

Review

Flexible engineering of advanced phase change materials

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SUMMARY

Liquid phase leakage, intrinsic rigidity, and easy brittle failure are the longstanding bottlenecks of phase change materials (PCMs) for thermal energy storage, which seriously hinder their widespread applications in advanced energy-efficient systems. Emerging flexible composite PCMs that are capable of enduring certain deformation and guaranteeing superior mutual contact with integrated devices are considered as a cutting-edge effective solution. Flexible PCMs-based thermal regulation technology can reallocate thermal energy and regulate the temperature within an optimal range. Currently, tireless efforts are devoted to the development of versatile flexible PCMs-based thermal regulation devices, and a big step forward has been taken. Herein, we systematically outline fabrication techniques, flexibility evaluation strategies, advanced functions and advances of flexible composite PCMs. Furthermore, existing challenges and future perspectives are provided in terms of flexible PCMs-based thermal regulation techniques. This insightful review aims to provide an in-depth understanding and constructive guidance of engineering advanced flexible multifunctional PCMs.

INTRODUCTION

Thermal regulation technology is an efficient approach to reallocate thermal energy for both heating and cooling of the human body, buildings and electric batteries and so on (Chen et al., 2020d; Moore and Shi, 2014; Wang et al., 2020b; Weinstein et al., 2018; Zhang et al., 2020). Although various thermal regulation technologies have been developed in the past years, they suffer from some intrinsic drawbacks (Hsu et al., 2016; Huang et al., 2016; Lin et al., 2021a; Tsai et al., 2020; Westwood et al., 2021). For example, integrating active air/liquid-cooling technology into rechargeable batteries can prevent overheating and thermal runaway at high temperatures, but they are usually bulky, heavy, complicated in structure, and high in power consumption. Moreover, it is necessary to heat the batteries at a low ambient temperature to achieve efficient working performance and safe operation of batteries (Kant et al., 2019; Lin et al., 2021a; Liu et al., 2019; Lizana et al., 2019; Yang et al., 2019; Zhu et al., 2019). Similarly, the thermal management devices of the human body in hot or cold environments are also crucial to human health. Various personal body heating/cooling technologies, such as photo heating, electric heating, ice cooling, water cooling, and air cooling, have been developed (Booten et al., 2021; Florindo et al., 2018; Hsu et al., 2017; Sipponen et al., 2020; Yang et al., 2017). However, these thermoregulation technologies usually restrict the mobility of the human body because of the heavy and complex wearable devices. Both the thermal regulation of human bodies and batteries can merely provide cooling or heating separately, but cooling and heating are usually simultaneously required under various conditions in many scenarios (Chen et al., 2020f; Ci et al., 2019; D'Alessandro et al., 2018; Waqas et al., 2018; Yan et al., 2021; Yang et al., 2021). In addition, thermal regulation needs to consider the diverse requirements of individuals, which can improve personal thermal comfort. It is worth noting that the traditional thermal regulation will not operate quickly once the external energy is removed. Therefore, it is of great importance to integrate heating/cooling thermal regulation into a small-scale system to adapt to a wider temperature range and extend the thermal conditioning time even in the case of removing external energy.

In response to the above critical issue, recently, an efficient solution based on solid-liquid phase change materials (PCMs) has been proposed which can regulate the temperature passively by utilizing large phase transition enthalpy of PCMs during the reversible crystalline-amorphous process (Hyun et al., 2014; Liu et al., 2021a; Velasco et al., 2021). Although PCMs can perform effective thermal regulation in various scenarios by absorbing and releasing thermal energy in the form of latent heat during the phase transition

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process, liquid PCMs are easy to flow, which restricts their widespread applications (Amaral et al., 2017; Chen et al., 2020g; Dai et al., 2021; Liu et al., 2021c; Saffari et al., 2017). To solve the liquid leakage issue of PCMs, diverse strategies have been developed to fabricate shape-stabilized composite PCMs such as core-shell encapsulation (microcapsule, CNTs, etc.), interface encapsulation (graphene, MXene, etc.) (Kumar et al., 2020; Shao et al., 2021a), and porous encapsulation (MOFs, EG, etc.) (Chen et al., 2020e, 2020h, 2021; Huang et al., 2020; Kashyap et al., 2019; Liu et al., 2021d; Wang et al., 2021b). Unfortunately, the shape-stabilized composite PCMs usually exhibit strong rigidity and poor flexibility, resulting in difficult installation, easy brittle failure and poor surface contact (Abdelrazik et al., 2020; Ashraf et al., 2017; Graham et al., 2020; Liu et al., 2020). The high thermal contact resistance caused by these problems is not conducive to efficient thermal regulation. To develop flexible PCMs-based thermal management devices, liquid phase leakage and solid phase rigidity of conventional PCMs should be addressed. Therefore, the thermal regulation systems based on PCMs are developing in the direction of flexibility, lightweight, intelligence, and wearability, which puts forward higher requirements for the mechanical strength and flexibility of PCMs.

Very recently, flexible engineering of PCMs technologies has attracted a lot of attention and offer a new avenue for significant improvement in the mechanical properties of PCMs while maintaining their energy storage capacity. High flexibility can guarantee that the thermal regulation materials contact the surface most fully under the condition of low installation pressure, and it is convenient to install and disassemble (Alam et al., 2019; Mandal et al., 2019; Wu et al., 2019c, 2021a). It is worth mentioning that mechanical flexibility and energy storage density are two contradictory evaluation factors for flexible composite PCMs. Flexible supporting materials are generally stretchable, twistable, foldable, and bendable and their flexible performances keep almost unchanged even though after suffering many deformation cycles. However, the flexibility of the supporting materials will be gradually destroyed with the increase of the content of PCMs. This is because PCMs tend to display a rigid state when solidified; the presence of a rigid component will restrict the flexible movement of supporting materials (Lin et al., 2022; Petruo et al., 2021; Ren et al., 2022). Currently, the two main methods for developing flexible thermal regulation systems based on PCMs are encapsulating PCMs into flexible supporting materials, which is a physical approach based on capillarity or hydrogen bonding, and grafting PCMs onto the supporting materials, which is a chemical approach based on grafting reaction. It should be noted that the supporting materials are importantly required no matter which method (Chen et al., 2018; He et al., 2019; Jing et al., 2019; Zayed et al., 2019) is adopted.

Recent reviews mainly concentrate on the encapsulation strategies, thermal conductivity enhancement, and applications of PCMs in energy conversion and storage (Aftab et al., 2018; Chandel and Agarwal, 2017; Chen et al., 2020g; Cheng et al., 2021; Frigione et al., 2019; Li and Mu, 2019; Shchukina et al., 2018; Wu et al., 2021b; Yuan et al., 2020), or focus on the preparations, properties and applications of flexible PCMs (Shi et al., 2021). However, an insightful understanding of flexible engineering of advanced PCMs is still insufficient. From the perspective of material science, herein, we systematically outline a comprehensive review of flexible PCMs based on different dimensional flexible additives, including 1D flexible additives, such as cellulose (Wei et al., 2019) and carbon nanotubes (CNTs) (Wang et al., 2021a); 2D flexible additives, such as graphene and their derivatives (Li et al., 2018), boron nitride (BN) (Wang et al., 2020a) (Yang et al., 2018) and MXene (Gong et al., 2021); and 3D flexible additives, such as EG (Wu et al., 2020c), foam (Chang et al., 2020) and other 3D flexible materials¹⁵⁷ (Figure 1). Moreover, we highlight fabrication techniques, flexibility evaluation strategies, advanced applications, current developments and further perspectives for flexible composite PCMs. This insightful overview aims to provide constructive guidance for the future development of advanced flexible PCMs.

FABRICATION TECHNIQUES OF FLEXIBLE COMPOSITE PCMS

The fabrication method of flexible composite PCMs is one of the important considerations because various parameters such as stability, cost, thermal performance and mechanical flexibility of the composite PCMs are determined by its fabrication method. Pristine PCMs are inherently rigid. Generally, flexible supporting materials are exploited to encapsulate PCMs or PCMs are chemically bonded with the polymeric skeletons for the preparation of flexible composite PCMs. Typical fabrication methods of flexible composite PCMs are preparing composites composed of pristine PCMs and flexible supporting materials, or grafting PCMs onto the polymer matrix by atom transfer radical polymerization or Diels-Alder reaction (Cao et al., 2019; Shao et al., 2021b). Since their inception in 2015, cellulose, carbon nanotubes, graphene, MXene, boron nitride, expanded graphite, and foam-based flexible composite PCMs have attracted

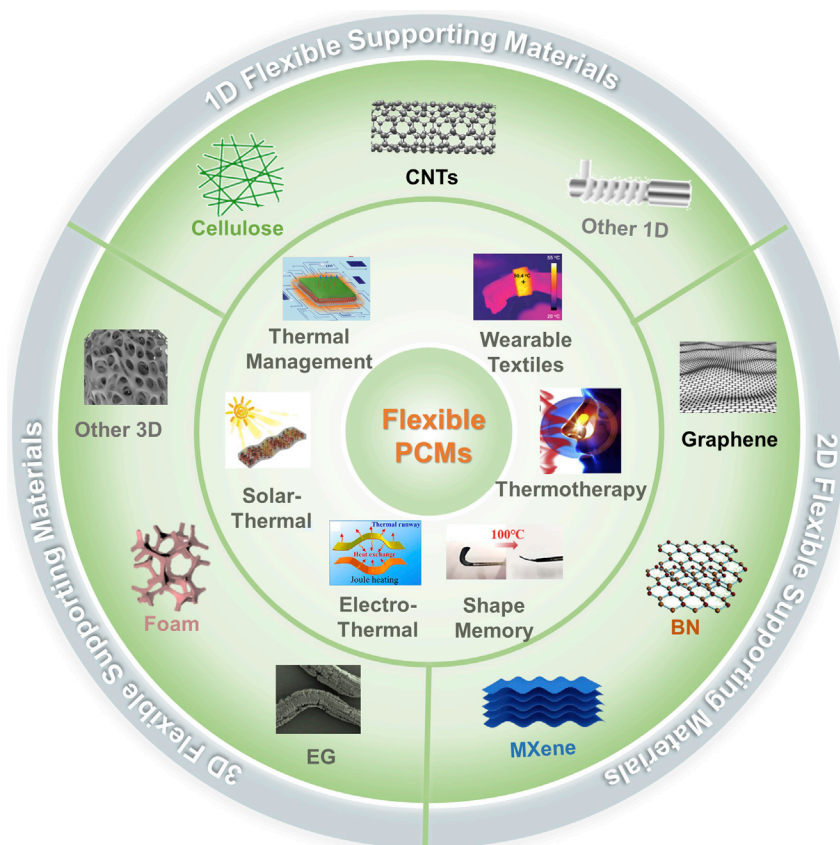


Figure 1. Layout structure of this review

Overview of using different dimensional supporting materials (1D, 2D, 3D) for preparation of flexible composite PCMs and advanced multifunctional applications: thermal management, wearable textiles, solar-thermal, electro-thermal, thermotherapy, and shape memory.

extensive interests from researchers and engineers because of their high energy storage density, excellent mechanical flexibility, and advanced multifunctional applications (Gong et al., 2021; Liu et al., 2021b; Qian et al., 2019). A timeline outlining major milestones towards the development of flexible composite PCMs is depicted in Figure 2. The five types of representative fabrication techniques for flexible composite PCMs will be as follows. We also summarized the advantages and disadvantages of five types of representative fabrication techniques for flexible composite PCMs (Table 1).

1. A commonly used method is spinning PCMs with other flexible materials such as polymer, CNTs, and graphene into the form of fibers via electrospinning process, producing phase change fibers (PCFs) (Wu et al., 2018). Fabricating PCFs exhibits some advantages, such as no encapsulation process required, easier preparation approach, controllable dimensions and high cost-efficiency. A number of thermoregulating textiles have focused on functional materials to integrate PCMs into fabrics (Gao et al., 2017; Pakdel et al., 2019). Li et al. fabricated flexible fluorocarbon (FC) resin/graphene/PEG fibers, which could be tied into a knot or woven into fabrics (Li et al., 2018). The fracture strength and Young's modulus of the fiber reached 12.7 MPa and 1.2 GPa, respectively. This flexibility is attributed to the coherent core-shell structure of FC/graphene/poly(ethylene glycol) (PEG) fiber. Similarly, ultrafine composite fibers of PEG and cellulose acetate (CA) were generated using uniaxial electro-spinning (Chen et al., 2011). Different amounts of PEG were mixed with CA spinning fibers with low concentrations of PEG resulted in PEG/CA fibers with a smooth surface. The content of PEG played the key role in thermoregulating performance of the spun fibers. Regardless of 1D, 2D or 3D materials, this technique can be used to prepare flexible composite PCMs, showing universal applicability.

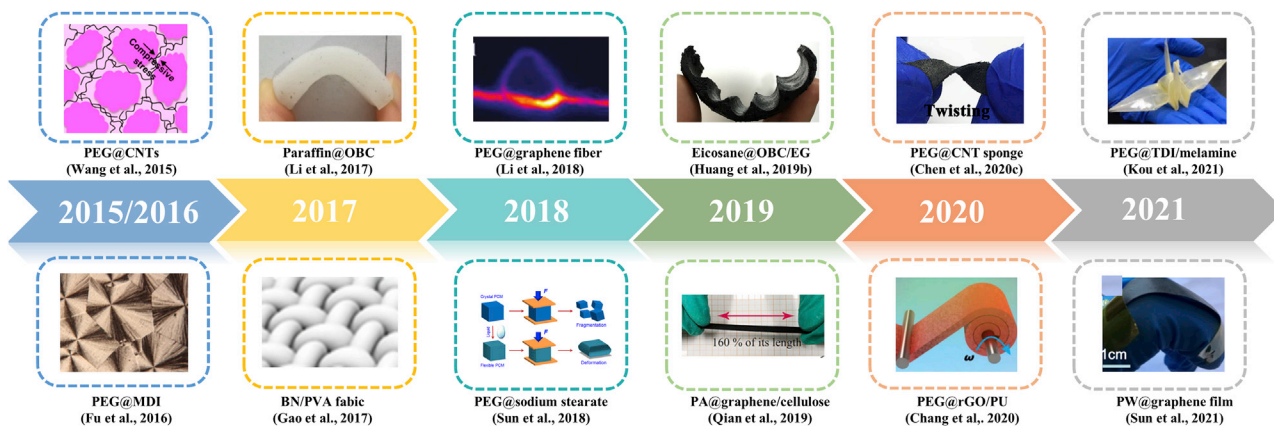
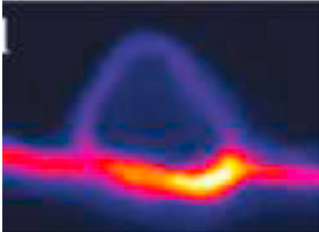
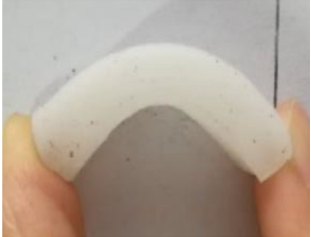





Figure 2. A timeline of the historic development of flexible composite PCMs

2. The second technique is based on polymer crosslinking network to encapsulate PCMs like olefin block copolymer (OBC), styrene butadiene styrene (SBS), polydimethylsiloxane (PDMS) etc. These polymers are intrinsically flexible and can be formed into 3D flexible porous structure to encapsulate PCMs. For example, Zhang et al. fabricated a 3D network of polymerized polyacrylamide (PAM) using a molecular self-assembly method, which showed an ultimate stretch length ratio of 530% and a tensile strength of 26 kPa (Zhang et al., 2021). OBC could realize shape deformation and shape recovery upon exposure to external stimuli, and physical blending between the elastic OBC and paraffin wax (PW) may impart the PW/OBC blends with shape variation property via temperature as a stimulus (Zhang and Feng, 2013). Specifically, when the temperature was below the melting temperature of PW, the PW/OBC blends showed a rigid state because of the existence of PW crystals. Once the temperature was above the melting temperature of PW, PW/OBC blends became softened and thus could be easily deformed into other shape. Therefore, the mechanical state of PW/OBC blends from rigidity to flexibility was reversible by triggering the phase transition of PW. In addition, other additives with specific functions could be also introduced into elastic crosslinked network, such as CNTs, MXene, BN, so that flexible composite PCMs can be tuned to obtain specifically tailored optical, electric, and thermal properties. In another sample, flexible solar-responsive composite PCMs consisting PW and CNTs-filled OBC were prepared by Qi et al. (2019). Flexible PW@OBC/CNTs composite PCMs simultaneously exhibited solar-thermal energy storage and solar-driven shape memory capability even a small adding amount of CNTs. In brief, this fabrication technique is simple and low-cost, but its flexibility is limited by the melting temperature of PCMs.
3. The third technique is based on off-the-shelf foam-like melamine foams (MF) and polyurethane (PU) foam to encapsulate PCMs. These foams often endow flexible composite PCMs with shape memory capability. However, the flexibility or comfort of composite PCMs may be compromised if the content of PCMs is high. In addition, some researches endow flexible composite PCMs with solar-thermal, electro-thermal conversion functions via integrating CNTs, graphene and MXene with PCMs. Xiao et al. prepared flexible PEG@Cu/MF composite PCMs with 3D interconnected thermal-conductive additive network via electroless copper (Cu) plating on porous MF (Xiao et al., 2021). The tensile strength of Cu/MF foam reached 72.37 kPa, which was increased by nearly 2 times compared with pristine MF under the same strain of 11%. The unique binary structure of MF/PCMs blends might combine the advantages of both PCMs and MF, which imparted MF/PW blends with not only a high latent heat but also excellent shape memory properties. However, there are still some shortcomings. The flexibility of prepared MF-based PCMs was overemphasized, whereas these PCMs exhibit low fracture strength and insufficient mechanical loading capacity. In addition, the thermal conductivity of PCMs prepared by the thermally insulating MF was still not significantly improved even with the addition of thermally conductive additives.
4. The fourth technique is based on designing aerogels with special 3D network structure like CNT aerogel, rGO aerogel, BN aerogel and the like, displaying high mechanical flexibility. Cheng et al. fabricated a meet-demand flexible monolithic composite PCMs with a folded layer-bridge 3D network using a directional freezing method (Cheng et al., 2020). The flexible composite PCMs

Table 1. The advantages and disadvantages of five types of representative fabrication techniques for flexible composite PCMs

Fabrication techniques	The advantages and disadvantages
<p data-bbox="150 384 464 409">Fiber based flexible composite PCMs</p> 	<ul style="list-style-type: none"> ✓ Easy preparation approach ✓ Controllable dimensions ✓ High cost-efficiency ✓ Suitable wearable applications ✗ Low energy storage capacity ✗ Poor shape stability at high temperature
<p data-bbox="150 688 509 714">Polymer network based flexible composite</p> 	<ul style="list-style-type: none"> ✓ Easy preparation approach ✓ Excellent compatibility ✓ Excellent mechanical stretchability ✓ High foldability ✗ Limited flexibility by melting temperature ✗ Low PCM content
<p data-bbox="150 1001 469 1026">Foam based flexible composite PCMs</p> 	<ul style="list-style-type: none"> ✓ Well-controlled tailorability ✓ High compressibility/restorability ✓ Well shape memory property ✗ Low thermal conductivity ✗ Leakage-proneness
<p data-bbox="150 1314 488 1339">Aerogel based flexible composite PCMs</p> 	<ul style="list-style-type: none"> ✓ High thermal conductivity ✓ Multi-responsive functionality ✓ High stability and durability ✗ High cost and energy consumption ✗ Relatively poor mechanical strength
<p data-bbox="150 1619 453 1644">Solid-solid flexible composite PCMs</p> 	<ul style="list-style-type: none"> ✓ Inherent flexibility ✓ Without requiring supporting materials ✓ Excellent mechanical properties ✓ Well functionalized modifiability ✗ Non-recyclability ✗ Non-processability ✗ Non-malleability

displayed excellent mechanical properties, such as high tensile strength of 2.42 MPa and bending resistance of >100 cycles and outstanding thermal properties, such as high crystallinity of close to 100% and encapsulation ratio of 92.6 wt%. In addition, a CNT array (CNTA) was synthesized by chemical vapor deposition, which could modulate the nanotube density by direct lateral compression (Liu et al., 2013b). Compared with traditional CNT aerogels (Hirsch, 2010) made of randomly overlapped nanotubes, CNTA with a high porosity could be formed by single-walled or multiwalled CNTs with different diameters. The original empty CNTA could be compressed laterally to a large strain (40%) and returned to original size elastically, providing a controllable way to tailor the CNT distribution and density. This technique can utilize high thermally conductive materials with superior solar absorption, such as CNTs and graphene, to assemble 3D flexible networked supporting materials, thereby obtaining flexible composite PCMs with some advanced applications.

5. The fifth technique is based on the Diels-Alder reaction or the atom transfer radical polymerization reaction to graft PCMs onto the supporting materials, referring to solid-solid PCMs (SSPCMs) (Fu et al., 2016; Zhou et al., 2018). Compared with solid-liquid PCMs, it is a more promising method to fabricate SSPCMs by integrating PCMs into the polymeric skeletons through permanent chemical bond. Surprisingly, SSPCMs have more reliable chemical stability and thermal stability without leakage or migration over the phase change process. Du et al. fabricated flexible SSPCMs by grafting PEG into nanofibrillated cellulose (NFC)/graphene hybrid aerogels (Du et al., 2020b). The obtained SSPCMs not only could recover the original height after 60 compressive cycles with a strain of 50%, but also showed a high solar-thermal conversion efficiency of 84.7%. Similarly, Qian et al. grafted the poly-(hexadecyl acrylate) polymer (PA16) onto a cellulose by atom transfer radical polymerization, followed by the introduction of modified graphene (GN16) (Qian et al., 2019). The obtained SSPCMs exhibited excellent thermally induced flexibility and were prone to various deformations under the action of external forces because of the relatively low coefficient of linear thermal expansion of the cellulose backbone and the high degree of cross-linking among the alkyl chains (Klemm et al., 2005; Xiong et al., 2018). Nevertheless, this advantage of chemical cross-links may present new problems, including non-recyclability, non-processability or non-malleability, which enormously hinders the achievement of comprehensive and sustainable development (Sundararajan et al., 2018). Although considerable efforts have been dedicated to constructing flexible composite PCMs by chemically grafting pristine PCMs with different flexible polymers, such as polyethylene, polymethyl and polyurethane, it is still a great challenge to design and prepare intrinsic flexibility composite PCMs with shape-conformability and foldability for wearable thermal managements. The “elastic” property of cross-linked polymers greatly limits the application of SSPCMs under high temperature conditions because the “elastic” property may suffer a sharp shrink at a high temperature.

FLEXIBILITY EVALUATION STRATEGIES OF COMPOSITE PCMS

To date, a standardized or normalized evaluation method has not been proposed for the flexibility evaluation of composite PCMs. Flexible composite PCMs usually encapsulate pristine PCMs into the supporting materials with high mechanical flexibility which still maintain the high mechanical integrity upon bending, folding or even rolling. There are two methods to evaluate the flexibility of composite PCMs, a qualitative method and a quantitative method.

Flexibility evaluation strategies can be qualitatively expressed as no significant changes, similar to the initial state or minimal loss after undergoing multiple bending cycles. Namely, composite PCMs can be bent into large angles, or be shaped into various desired structures, and quickly recover to their original shapes, indicating their excellent flexibility.

In addition to a qualitative method, the flexibility of composite PCMs can be quantitatively characterized by elastic modulus, tensile fracture strength, elongation at break, elastic response rate. For example, the stress and strain change linearly at the initial stage of material stretching, and the elastic modulus of the material can be estimated according to the change based on stress-strain curve. Similarly, a tensile fracture strength or an elastic response rate can be obtained via a tensile test or compressive test, respectively.

ADVANCED FLEXIBLE COMPOSITE PCMS

Flexible multifunctional composite PCMs not only require excellent thermal regulation properties, but also require high mechanical property upon bending or folding. Given that PCMs have low mechanical

properties, fabricating flexible composite PCMs with an excellent flexibility requires introducing highly flexible components into the PCMs with flexible fabrication technologies. Among them, 1D materials tend to intertwine with each other when prepared, which makes them likely to be assembled into flexible supporting materials. In addition, 2D materials can form an overlapping structure when they are stacked layer-by-layer, which contributes to their highly flexible performance. Moreover, 3D materials have more junction sites among building blocks and have more porous structure themselves, provide more benefits for multifunctional composite PCMs with highly flexible performance. Through the use of various components (1D, 2D, and 3D) combinations and seeking some synergistic effects effect, many studies have shown improved flexibility. This section briefly summarizes and compares to the results of adding components in different dimensions to the mechanical properties and advanced applications of PCMs, and analyzes the reasons for the above results.

1D flexible composite PCMs

1D materials usually have a high aspect ratio, which are easier to construct an effective conductive pathway/network structure. The phonons can travel ballistically through the conductive pathway without scattering, realizing high thermal conductivity enhancement in PCMs. To meet the demands of flexible composite PCMs, numerous 1D material platforms are possible choices for flexible composite PCMs. 1D nanomaterials, including cellulose, CNTs, and other 1D materials, tend to be entangled with each other to assemble flexible supporting materials. The flexibility of composite PCMs can be achieved via constructing flexible porous supporting materials with 1D materials and via cross-linking reaction with 1D polymer molecular skeleton. Some 1D flexible composite PCMs not only hold traditional temperature regulation capability, but also can convert solar energy or electricity energy into thermal energy and then stored into PCMs in the form of latent heat during the solar-thermal and electro-thermal energy conversion process. In addition, 1D flexible composite PCMs can be employed in some cutting-edge applications such as the thermal management of devices, shape memory capability, thermotherapy and wearable textiles (Gerkman and Han, 2020; Hassan et al., 2020; Ibrahim et al., 2017).

Cellulose-based flexible composite PCMs

As a polymer, cellulose possesses excellent processability, and can be made into various shape monoliths for practical applications. The multi-chemically cross-linking cellulose nanofiber (CNF) sponge was selected as the scaffold for PCMs-based thermal conversion systems owing to its easy fabrication, 3D porous network structure, and high mechanical strength (Huang et al., 2019a). Therefore, integrating CNF and PCMs can construct flexible composite PCMs with temperature regulation capability.

Flexible phase change fibers (PCF) based on polyethylene glycol (PEG)@cellulose acetate were prepared via electrospinning (Chen et al., 2011). The temperature of flexible PEG@cellulose acetate PCF was maintained about 58°C (close to the melting temperature of PEG) while cellulose acetate fibers quickly raised to the temperature of heating stage (90°C), indicating that PCF could spontaneously adjust the temperature with the change of ambient temperature. On the other hand, the fracture strength and strain of PCF were 4.0 MPa and 6% whereas those of cellulose acetate fibers were about 8.5 MPa and 10%, respectively. The reduced mechanical strength was attributed to the introduction of PEG, which broken the continuous phase structure of cellulose acetate. Moreover, flexible PCF would lose flexibility if PCMs content is much larger than cellulose content. The temperature regulation capability of PCF will decrease if cellulose content is larger than PCMs content. Therefore, the content balance between PCMs and cellulose is a main consideration for achieving temperature regulation and excellent flexibility of composite PCMs. Regarding the issue above, Yazdani et al. exploited flexible PCF organogelator to achieve 85 wt% PEG encapsulation (Yazdani et al., 2021). The tensile strength and strain of PCF were 28 MPa and 1% when PCF failed whereas those of pristine PEG were too weak to measure. Apart from single cellulose, certain researches gradually focused on hybrid cellulose for the preparation of flexible composite PCMs. A flexible cellulose fibers/PU hybrid aerogel was prepared via freeze-drying methods and wet coagulating methods to encapsulate octadecane (Wang et al., 2020d). The resultant flexible hybrid aerogel was lightweight (<0.12 g/cm³), highly porous (>89.72%) and could quickly regress to their original shapes even when bent and twisted, showing superb flexibility (Figure 3A). Hybrid cellulose based supporting materials can construct more porosity to enhance thermal energy storage density. Flexible octadecane@cellulose fiber/PU composite PCMs exhibited a high latent heat of 223.3 J/g, excellent shape stability and thermal stability. Moreover, these composite PCMs demonstrated shape memory properties. They could be fixed into various shapes at 20°C or lower, and quickly recovered to the original shape above the melting point of octadecane

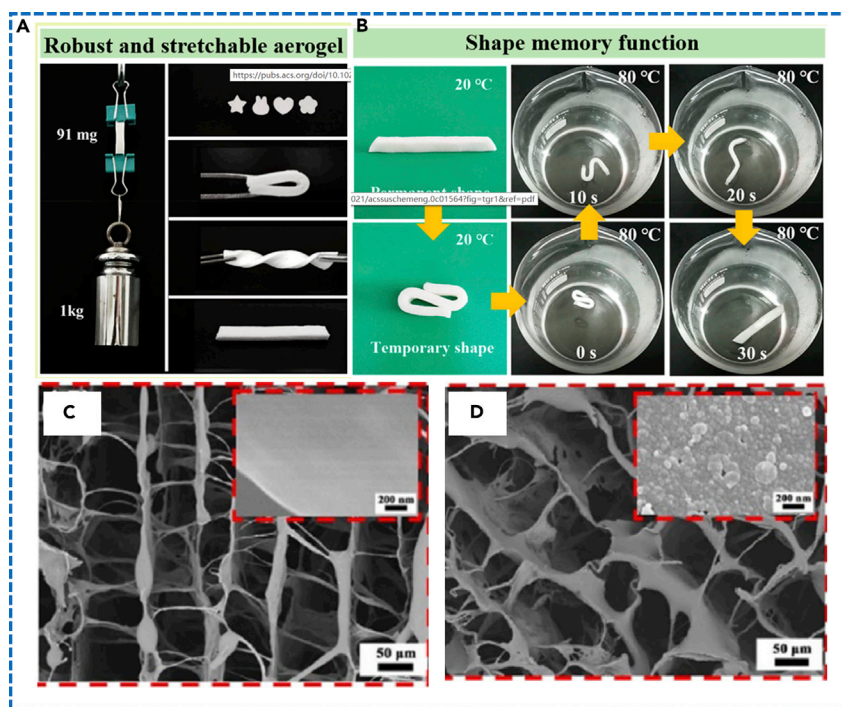


Figure 3. Cellulose-based flexible composite PCMs

(A–B) Photographs of mechanical property and shape memory process of octadecane@CNF/PU. Adapted from Wang et al. (Wang et al., 2020d) with permission; copyright 2020, American Chemical Society.

(C–D) SEM images of CNF sponge and PPy/CNF sponge. Adapted from Chen et al. (Chen et al., 2020a) with permission; copyright 2020, Elsevier.

(Figure 3B). Cellulose serves as a polymer with excellent processability, it is often prepared into fibrous form without other auxiliary additives. However, there are some factors to be considered, such as the selected polymer type (solubility, molecular weight, and melting point) and the properties of polymer solvent (viscosity, temperature, and surface tension). Usually, to achieve high flexibility, thermal storage density is inevitably reduced. Flexible cellulose based PCF can be woven into thermo-regulating textiles for various wearable applications.

Cellulose can be integrated with certain high conductive additives to achieve electro-thermal conversion owing to its superior processability. A cellulose nanofiber sponge coated with polypyrrole (PPy@CNF) was constructed to prepare flexible PEG@PPy/CNF composite PCMs for electro-thermal conversion (Chen et al., 2020a). PPy was integrated well with CNF sponge via hydrogen bonding interactions between the hydroxyl groups in CNF and imino groups of pyrrole ring (Figures 3C–3D). The uniformly deposited PPy on the CNF sponge formed continuous conductive paths, which endowed flexible PEG@PPy/CNF composite PCMs with a good conductivity. Resultantly, cellulose-based flexible composite PCMs exhibited a high melting enthalpy (169.7 J/g) and a high electro-thermal efficiency (up to 85.1%) under an applied small voltage (1.9 V). Therefore, hybrid supporting materials by bringing high thermally conductive additives into cellulose not only enhance the flexibility, but also improve the electro-thermal conversion capacity of composite PCMs.

Pristine cellulose-based flexible composite PCMs cannot be directly triggered for solar-thermal conversion owing to the low thermal conductivity and poor trapping ability. Cellulose-based flexible composite PCMs can also regularly utilized in solar-thermal conversion via adding photoabsorption materials such as CNTs and graphene. In a study, graphene with high thermal conductivity and superior photoabsorption capacity was introduced into flexible cellulose-based composite PCMs grafting comb-like poly-(hexadecyl acrylate) polymer (PA16) by atom transfer radical polymerization for solar-thermal conversion. The graphene-modified flexible cellulose-based composite PCMs showed an enhanced thermal conductivity (1.32 W/m·K, 9 wt% graphene) and phase change enthalpy (103 J/g, 5 wt% graphene) (Qian et al., 2019).

Resultantly, graphene-based flexible composite PCMs exhibited a sharp increase from 10 to 35°C whereas the temperature of PA@cellulose composite PCMs slowly increased to 35°C under the direct solar irradiation. This could be ascribed to the function of graphene nanosheets as high-performance photon captors and material heaters. Overall, graphene not only improved the solar-thermal conversion capacity, but also guaranteed the flexibility of composite PCMs. In addition, when the temperature was above the melting point of PA16, flexible composite PCMs adopted a free “S” shape, which could be maintained below the freezing temperature of PA16. Once the temperature reached or exceeded the melting point again, the original shape of composite PCMs could be restored. This result could be attributed to the strong self-aggregation of physically cross-linking and the entangled alkyl chains in comb-like PA16 polymer.

Apart from the above situation, cellulose based flexible composite PCMs can achieve simultaneous integration of electro-thermal conversion and solar-thermal conversion via adding graphene. Incorporating PEG into the flexible cellulose/graphene hybrid-coated MF could reach the simultaneous realization of electro-thermal and solar-thermal conversion (Wu et al., 2019b). The electro-thermal and solar-thermal conversion efficiencies of flexible PEG@cellulose/graphene/MF composite PCMs were 66.13 and 89.88%, respectively. These results proved that graphene is an effective photon absorber and nanoheating unit, which can efficiently convert solar energy into thermal energy and then transfer thermal energy.

In summary, cellulose is a kind of easy-to-process and easy-to-mixed 1D polymer material. Thus, it is often mixed with PCMs to prepare fibrous fabrics via direct spinning methods. However, 1D nanomaterials still have the limitation of a relatively smaller contact area with the PCMs for its nanoscale diameter and thus the surface areas of 1D nanomaterials are not utilized effectively. Therefore, it is often integrated with 3D foams such as MF or PU to realize more contact area with PCMs. In addition, cellulose can be combined with other materials with high electrical conduction and photoabsorption capabilities (graphene, poly-pyrrole) to prepare flexible composite PCMs for electro-thermal and solar-thermal conversion.

CNTs-based flexible composite PCMs

Different from 1D cellulose polymer, carbon nanotubes (CNTs) not only possess remarkable mechanical properties, but also inherently possess strong photoabsorption and electrical conduction capacities (Chen et al., 2020d, 2020g; Tang et al., 2021). CNTs have been widely used for flexible wearable composite PCMs owing to their unique properties such as high thermal conductivities (2000–6000 W/m·K), high flexibility and superior mechanical properties (Hirsch, 2010). Therefore, CNTs-based flexible composite PCMs can display excellent electro/solar-thermal conversion capacity besides temperature regulation function. However, it is essential to assemble individual CNTs into 3D free-standing macroscopic structure with high mechanical flexibility from the perspective of practical applications. Ma et al. (2020) fabricated multi-responsive phase change fibers (PCF) by spray-coating PW@crystalline polysiloxanes/MWCNTs solution, followed by *in situ* curing. Thermal conductivity of flexible composite PCMs was 1.16 ± 0.05 W/m·K. When the applied voltage (8.0 V) was exerted, surface temperature of flexible composite PCMs increased a small plateau (56°C) rapidly. The solar-thermal conversion efficiency of flexible composite PCMs was approximately 65% under 1.0 sun, which could be attributed to large numbers of MWCNTs, extensive small-scale porosities as microcavities to enhance solar-absorption.

CNTs based flexible composite PCMs can be fabricated not only into fibers, but also into films. Composite PCMs with electro-thermal conversion and storage function have shown a great potential in the thermal management of power vehicles, electronic devices, and off-peak electricity storage systems. A flexible single-walled CNTs (SWCNTs) scaffold-based PCMs film was obtained by volatilization synchronously for electro-thermal conversion (Chen et al., 2020b). Composite PCMs films exhibited a reversible flexibility with arbitrary bending. The highest electro-thermal conversion efficiency was up to 91.3% under an input voltage of 5 V. Redundant eicosane covered on the surface of CNTs could greatly increase the resistance of composite PCMs, which needed a higher input voltage for electro-driven thermal storage. Although the higher the PCMs content, the higher the thermal storage density, but the greater the thermal resistance, the higher the input voltage. Finally, appropriate PCMs content should be infiltrated if energy efficiency is considered. Apart from electro-thermal conversion function of flexible PCMs, CNTs possess strong photoabsorption and solar-thermal conversion function because of their π -conjugated structures, thereby making them a promising candidate for IR detecting applications (Kong et al., 2021; Schnorr and Swager, 2011). A multi-walled CNTs (MWCNTs) based composite PCMs film was fabricated by Wang et al. (2015),

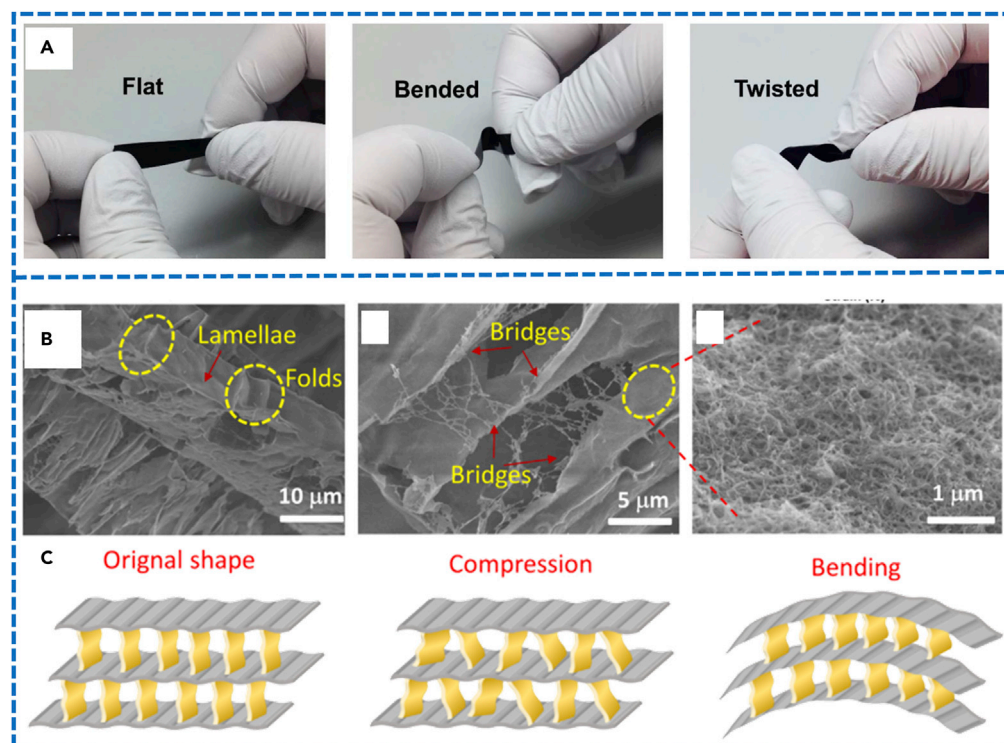


Figure 4. CNTs-based flexible composite PCMs

(A) Photographs of flexible composite film under bending and twisting. Adapted from Wang et al. (Wang et al., 2015) with permission; copyright 2015, American Chemical Society.

(B–C) SEM images and schematic illustrations of the supporting material. Adapted from Cheng et al. (Cheng et al., 2020) with permission; copyright 2020, Elsevier.

which exhibited robust flexibility and could easily be stretched and bent. The IR-regulated on/off electrical conductivity ratios of MWCNTs-based composite PCMs film were 11.6 ± 0.6 and 570.0 ± 70.5 times at IR powers of 730 and 2360 mW/cm², respectively. During the heating process, the melted localized PEG crystalline regions caused a localized volume expansion and subsequently generated a compressive internal stress on the cross-linking elastic regions where the MWCNTs resided (Figure 4A). The excellent photoabsorption and thermal conversion capabilities of MWCNTs affected the thickness of the interfacial PCMs between adjacent conductive MWCNTs, thereby affecting the electron tunneling efficiency between MWCNTs.

Apart from CNTs-based flexible PCF and flexible PCMs films, CNTs can be combined with OBC to establish cross-linking network, thereby encapsulating PCMs to fabricate flexible composite PCMs. Flexible solar-responsive composite PCMs consisting PW and CNTs-filled olefin block copolymer (OBC) were prepared by Qi et al. (2019). Flexible PW@OBC/CNTs composite PCMs simultaneously exhibited solar-thermal energy storage and solar-driven shape memory capability even a small adding amount of CNTs. The shape fixing ratio and recovery ratio of PW@OBC composite PCMs were 97.1 and 86.0%, suggesting good shape fixing and recovery effect. In addition, compared with PW@OBC composite PCMs (0.09MPa), the tensile strength of flexible PW@OBC/CNTs composite PCMs was increased to 0.17 MPa, showing over 88.9% increment.

To make full use of the advantages of CNTs to meet the practical applications of composite PCMs, 1D CNTs can be made into 3D CNT sponges. The designed structure of CNTs sponge is significant for mechanical flexibility and thermal properties of flexible PCMs. Cheng et al. (2020) utilized a flexible CNTs/chitosan(CS)/poly(vinyl alcohol) (PVA) supporting material for the preparation of CNTs-based flexible composite PCMs using a directional freezing method. The obtained flexible CNTs/CS/PVA material possessed certain inter-penetrations of CS and PVA among the CNTs during the directional freezing and freeze-drying, thereby showing a high compressibility because of the formed folded layers and the

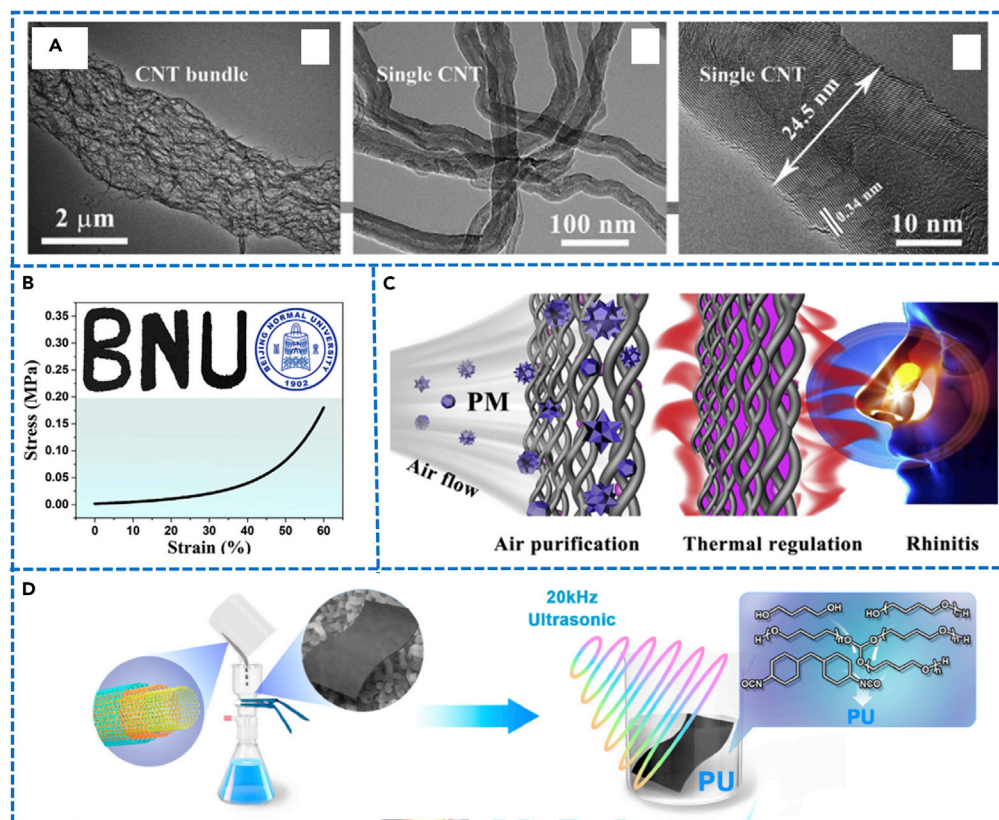


Figure 5. CNTs-based flexible composite PCMs

(A) TEM images of CNT sponge.

(B) Stress-strain curve of CNT sponge.

(C) Schematic illustration of the thermotherapy. Adapted from Chen et al. (Chen et al., 2020c) with permission; copyright 2020, Elsevier.

(D) Schematic illustration of the PU/CNTs nanocomposites. Adapted from Wang et al. (Wang et al., 2021a) with permission; copyright 2021, Elsevier.

bridges (Figure 4B). The fracture tensile stress of composite PCMs was 2.39 MPa in the freezing state, which was approximately 2 times higher than that of the flexible supporting materials (1.29 MPa). Importantly, flexible composite PCMs always maintained an excellent flexibility no matter whether PEG confined in supporting materials was in the freezing or melting states (Figure 4C). In addition, the resulting flexible composite PCMs displayed a high crystallinity of close to 100% and a high PEG encapsulation ratio of 92.6 wt %, which indicated that integrating certain polymers with CNTs could design flexible macroscopic assemblies for direct applications. By taking advantage of the bendability and stable heat-releasing temperature of monolithic PCMs, they can be directly applied to human thermal comfort and thermotherapy at the desired temperatures by absorbing and releasing large amounts of thermal energy. CNTs bundles assembled flexible hierarchical framework based composite PCMs was fabricated by Chen et al. (2020c) for thermotherapy of allergic rhinitis. Hierarchically interconnected 3D freestanding flexible CNTs sponge was constructed using table salt as a sacrificial template (Figure 5A). The CNT sponge could be strained to 60% height reduction at a low stress of 0.17 MPa because of high porosity and the squeezing of inter-tube pores. After the release of external force, it could restore to nearly its original shape (Figure 5B). Strikingly, the authors designed an advanced portable integrated functional mask for the thermotherapy of allergic rhinitis, in which pristine CNTs sponge served as an excellent particulate matter capturer and flexible PEG-infiltrated CNTs sponge served as a superior thermal regulator (Figure 5C). Strikingly, flexible CNTs sponge involved composite PCMs harvested high-performance thermotherapy (~33 min of the plateau at ~43.5°C). The corresponding medical results indicated that the designed thermotherapy mask could significantly reduce the inflammatory injury of nasal mucosa.

Currently, a few efforts have concentrated on solid-solid PCMs, in which PCMs are chemically bonded with the polymeric skeletons. Generally, cross-linking polyurethanes, epoxy resins, polystyrenes and polyesters have been considered as popular candidates in recent years. However, the thermal conductivity of flexible polyurethanes (PEG based solid-solid PCMs) based composite PCMs is very low (0.10–0.50 W/m·K) because of the complex morphology of macromolecular chains. Generally, CNTs can increase the thermal conductivity of polyurethanes via solution assisted infiltration methods. Flexible polyurethanes@CNTs composite PCMs were fabricated via the ultrasonic-assisted forced infiltration strategy (Figure 5D). The resulting PU@CNTs composite PCMs presented an excellent mechanical stability (elongation at break of 211.7%, tensile strength of 5.97 MPa, and 360° bending available) and a superior thermal conductivity (6.03 W/m·K) (Wang et al., 2021a). Similarly, Shi et al. (2020a) incorporated functionalized CNTs in the PU (PEG based solid-solid PCMs)-based PCMs by controlling the molecular weight of PEG and figuring out the optimum selection through the tradeoff between flexibility and thermal storage capacity. The deformation of shape could be maintained rehabilitate at both above or below the crystallization point of PCMs. In addition, the stabilized performance over 25 stretching cycles guaranteed the long-term stability of flexible composite PCMs. The thermal conductivity of flexible PU@CNTs composite PCMs with only 5 wt% CNTs was improved by 2.3 times compared with pristine PU, and the solar-thermal energy storage efficiency reached 85.9% at 125 mW/cm² of irradiation power. Resultantly, flexible PCMs film could maintain a higher temperature for ~3800 s than that of bare skin (33.5°C) owing to the stable temperature range of phase transition, whereas cotton fabric quickly dropped to the temperature of bare skin after 800 s. When the charged flexible PCMs film was pasted on arm skin, it could release thermal energy uniformly and provide a valid thermal management for human body.

Attractively, combining SSPCMs with CNTs aerogels to prepare flexible composite PCMs is a very promising choice for various advanced applications. Highly conductive flexible composite PCMs were fabricated by Aftab et al. (2019) through infiltrating polyurethanes molecules into the pores of CNTs sponge (CNTS). Flexible PU@CNTS composite PCMs presented a high axial thermal conductivity (2.40 W/m·K) and a high thermal energy storage density of 132 J/g. Along the axial direction, the thermal conductivity of PU@CNTS composite PCMs was 2.40 W/m·K at 25°C, about 10 times higher than pristine polyurethanes. The polyurethanes@CNTS composite PCMs could be driven by either solar irradiation or by applying a small voltage. The electro/solar-thermal energy storage efficiency reached 94% at 2 V and 95% at 150 mW/cm² intensity, respectively, which could be attributed to high thermal transport rate of aligned and percolated CNTs in a composite structure, thereby reducing the charging time.

In some cases, CNTs blended with PCMs can be fabricated into fibers or films directly via spinning or spray-coating methods (Li and Mu, 2019; Li et al., 2019). In terms of this situation, the content of PCMs is restricted by maintaining mechanical flexibility of flexible composite PCMs. Therefore, CNTs are often exploited into 3D CNTs sponge with 3D network structure via freeze-drying methods. On the one hand, high flexibility of CNTs sponge based composite PCMs can be realized. On the other hand, enhanced thermal conductivity and solar absorption can also be reached via CNTs based 3D network.

Other 1D-based flexible composite PCMs

Integrating personal thermoregulation technologies into wearable textiles has enabled extensive and profound technological breakthroughs in energy savings, thermal comfort, wearable electronics, intelligent fabrics (Peng and Cui, 2020; Tabor et al., 2020). Nevertheless, previous studies have suffered from long-standing issues such as limited working temperature, poor comfort, and weak textile reliability (Gu et al., 2020; Li et al., 2021b). Encapsulating PCMs into fibers is a facile and effective approach to solve the leakage problem and improve the thermal performances of flexible textiles (Tang et al., 2018).

Flexible composite PCMs can be melt spun of polyamide 6 (PA6) into PCFs via a molecular chain structural selection strategy and nano-hybridization technique. The obtained PCFs could delay temperature rise for 591 s, suggesting a temperature buffering effect (Figure 6A) (Xia et al., 2021). Here, fumed silica nanoparticles were used as the inorganic carriers to adsorb PCMs and the interaction between fumed silica nanoparticles formed a fluffy network, providing an enhanced physical adsorption capacity as well as high thermal conductivity. In another sample, Wu et al. (2020b) prepared a skin-friendly personal insulation textile and a thermoregulation textile that could perform both passive heating and cooling using the same piece of textile with zero energy input. By filling these microstructural fibers with biocompatible PEG and coating them with polydimethylsiloxane (PDMS), flexible PCFs exhibited better thermal conditioning

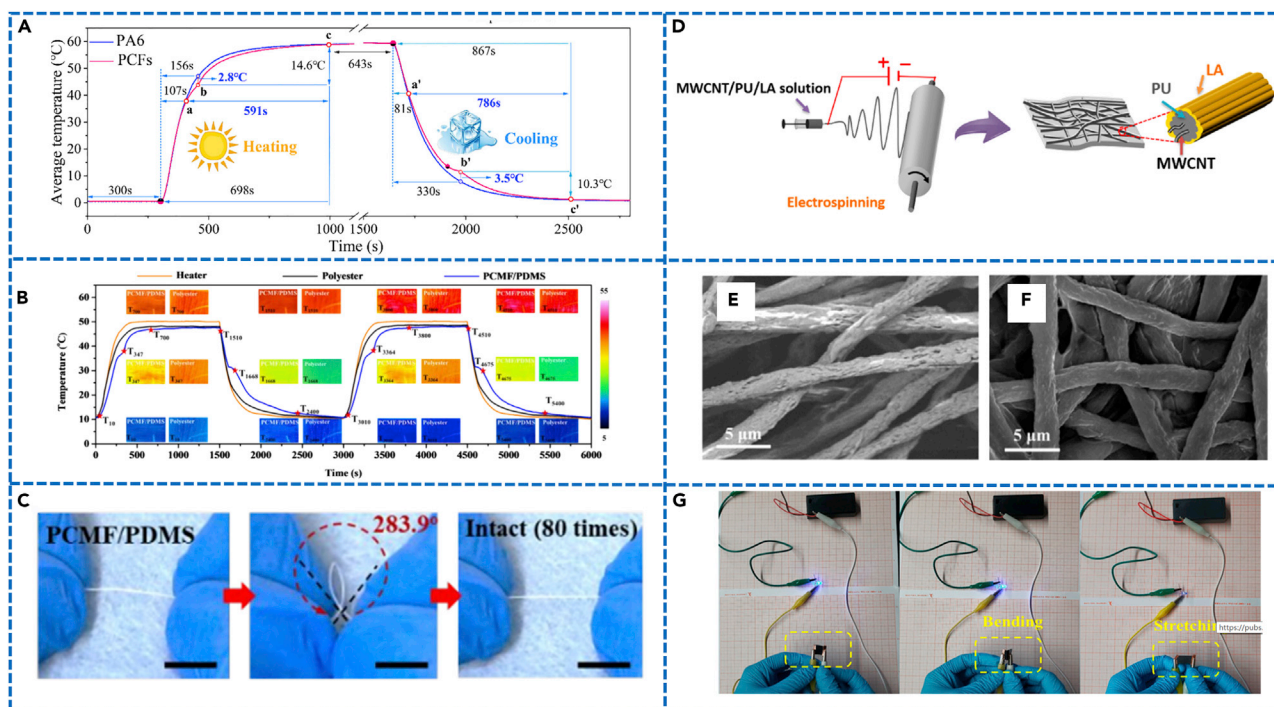


Figure 6. Other 1D-based flexible composite PCMs

(A) Temperature-time curves of PCFs and PA6 fibers. Adapted from Xia et al. (Xia et al., 2021) with permission; copyright 2021, Elsevier.
 (B) Temperature-time curves of the heater, polyester and PCMF/PDMS textiles.
 (C) Photographs of PCF/PDMS bending tests. Adapted from Wu et al. (Wu et al., 2020b) with permission; copyright 2020, American Chemical Society.
 (D) Schematic illustration of PEDOT:PSS-coated MWCNTs/LA/PU fabrics.
 (E–F) SEM image of 1% CLPF₂ and 1% CSF₂.
 (G) The LED circuit with 5% CSF_{1.5} sample as a circuit conductor when bent and stretched. Adapted from Niu et al. (Niu and Yuan, 2021) with permission; copyright 2021, American Chemical Society.

comfort than commercial thermal textiles (Figure 6B). This strategy offers feasible and adaptive options for personal cooling/heating scenarios and enables scalable manufacturing for practical applications. Moreover, PDMS-coated PCFs further enhanced the hydrophobic and mechanical properties. The flexible PCFs@PDMS on the gloves exhibited outstanding thermal regulation abilities in cold and hot environments, validating its excellent thermal reliability and stability (Figure 6C).

Poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(styrenesulfonate) (PSS) have been widely used in the applications of electrostatic coatings, wearable and implantable devices owing to their high conductivity, transmission, flexibility, and processability in water (Zhang et al., 2020). Therefore, it is an effective way to improve the conductivity of textiles through a combination with PEDOT:PSS. The MWCNTs/lauric acid (LA)/PU fabrics were fabricated by electrospinning and dip-coating conductive polymer PEDOT:PSS on the nanofibers (CSFs) (Niu and Yuan, 2021) (Figure 6D). The surface of the fibers became relatively smooth after coating, indicating that the fiber was completely wrapped by a layer of PEDOT:PSS (Figures 6E–6F). The latent heat of CSFs reached up to 124.30 J/g, which was 67% that of pristine LA. The special structure of CSFs enabled them to respond to various external stimuli, such as electrical, infrared, and sunlight. They exhibited effective energy conversion and storage properties, with a solar energy conversion efficiency of 82.8%. An electric circuit connected with a LED lamp was built using 5% flexible CSFs as conductor (Figure 6G). Strikingly, LED lamp still held the solar when 5% CSFs was bent and stretched.

Similarly, Umair et al. (2019b) designed flexible composite PCMs composed of carbonized cotton cloth as a conductive supporting structure, PW as a latent heat storage material and thermoplastic PU as a protective layer. As a result, PW@carbon cloth/PU composite PCMs showed exceptional bending and twisting deformation modes at room temperature. The charging processes of PW@carbon cloth/PU composite PCMs lasted for 150 s and 70 s at 3 V and 4 V, respectively, which spanned the range from room temperature to

the end point of the melting platform. The flexible PW@carbon cloth/PU composite PCMs can function as a flexible Joule heater for low temperature (<50°C) thermal management applications. The bending dynamic test simulated by finger-joint motion exhibited sharp electrical signals with a superior repeatability. The change in conductance upon finger motion was because of the stretching and relaxation of the fibrous network of carbon cloth, which caused a decrease and increase in the number of conductive contact points, respectively.

Except for the assembly from the cellulose and CNTs, other 1D supporting materials exhibit the great practicability to prepare flexible composite PCMs because of the desirable mechanical property. In this regard, the composite PCMs composed of numerous well-ordered 1D fibers can maintain the flexibility. Besides, 1D supporting materials can construct an effective linear thermal conductivity pathway/network structure to increase the thermal conductivity PCMs.

2D flexible composite PCMs

2D materials, such as graphene, BN, MXenes, are widely used in the fields of thermal management, photoelectric devices, thermoelectric devices because the carrier transport and heat diffusion are confined to the 2D plane (Min et al., 2018; Zhang et al., 2020b). The 2D plane can establish surface thermal conductivity transmission because of the unique advantages of being atomically thin and mechanically flexible. Therefore, the addition of 2D materials can improve the low thermal conductivity of PCM. Recently, 2D nanomaterials integrating PCMs have emerged as a novel material platform to fabricate flexible thermal energy storage devices. 2D nanomaterials endow PCMs with fascinating mechanical properties, including bending/folding strength as well as excellent flexibility. Because the large overlapping area between each nanosheet has the great benefit to allow the physicochemical properties to remain unaffected during bending or folding, contributing to ultrahigh flexibility. In this section, we provide a detailed overview of 2D flexible composite PCMs for solar-thermal, electro-thermal conversion, shape memory, thermal therapy and efficient heat transfer.

Graphene-based flexible composite PCMs

Graphene with 2D cellular lattice structure has been extensively studied in thermal energy storage fields because of the large specific surface area, high electrical and thermal conductivity, and excellent optical characteristics. Based on these superior properties, graphene-based flexible composite PCMs with novel functions have been designed and constructed. Smart fiber, a fundamental unit of textiles, is an excellent choice for advanced flexible and wearable device with various functions.

Li et al. (2018) fabricated flexible smart fibers with reversible heat conversion and storage performance by impregnating PCMs into graphene aerogel fibers. The obtained smart fibers showed tunable temperature and phase change enthalpy, as well as excellent super-hydrophobicity after coating fluorocarbon (FC) resin. Moreover, the smart fibers exhibited excellent strength and elasticity, which could be tied into a knot or woven into fabrics. The fracture strength of FC/graphene/PEG fiber reached 12.7 MPa, which was 70% higher than graphene/PEG fiber and 775% higher than graphene aerogel fiber. The Young's modulus of FC/graphene/PEG fiber reached 1.2 GPa, which was four times higher than graphene/PEG fiber and 48 times higher than graphene aerogel fiber. This enhancement effect is attributed to the coherent core-shell structure of FC/graphene/PEG fiber. Attractively, the smart fibers could respond to the external stimuli (electrical/thermal/photonic), holding great potentials in wearable fabrics and electrical devices (Figure 7E). To further improve the mechanical strength, the author used graphene aerogel fibers to prepare macroscopically densified graphene aerogel film by a press-forging method, followed by the infiltration of paraffin to obtain flexible graphene aerogel/PCMs smart films (Li et al., 2021a) (Figure 7A). The obtained composite PCMs films exhibited a fracture strength of up to 29.6 MPa, which was 3–20 times higher than those of previous reports (Aftab et al., 2018; Chen et al., 2012; Zhan et al., 2020) (Figures 7B–7D). Moreover, it could be bent into a 180° camber and the surface maintained well without fracture at room temperature or above the melting point of paraffin, indicating the flexibility.

In addition to the graphene fiber and graphene film, graphene can also be designed into 3D flexible porous supporting materials. Zhao et al. (2016) fabricated a flexible graphene foam/multilayer graphene flakes/polydimethylsiloxane (PDMS) composite. Compared with pristine PDMS, the thermal conductivity of composite PCMs reached 1.08 W/m·K with a 340% increase due to the constructed effective thermal transportation paths from synergistic effect between graphene foam and graphene flakes. The Young's modulus of

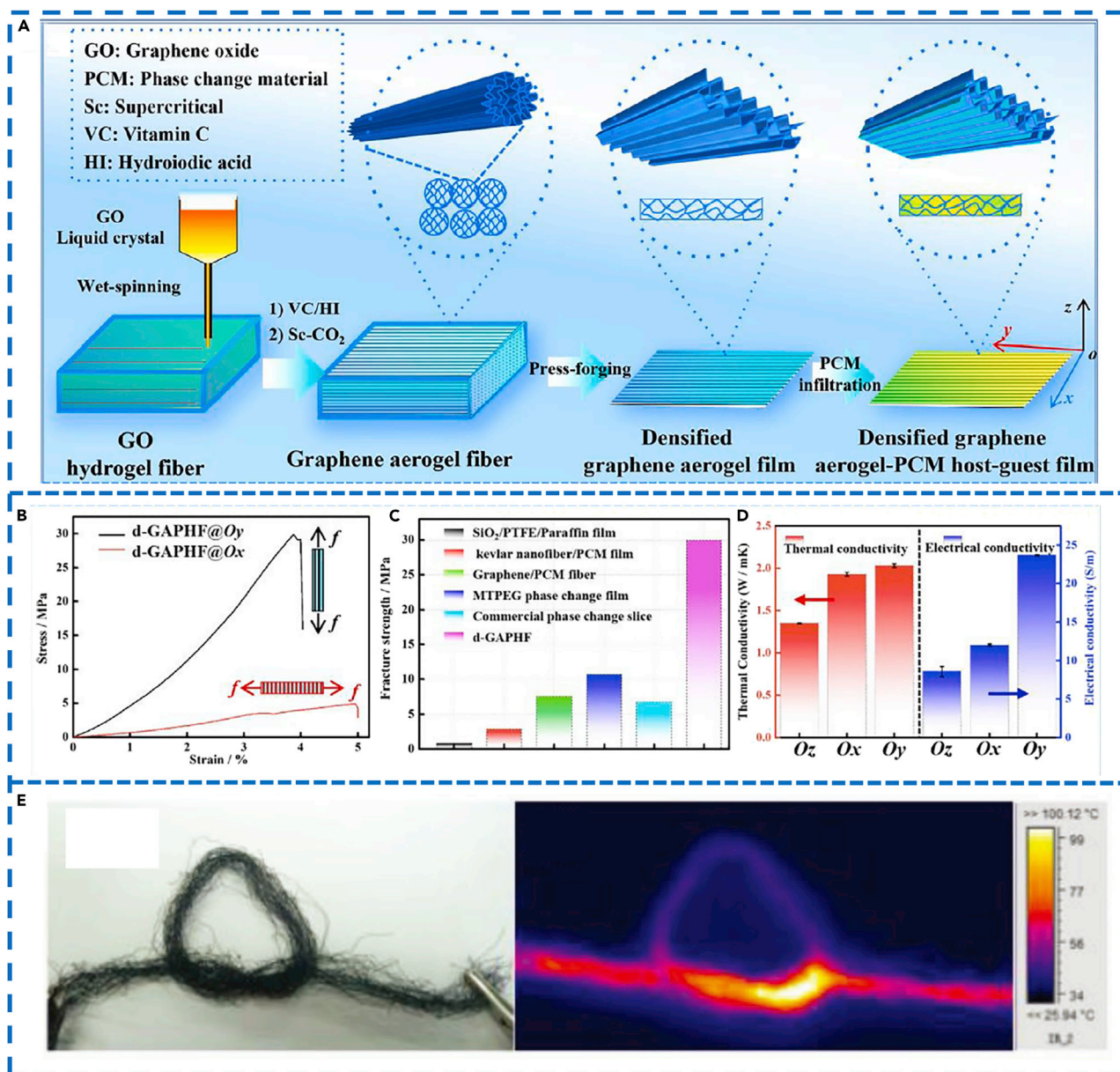


Figure 7. Graphene-based flexible composite PCMs

(A) Synthetic illustration of composite PCMs films.

(B–D) Stress-strain, fracture strength, thermal conductivity and electrical conductivity of composite PCMs films. Adapted from Li et al. (2021a) with permission; copyright 2021, Elsevier.

(E) Photograph and IR image of the fiber bundle after being tied into a knot under a 30 V. Adapted from Li et al. (2018) with permission; copyright 2018, John Wiley and Sons.

composite PCMs increased about 280% compared with pristine PDMS. The excellent thermal and mechanical properties make it a possible application in thermal management of electronics. In this work of Sun et al. (2021), a flexible graphene aerogel based porous framework was designed and constructed to infiltrate paraffin (Figure 8A). The as-prepared composite PCMs exhibited an excellent flexibility even after an extensive bending process because of PVDF-HFP polymer-enhanced structural strength, which was beneficial to the attachment on a human model. The obtained composite PCMs showed a phase change enthalpy of 154.64 J/g and kept almost unchanged after 500 cycles, demonstrating the excellent thermal property and long-term cycle stability. Moreover, the solar-thermal conversion efficiency of composite

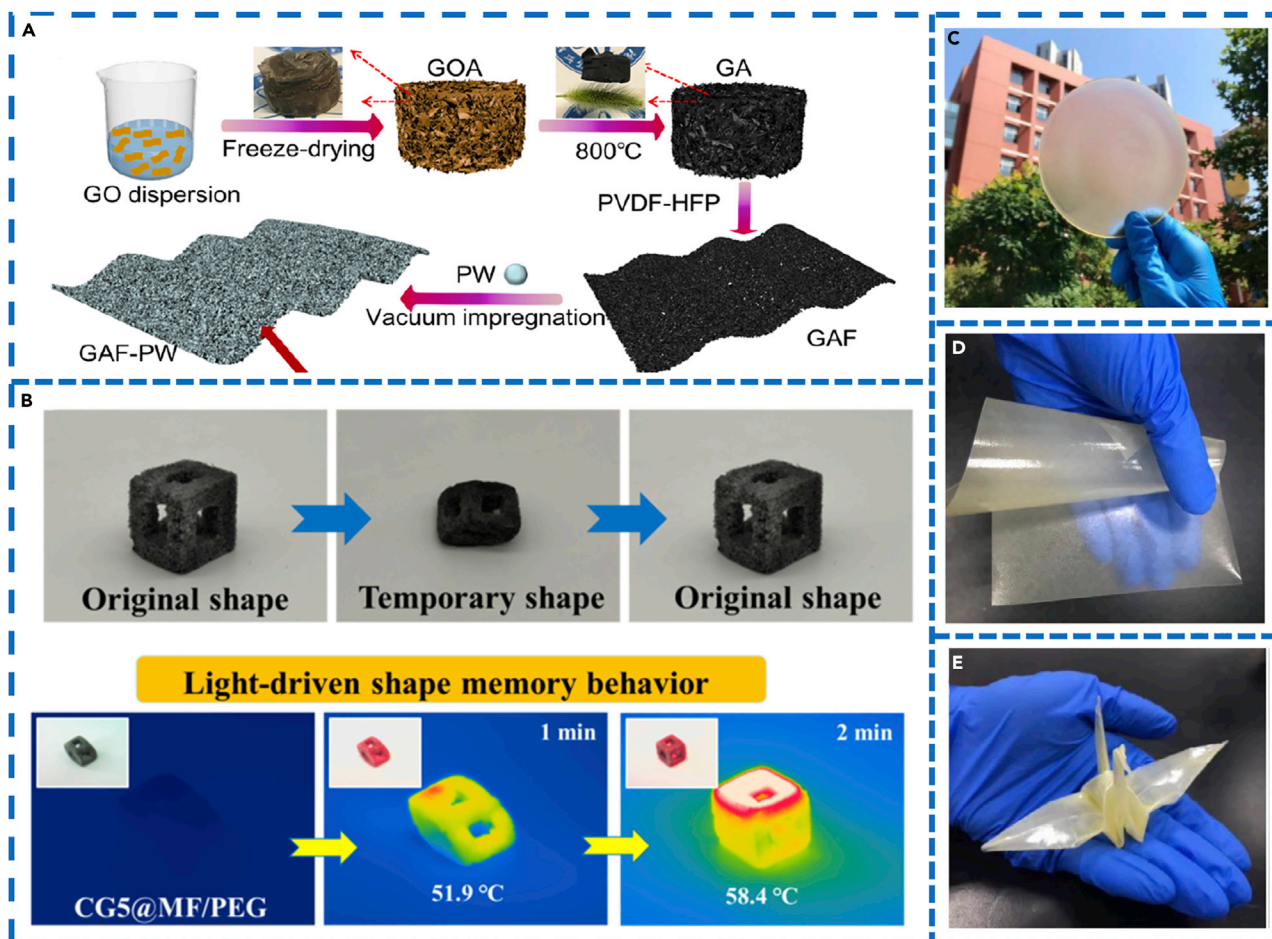


Figure 8. Graphene-based flexible composite PCMs

(A) Synthetic illustration of composite PCMs. Adapted from Sun et al. (Sun et al., 2021) with permission; copyright 2021, Elsevier.

(B) Photographs and IR images of the shape memory behaviors of CG5@MF/PEG. Adapted from Wu et al. (Wu et al., 2019b) with permission; copyright 2019, American Chemical Society.

(C–E) Photographs of MTPEG10000 film with different shapes. Adapted from Kou et al. (Kou et al., 2021) with permission; copyright 2021, Elsevier.

PCMs was evaluated to be 96.0% because of the superior ability of graphene converting solar energy into thermal energy.

In addition to single graphene as flexible carrier, a hybrid graphene/foam supporting skeleton can be also applied to improve the flexibility of composite PCMs. Wu et al. (2019b) fabricated flexible composite PCMs with solar/electro-driven shape memory and thermal energy storage functions by incorporating PEG into cellulose nanofiber/graphene hybrid-coated melamine foam (CG@MF). The CG@MF could be compressed to 90% strain and recovered to its initial shape after releasing the compression, confirming the excellent mechanical stability and recoverability (Figure 8B). The obtained composite PCMs exhibited a melting enthalpy of 178.9 J/g and a thermal conductivity of 0.26 W/m·K with a 188.9% enhancement. Moreover, the composite PCMs demonstrated a solar-thermal conversion efficiency of 89.9% and an electro-thermal conversion efficiency of 66.1%. The MF's high elasticity and graphene's excellent solar/electric thermal conversion performance make it have a significant solar/electro-driven shape memory function. Moreover, the authors further utilized reduced graphene oxide (rGO) to investigate the solar-thermal conversion ability and thermal/solar-actuated shape memory property (Wu et al., 2020a). Because of the abundant porosity of MF/rGO foam and excellent photon capture capability, composite PCMs showed a high latent heat of 144.8 J/g and good solar-thermal conversion and storage ability. More importantly, MF/rGO foam could recover their initial shape without structural fatigue even after hundreds of compression or distortion deformation cycles, which was attributed to the π - π interactions between rGO sheets and MF

skeletons. Therefore, composite PCMs exhibited reversible thermal/solar-actuated shape deformation and recovery.

In addition to the flexible supporting materials, the grafting/cross-linking technology is another excellent choice to fabricate flexible solid-solid PCMs (SSPCMs). Moreover, the phase transition temperature and enthalpy can be adjusted by selecting different molecular weights and types of PCMs. [Du et al. \(2020b\)](#) fabricated flexible SSPCMs by grafting PEG into nanofibrillated cellulose (NFC)/graphene hybrid aerogels. The obtained SSPCMs not only could recover the original height after 60 compressive cycles with a strain of 50%, but also showed a high solar-thermal conversion efficiency of 84.7%. Similarly, [Qian et al. \(2019\)](#) grafted the poly-(hexadecyl acrylate) polymer (PA16) onto a cellulose by atom transfer radical polymerization (ATRP), followed by the introduction of modified graphene (GN16). The obtained SSPCMs exhibited a phase change enthalpy of 103 J/g and a thermal conductivity of 1.32 W/m·K. The solar-thermal conversion efficiency of SSPCMs reached 89.0% at a 9 wt% GN16 loading. Moreover, the SSPCMs exhibited excellent thermally induced flexibility and were prone to various deformations under the action of external forces due to the relatively low coefficient of linear thermal expansion of the cellulose backbone and the high degree of cross-linking among the alkyl chains ([Klemm et al., 2005](#); [Xiong et al., 2018](#)).

To further enhance the thermal and electrical conductivities of flexible SSPCMs with multiresponsive functions, [Cao et al. \(2019\)](#) fabricated PA16/graphene SSPCMs via a solvent-free Diels-Alder (DA) reaction. The PA16/graphene SSPCMs exhibited a thermal conductivity of 3.96 W/m·K and an excellent electric conductivity of 219 S/m, showing great potential in solar-thermal and electron-thermal energy conversion and storage. [Kou et al. \(2021\)](#) prepared an intrinsically flexible solid-solid PCMs film by polymerically chemical grafting of melamine and toluene-2,4-diisocyanate (TDI) with PEG. The phase change temperature of resultant flexible PCMs film was tunable by varying PEG molecular weights. The flexible PCMs film still kept a relatively high latent heat of 118.7 J/g and remarkably shape foldability even after 1000 heating-cooling cycles ([Figures 8C–8E](#)). The obtained flexible PCMs film with PEG 10000 exhibited a high tensile strength of 10.7 MPa and a strain of 8.2%, revealing highly mechanical property. Furthermore, a flexible graphene film was transferred onto the flexible PCMs film to construct a wearable thermal management device with a high electro-thermal conversion efficiency of 94% at 1.5 A. In summary, pristine PCMs can be grafted into graphene or graphene base hybrid materials to gain flexible composite PCMs. This kind of SSPCMs using this technique have more reliable chemical stability and thermal stability without leakage or migration over the phase change process ([Sundararajan et al., 2018](#)). Nevertheless, this chemical cross-links may present new problems, containing non-recyclability, non-processability or non-malleability, which enormously hinder the achievement of comprehensive and sustainable development and advanced applications.

In brief, graphene is considered as an advanced flexible energy storage carrier material with great potential because of its high mechanical strength and flexibility, good conductivity without additional conductive layer, large specific surface area and high temperature resistance. Besides, their tremendous functional groups can be easily modified, which can improve the dispersion of graphene in many solvents. In addition to graphene fibers and graphene films, 3D interconnected porous graphene framework can be also employed for flexible wearable devices. Currently, graphene is regularly combined with SSPCMs to obtain flexible composite PCMs for electro-thermal conversion, photo-thermal conversion and thermal management devices.

BN-based flexible composite PCMs

Boron nitride (BN), also called “white graphite”, has a similar graphite lamellar structure, which is loose and light. Currently, although few researches focus on fabricating flexible composite PCMs with BN, it is a kind of potential materials for fabrication of flexible composite PCMs. To effectively cool the portable and wearable 5G electronics, [Wang et al. \(2020a\)](#) first fabricated flexible boron nitride (BN) aerogel films with controllable thickness (50–200 μm) by a pyrolysis process of precursor (M·2B monolith). After paraffin was infiltrated in BN aerogel films, the BN-PCMs composite films were prepared. In the BN-PCMs composite films, BN aerogel component served as the thermal insulation layer to reduce heat diffuse from electronics to skin, and paraffin component could buffer temperature variation by solid-liquid phase transition that could absorb the undesired heat and maintain a constant temperature ([Figures 9A–9B](#)). The M·2B monolith could be cut into different shapes and slices with a thickness of hundreds of micrometers, indicating the excellent machinability ([Figure 9C](#)). Benefitting from the robust nanoribbon network of M·2B

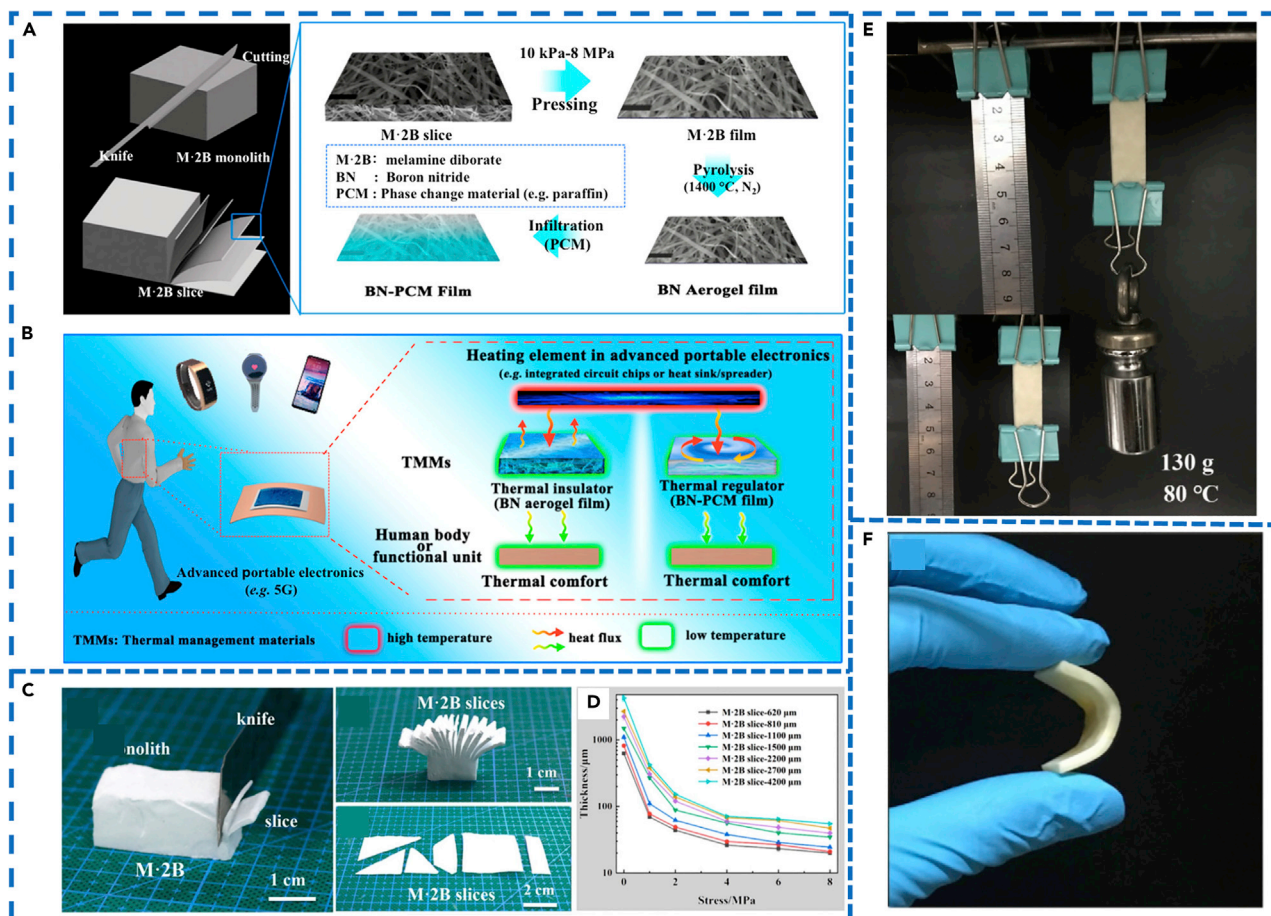


Figure 9. BN-based flexible composite PCMs

(A) Synthetic illustration of BN-PCMs composite film.

(B) Schematic of thermal management mechanisms based on BN aerogel film and BN-PCMs composite film.

(C) Photograph of M·2B slice and the M·2B monolith.

(D) Relationship between the thickness of M·2B film and stress. Adapted from Wang et al. (Wang et al., 2020a) with permission; copyright 2020, American Chemical Society.

(E–F) Shape stability of CBP-3 under different external forces. Adapted from Yang et al. (Yang et al., 2020) with permission; copyright 2020, Elsevier.

monolith, BN aerogel films inherited the excellent mechanical flexibility, whose Young's modules reached 1.14 MPa. The tensile strength and ultimate strain of BN aerogel films were about 83 kPa and 0.8%, respectively (Figure 9D). Furthermore, BN aerogel films further could be bent into a camber without cracks even though it was immersed into liquid nitrogen, indicating the excellent flexibility. This superior flexibility was attributed to the synergistic effect between the honeycomb cellular structure and the interconnecting junctions between BN nanoribbons (Lu et al., 2019a; Ren et al., 2019; Si et al., 2018; Su et al., 2018). To evaluate the thermal management performance of BN-paraffin composite films, the film was placed on the backside of a working smart 5G phone. After 1 min, the temperature of composite film increased from 31.5°C to 35.6°C, which was still lower than the original temperature (45°C). As the BN-paraffin composite film was removed, the temperature of phone would reach to 45°C rapidly again, indicating that the flexible BN-paraffin composite films could restrain electronics overheating and maintain a relatively constant low temperature state.

Contrary to the above, BN nanosheets were doped into cellulosic scaffolds to improve the inherent low thermal conductivity of PCMs in the study of Yang et al. (2020). The resulting composite PCMs exhibited an enhanced thermal conductivity of 0.40 W/m·K with an increase of 42.8% at a 1.9 wt% loading of BN nanosheets. This enhanced thermal conductivity was attributed to the formation of a complete thermally conductive network, which is different from the above aerogels with a typical porous network. The porous

network could isolate heat into the special space and reduce the heat exchange, which contributed to the superlow thermal conductivity. Attractively, the composite PCMs exhibited a high fusion enthalpy of 169.3 J/g and a high solidification enthalpy of 176.1 J/g, as well as stable cycling reliability, indicating the excellent thermal management capability. Significantly, the composite PCMs with a high loading of 95.6 wt% showed excellent flexibility against pressure, tension and bending. The composite PCMs exhibited a 90% high shape retention without leakage at 85°C when they were conducted tensile deformation (Figures 9E–9F). The flexibility was mainly ascribed to the melting of PEG, which lost the rigidity at solid state.

Thermal management of electronics based on BN not only can dissipate the undesired heat from the heating elements through the fast heat transportation, but also can isolate the thermal energy through porous aerogels with superlow thermal conductivity. Whatever way, flexibility is very important during the manipulation process and practical applications. It is a promising direction to combine BN with other different dimensionality flexible supporting materials for advanced flexible composite PCMs in the future.

MXene-based flexible composite PCMs

As a two-dimensional transition metal carbonitride, MXene has attracted much attention in the field of solar-thermal conversion due to the excellent photoabsorption ability derived from its local surface plasmon resonance (LSPR) effect (Du et al., 2020a; Fan et al., 2019; Sheng et al., 2020). Based on this advantage, Shao et al. (2021b) fabricated composite PCMs by introducing MXene into flexible melamine foam (MF), followed by the encapsulation of PEG (Figure 10A). The solar-thermal conversion efficiency of resulting composite PCMs reached 92.7% because of the constructed MXene network along the MF skeleton (Figure 10B). Moreover, the MF@MXene sponge could recover to its original shape from the compression shape upon releasing force immediately, indicating remarkable shape flexibility and recovery effects. After the infiltration of PEG, the composite PCMs showed an excellent solar-actuated shape memory property. The composite PCMs recovered to their initial shape from temporary “U” shape with a 100% shape recovery ratio, whereas the MF/PEG still maintained its temporary shape upon the irradiation of the NIR lamp. It was noted that the shape recovery rate was improved with the increase of MXene content (Figure 10E). This is because composite PCMs can absorb solar energy and convert it into heat, causing the temperature to gradually rise to the melting point of PEG. The composite PCMs at this soft state could be simply deformed into a temporary shape and the temporary shape could be fully fixed by cooling the temperature to the solidification point of PEG. When the composite PCMs were irradiated by the solar again, they could be recovered to initial shape (Figure 10C). Because of the excellent thermal/solar energy storage property and shape memory function of composite PCMs, they possessed feasibility and practicality on human thermal comfort. The authors evaluated the thermotherapy effect of composite PCMs as a heat eye-patch, which could be closely attached on human eyes and provided an about 6 min thermotherapy time with an appropriate temperature around 37°C (Figure 10D).

In addition to the direct use of flexible supporting materials with strong mechanical property, chemical cross-linking is another strategy used to fabricate flexible composite PCMs. Gong et al. (2021) fabricated flexible polyurethane/MXene/PEG SSPCMs with improved solar-thermal conversion efficiency by a polyurethane cross-linking reaction between-NCO derived from HDIT and-OH derived from the MXene and PEG (Lu et al., 2019b). The resulting composite PCMs exhibited an increased tensile strength with the increase of MXene content and showed a maximum tensile strength of 12.05MPa at a 2 wt% loading of MXene (Figure 10F). However, the tensile strength would decrease as the content of MXene continued to increase, which may be attributed to the agglomeration of MXene. Moreover, composite PCMs also possessed excellent flexibility and tear resistance without leakage at room temperature or after heat treatment (Figure 10G). This may be attributed to the formation of a 3D cross-linking network hexamethylene diisocyanate trimer (HDIT), MXene and PEG. Furthermore, the solar-thermal conversion efficiency of resulting composite PCMs reached 91.2% due to the LSPR effect of MXene (Shao et al., 2021b; Xu et al., 2018). These results demonstrated that the composite PCMs with excellent flexibility and solar-thermal conversion efficiency showed great application potential in the thermal management field of flexible wearable devices.

Although unremitting efforts have been made in the design of flexible MXene based materials, the development of MXene based flexible composite PCMs has rarely been reported. Current reports mainly concentrate on the thermal management of human body. The basic researches of MXene based flexible composite PCMs should be intensified to achieve more excellent thermal management capabilities.

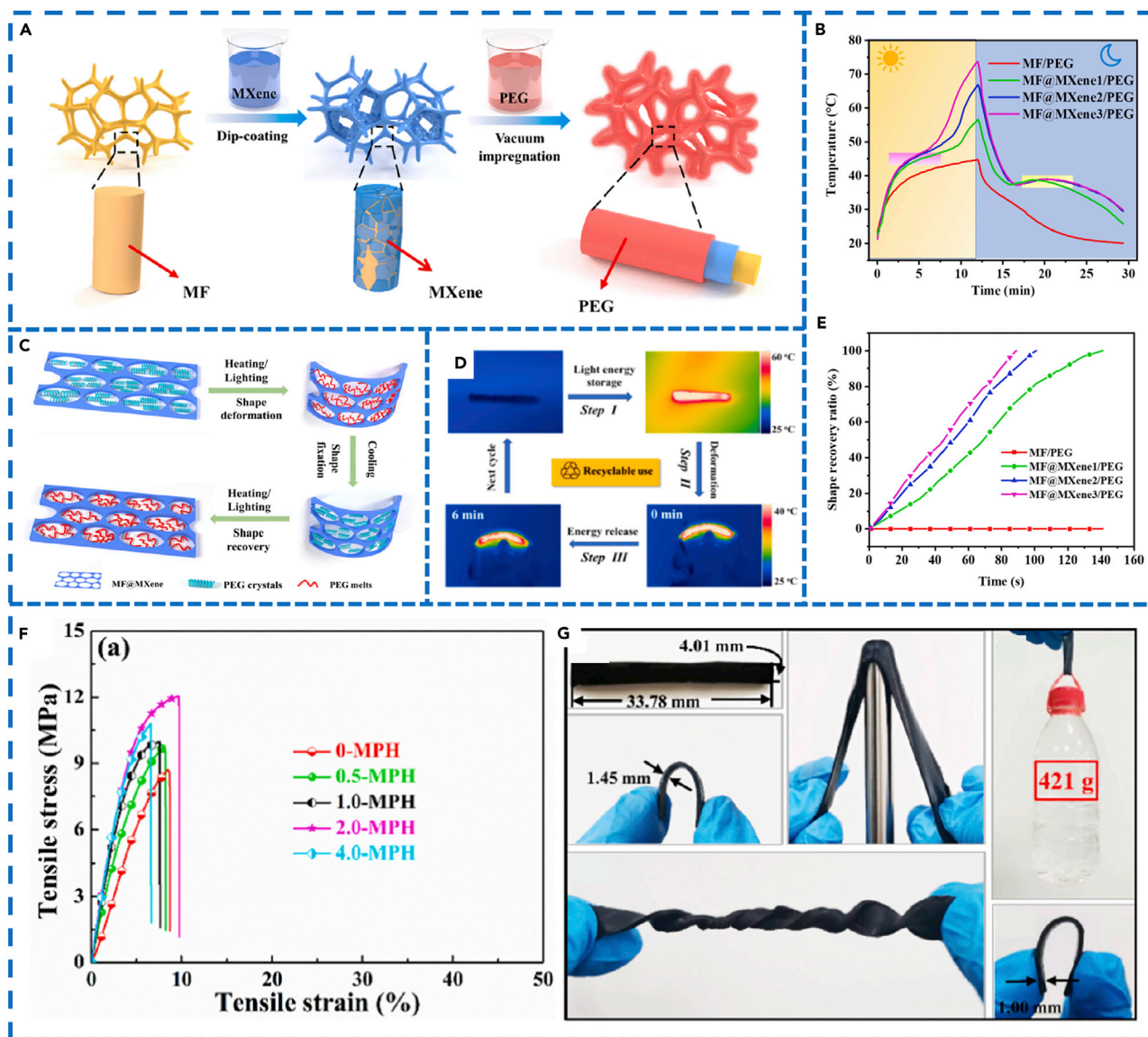


Figure 10. MXene-based flexible composite PCMs

(A) Synthetic illustration of MF@MXene/PEG.

(B) Solar-thermal curves of composites PCMs.

(C) Schematic of the solar-actuated shape memory process of MF@MXene/PEG.

(D) IR images of the temperature evolutions in different steps.

(E) Variation curves of the shape recovery ratio-irradiation time. Adapted from Shao et al. (Shao et al., 2021b) with permission; copyright 2021, Elsevier.

(F) Stress-strain curves of SSPCMs at room temperature.

(G) Mechanical properties of SSPCMs after heat treatment at room temperature. Adapted from Gong et al. (Gong et al., 2021) with permission; copyright 2021, Elsevier.

3D flexible composite PCMs

Recently, numerous 3D flexible materials have been constructed with micro-nano materials as the basic units through various preparation methods (Maleki et al., 2019, 2020; Shchukina et al., 2018). These 3D flexible materials show great potential in thermal management, energy conversion, and wearable devices because of the superior mechanical properties and porous structures (Ali, 2020; Liu et al., 2018; Umair et al., 2019a; Varzi et al., 2018; Zhang et al., 2020a). 3D materials have higher thermal transfer efficiency than 1D and 2D materials because the thermal contact resistance decreases with increasing dimensions. Besides, owing to intrinsic 3D-conductive network, an effective conductive pathway/network structure

can be formed. In this section, we summarized the mechanical properties and thermal management properties of 3D flexible composite PCMs.

EG-based flexible composite PCMs

Expanded graphite (EG), a kind of porous vermicular graphite derivative, is obtained by thermal exfoliation of chemically intercalated graphite flakes. The volume and surface of EG instantly expand in high temperature, so EG shows loose, porous and bending structure. The vermicular graphite can incorporate with each other to strengthen its softness, resilience and plasticity. To solve the strong rigidity and low thermal conductivity issues of pristine PCMs, Li et al. (2017) fabricated thermal sensitive flexible composite PCMs by using olefin block copolymer (OBC) and EG instead of conventional supporting materials to encapsulate paraffin (Figure 11A). The resulting composite PCMs not only exhibited a latent heat storage capacity of 111.4 J/g, but also presented an enhanced thermal conductivity of 1.68 W/m·K at a 3 wt% loading of EG, which was 479% higher than that without any additives. Compared with conventional rigid PCMs, the resulting composite PCMs exhibited superior softness and flexibility when they were slightly heated higher than the melting point of paraffin (Figure 11B). Noticeably, the contact gap between the flexible composite PCMs and the device was lower than 30 μm with a minimum of zero, which was far lower than that of conventional PCMs. More importantly, the transformation from rigid to flexibility responding to temperature is reversible. The predominant flexibility of composite PCMs with enhanced thermal conductivity contributes to the application of PCMs in energy storage thermal management fields.

Wu et al. (2020c) prepared highly thermally conductive flexible composite PCMs by using OBC and EG network as the supporting material to infiltrate paraffin, followed by the mechanical compression to form an aligned and interconnected percolation network. Compared with strong rigid paraffin/EG at 25°C, the strain of composite PCMs reached 5.4% at an external force of 2.2 MPa. The strain was enhanced with the increased temperature and reached about 14% at an external force of 2.5 MPa at 50°C, which was attributed to the mobility of molecule chain of paraffin within the network when the temperature exceeded the melting point of paraffin (Lv et al., 2016). The thermal conductivities of composite PCMs reached 4.20–32.80 W/m·K at EG loadings of 5–40 wt% because of the anisotropic structure. Moreover, the resultant flexible composite PCMs films could cool the commercial lithium-ion battery more than 12°C, indicating efficient thermal management capability.

Similarly, some analogous OBC/EG researches have also been reported and the results showed that the battery temperature could be effectively cooled down in comparison to natural cooling with the applied flexible composite PCMs (Huang et al., 2019b; Lin et al., 2021b). For example, flexible styrene butadiene styrene (SBS)@paraffin/EG composite PCMs were prepared based on a chain shutting technology of multi-block thermoplastic elastomers (Huang et al., 2021a). The resultant composite PCMs at a 4 wt% loading of EG exhibited a tensile strength of 0.38 MPa and a bending strength of 0.75 MPa. It is worth noting that the mechanical properties of composite PCMs tended to decrease as the content of EG further increased. The flexible mechanism of composite PCMs was illustrated in Figure 11C. When the temperature was above the melting temperature of paraffin, composite PCMs would transform from rigidity to flexibility and could adapt well to the external forces. Moreover, when the flexible composite PCMs films were introduced into the battery module, the temperature could be always controlled below 46°C during a 5 C discharging process. To improve the tensile strength thermal conductivity and photo-thermal efficiency of PCMs, Cai et al. (2021) used EG and thermoplastic elastomer to encapsulate the paraffin for the preparation of flexible composite PCMs. The obtained flexible composite PCMs showed a melting enthalpy of 124.6 J/g and a high thermal conductivity of 2.20 W/m·K (Figure 11D). The tensile strength and breaking elongation of composite PCMs reached 2.1 MPa and 220%, respectively (Figure 11E). Moreover, flexible composite PCMs demonstrated a good photo-thermal conversion efficiency of 75.2% (Figure 11F).

In brief, EG usually plays a role in enhancing thermal conductivity in EG based flexible composite PCMs, which could guarantee effective thermal management for human body and wearable electronic devices. In addition, EG can also contribute to the improvement of mechanical properties of EG based flexible composite PCMs.

Foam-based flexible composite PCMs

Foam demonstrates superior characteristics such as cheap, lightweight, stable, and compatible traits. MF (melamine foam) has an interconnected network with high open porosity of 99% and pore size of about

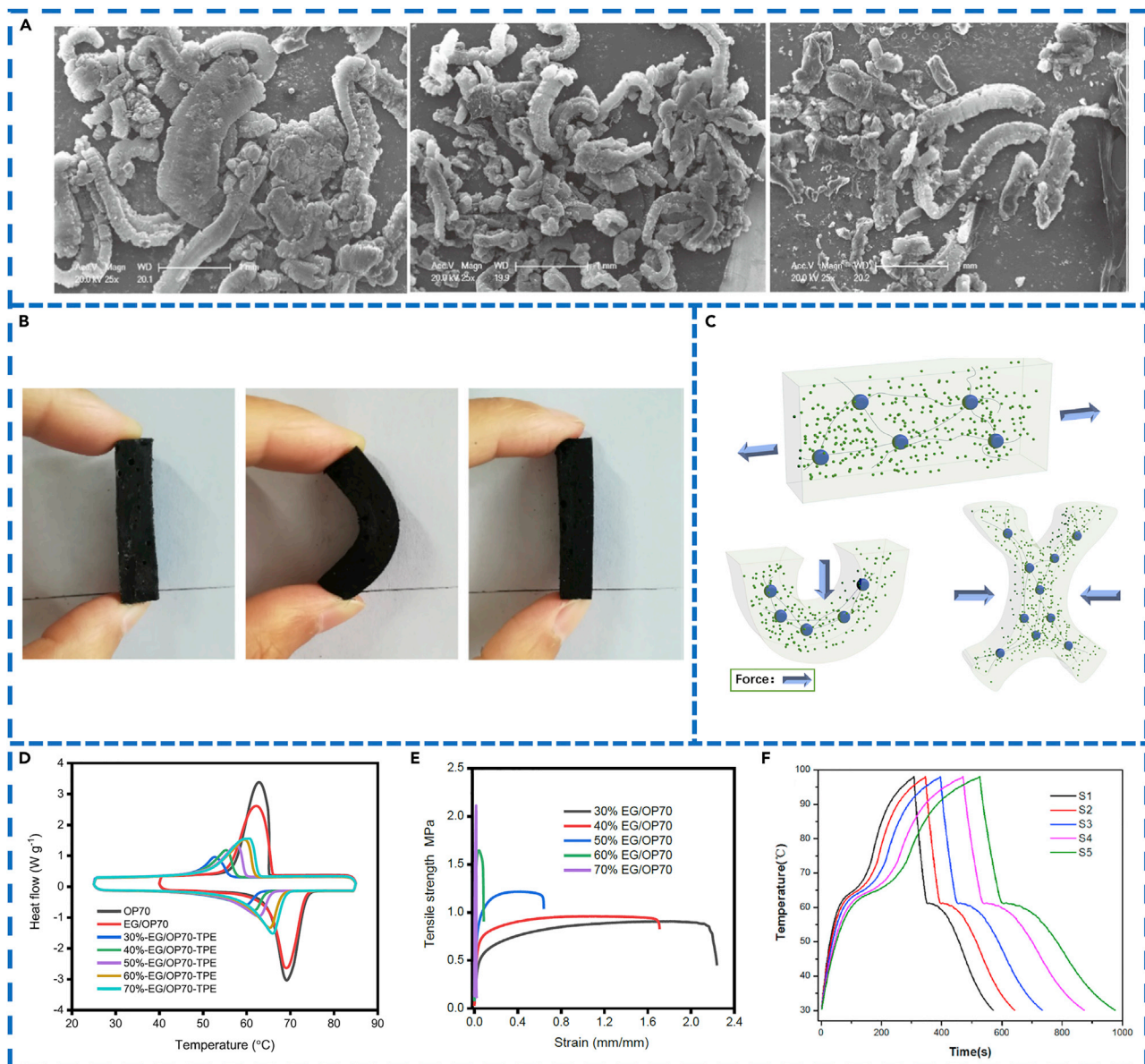


Figure 11. EG-based flexible composite PCMs

(A) SEM photographs of EG.

(B) Illustrations of bending deformation for flexible PCMs above paraffin melting point. Adapted from Li et al. (Li et al., 2017) with permission; copyright 2017, Elsevier.

(C) Mechanism models of the flexible SBS@PA/EG. Adapted from Huang et al. (Huang et al., 2021a) with permission; copyright 2021, Elsevier.

(D) DSC curves of composite PCMs.

(E) Tensile strength of composite PCMs.

(F) Solar-thermal curves of composite PCMs. Adapted from Cai et al. (Cai et al., 2021) with permission; copyright 2021, Elsevier.

100 μm . Moreover, MF possesses excellent elasticity, meaning that MF can be deformed and quickly recovered to its original shape without structural fatigue. Therefore, combining MF and PCMs is considered as a feasible routine for preparing 3D flexible composite PCMs.

Flexible PW@MF composite PCMs with thermal energy storage and shape memory functions was prepared through vacuum impregnation (Jing et al., 2019). MF could not only prevent the leakage of PW but also serve as a permanent phase for shape recovery. The stored resilience of MF could be released and drive

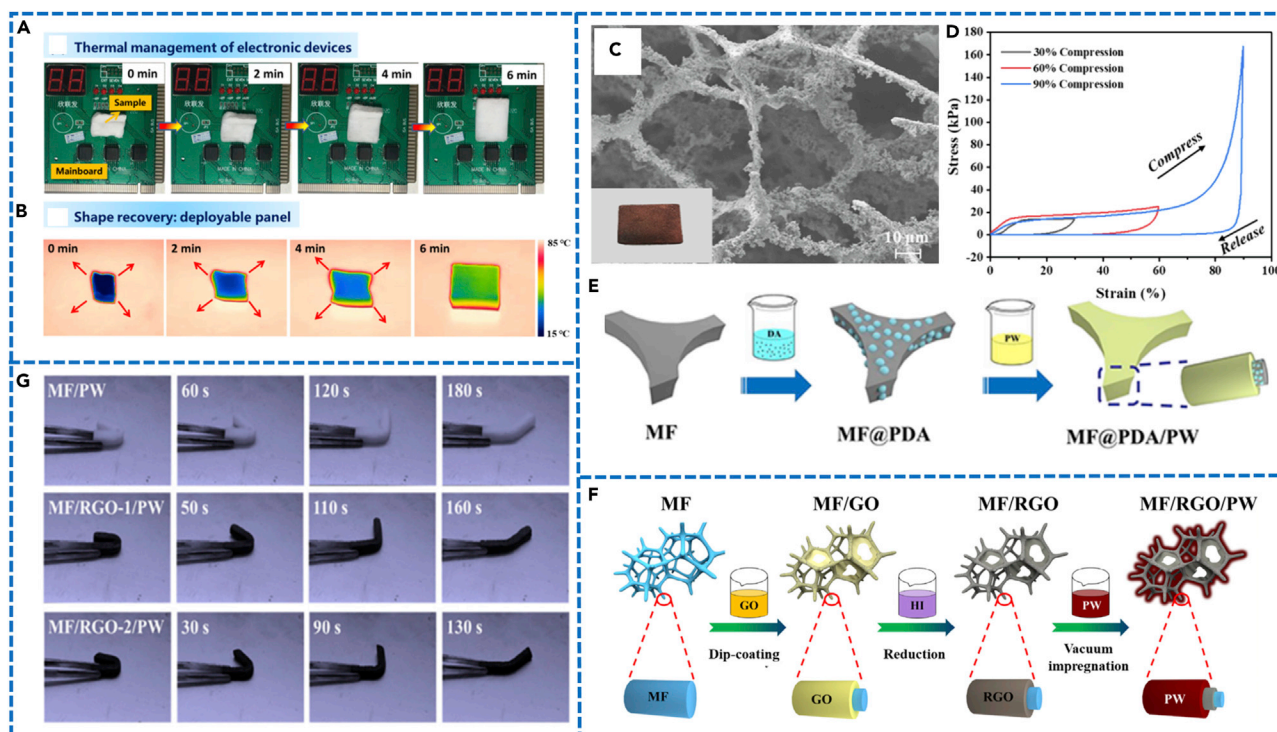


Figure 12. Foam-based flexible composite PCMs

(A) Photographs of composite PCMs used for thermal management of electronic devices.

(B) IR images of the shape recovery from a compressed shape to a square shape. Adapted from Jing et al. (Jing et al., 2019) with permission; copyright 2019, American Chemical Society.

(C) SEM image of Cu/MF foam.

(D) Stress-strain curves of Cu/MF foam under various strains. Adapted from Xiao et al. (Xiao et al., 2021) with permission; copyright 2021, Elsevier.

(E) Synthetic illustration of PW@PDA/MF. Adapted from Wu et al. (Wu et al., 2019a) with permission; copyright 2019, American Chemical Society.

(F) Synthetic illustration of PW@rGO/MF composite PCMs.

(G) Thermal-actuated shape recovery behaviors. Adapted from Wu et al. (Wu et al., 2020a) with permission; copyright 2020, Elsevier.

flexible PW@MF composite PCMs to recover their original shapes. Upon heating above the melting temperature of PW, composite PCMs became flexible and could be easily deformed to a temporary shape (Figure 12B). The thermal conductivity of flexible PW@MF composite PCMs was only about $0.30 \text{ W/m}\cdot\text{K}$ owing to MF with low thermal conductivity, which was lower than those of other thermally conductive PCMs. Combining MF with high thermal conductivity additives will help increase the thermal conductivity of flexible PCMs and accelerate the thermal charging/discharging rates (Figure 12A). Xiao et al. (2021) prepared flexible PEG@Cu/MF composite PCMs with 3D interconnected thermal-conductive additive network via electroless copper (Cu) plating on porous MF (Figure 12C). The tensile strength of Cu/MF foam reached 72.37 kPa , which was increased by nearly 2 times compared with that of pristine MF under the same strain of 11% (Figure 12D). The thermal conductivity of flexible PEG@Cu/MF was $0.33 \text{ W/m}\cdot\text{K}$, which is increased by nearly 6 times compared with that of PEG@MF, which could be attributed to the continuous thermal conductive Cu network constructed along with MF skeleton. Apart from the thermal conductivity enhancement, 3D Cu network also imparted MF@Cu/PEG with excellent electro-thermal energy conversion efficiency of 85.6% because of their inner 3D conductive network.

Except electro-thermal conversion function of MF based flexible composite PCMs, they also can be employed in solar-thermal conversion. Pristine PCMs are not capable of directly driving solar-thermal conversion because of their poor solar capture ability (Latibari and Sadrameli, 2018). Polydopamine (PDA) is often utilized as solar-absorbing additive to improve the photo-thermal conversion efficiency of composite PCMs due to its high photoabsorption, photostability, and photo-thermal conversion efficiency (Li et al., 2016; Liu et al., 2013a). Wu et al. (2019a) prepared polydopamine (PDA)-coated MF based flexible PW@PDA/MF composite PCMs, which displayed a high phase change enthalpy (140 J/g) and high thermal storage

capability (90 wt%) (Figure 12E). The solar-thermal conversion efficiency of flexible PW@PDA/MF was calculated as 80.8% while PW@MF could not drive solar-thermal energy conversion. Therefore, PDA coating was an effective strategy to improve the solar-thermal energy storage properties of MF based flexible composite PCMs. Although MF itself lacks excellent solar-absorbing capability, carbon foam derived from MF is not only sensitive to solar sources, but also holds excellent flexibility of MF. Flexible carbon foam-based composite PCMs was fabricated by encapsulating n-eicosane into carbon foam skeleton that was precoated with Ti_2O_3 nanoparticles (Wang et al., 2019). The loading percentage of n-eicosane was 84 wt% and the phase change enthalpy of flexible composite PCMs was 200.6 J/g, which guaranteed excellent temperature regulation capability. The solar-thermal energy conversion of eicosane@ Ti_2O_3 /PDA/MF with a low volume concentration of Ti_2O_3 (7.5%) was 88.2% because Ti_2O_3 located on the surface of carbon foam served as the media for efficient photo-thermal conversion.

Similar to PDA, reduced graphene oxide (rGO) not only displays high solar capture ability, but also shows excellent mechanical and thermal transfer properties. Flexible PW@rGO/MF composite PCMs were fabricated with simultaneous shape memory and solar-thermal conversion functions (Wu et al., 2020a) (Figure 12F). PW@rGO/MF composite PCMs could be compressed or twisted, and completely recovered their original shape without significant structural fatigue. The temporary bended shape ("U" shape) could be fixed, after cooling to 20°C and releasing load of flexible composite PCMs. When the fixed samples were put on the heating stage at 80°C, they could restore their original straight shape (Figure 12G). Flexible composite PCMs exhibited solar/thermal-sensitive shape memory function by triggering the phase transition of PW. Similarly, Tao et al. prepared continuous MF frameworks wrapping with rGO via a simple circular impregnation and in-situ reduction process (Tao et al., 2020). The cube of resulting flexible PW@rGO/MF composite PCMs could recover easily without any shedding of rGO sheets, indicating rGO sheets were tightly adhered to the MF. As a result, flexible PW@rGO/MF composite PCMs achieved increased thermal conductivity (0.46 W/m·K), excellent energy storage density of 170.4 J/g (90 wt% PW) and efficient solar-thermal conversion efficiency of 85%. Based on the comprehensive performances of flexible PW@rGO/MF composite PCMs, domestic storage systems for solar-thermal water are designed to broaden the application of PCMs in the solar-thermal energy field.

Apart from commercial MF, PU foam is also utilized to encapsulate PCMs for preparing flexible composite PCMs. Flexible solar-absorbing composite PCMs were prepared by impregnating stearic acid (SA) into rGO-coated PU foam (Chang et al., 2020). Inspired by the behavioral spreading and folding of butterfly wings, this roll-to-roll charging strategy overcame the heat transfer limitation for fast solar-thermal energy harvesting within flexible composite PCMs. The thermal conductivity of SA@rGO/PU composite PCMs with a low loading of rGO (~1 wt%) was increased to 0.47 W/m·K whereas pristine SA was only 0.28 W/m·K. The effective improvement of thermal conductivity of flexible composite PCMs should be attributed to the formation of 3D conductive networks along the PU foam skeleton. Solar-thermal converted energy was stored within the flexible PW@rGO/PU composite PCMs (90 wt%) through the fast roll-to-roll direct illumination charging. After the charging process was completed, the rolled state minimized the exposed surface area, thus suppressing heat losses from the PCMs surfaces and facilitating a long-term storage of harvested solar energy. The flexible composite PCMs heat packs possessed a higher energy density and a comfortable temperature range, which was beneficial to thermotherapy application. Resultantly, thermotherapy temperature at 40°C could last for 15 min via wrapping two layers of charged PW@rGO/PU composite PCMs onto human arm or wrist, which was favourable to mitigating body pain or tiredness.

Graphene nanosheets are typical hydrophobic additives. They have poor dispersibility in aqueous solution, so it is difficult to ensure uniform dispersion of graphene nanosheets in MF. On the contrary, GO can promote the dispersion of graphene in the aqueous condition via strong π - π interactions between GO and graphene (Ye et al., 2015). Based on this strategy, flexible composite PCMs were fabricated based on commercial MF incorporated by GO and graphene (Xue et al., 2019). After hydrothermal reaction and carbonization, the composite aerogel still maintained 3D composite framework structure with rGO and graphene covering on the carbonized MF framework. The obtaining flexible composite PCMs exhibited a high phase change enthalpy retention rate (nearly 100% of PW), high thermal conductivity (1.46 W/m·K) and electrical conductivity (2.79 S/cm) at a filler content of 4.89 wt%. At a constant voltage of about 2.9 V, the current was about 0.21 mA in the composite PCMs. The electro-thermal energy conversion efficiency of composite PCMs was calculated about 62.5%. These results indicated that flexible composite PCMs could be used in temperature protection of microelectronic devices.

In brief, foam (MF, PU foam and carbon foam) is conducive to enhancing the mechanical properties of PCMs due its continuous 3D network and appropriate pore structure. However, commercial foams show low thermal conductivity and poor solar capture capability. Therefore, adding high thermal conductivity additives (metal nanoparticles, graphene nanosheets, etc.) and solar absorbers (PDA, rGO, etc.) can efficiently improve the thermal properties of foam based flexible composite PCMs.

Other 3D-based flexible composite PCMs

Generally, the melting PCMs molecules adsorbed by the flexible network structure can move freely so that the corresponding composite PCMs exhibit elastic deformation and excellent flexibility. Therefore, encapsulating PCMs into a 3D flexible spatial network is a prospective way to prepare flexible composite PCMs. [Huang et al. \(2021c\)](#) reported a kind of flexible composite PCMs with shape memory and self-healing functions by encapsulating ethylene glycole distearate (EGDS) to the epoxy-based polymer matrix with SA segments anchored on the side chains using a photo-initiated polymerization method. The obtained composite PCMs exhibited reversible shape deformation and recovery behaviors, including three steps in the shape recovery successively: 1) a minor shape recovery at around 33°C due to the phase transition of SA segments; 2) an about 14% shape recovery at around 45°C due to the heterogeneous melting nucleation of EGDS; 3) a 100% shape recovery ratio after the solid-liquid phase transition of EGDS ([Figure 13B](#)). It was noted that the time for full shape recovery would increase with the increase of EGDS concentration due to the increments of fusion entropy. Moreover, composite PCMs exhibited a thermo-induced self-healing function because of the solid-liquid transition of EGDS and the interactions between SA segments and EGDS.

Similarly, [Zhang et al. \(2021\)](#) fabricated a 3D network of polymerized polyacrylamide (PAM) that formed hydrogen bonds with PEG2000 using a molecular self-assembly method. The obtained flexible composite PCMs loading 60 wt. % PEG2000 showed an ultimate stretch length ratio of 530% and a tensile strength of 26 kPa. Moreover, the length of composite PCMs with an initial length of 7.5 cm could increase to 19.6 cm without liquid leakage and fracture at a weight of 200 g and 55°C, indicating the excellent elasticity in the high temperature environment ([Figures 13D–13F](#)). This is because the filled melted PEG2000 could hinder the volume shrinkage of 3D network in the high temperature environment. However, the volume shrinkage of 3D network without PEG2000 reached 13%. Similarly, flexible eicosane/PAM biphasic organohydrogel was synthesized in the study of [Shen et al. \(2021\)](#). In contrast to the above, eicosane was insoluble in water. The compression stress of composite PCMs reached 476.4kPa at a 60% strain. The composite PCMs could almost recover to the initial shape when the compression was removed, indicating the remarkable toughness and self-recovery capacity. In addition, the temperature of miniature wooden model house covering composite PCMs was about 13°C lower than that of no gel-covering, indicating the efficient passive cooling capacity.

Thermoplastic elastomers, such as OBC ([Ma et al., 2020](#); [Qi et al., 2019](#); [Wu et al., 2020d](#)), PDMS ([Alfadhel et al., 2018](#); [Owuor et al., 2018](#); [Shi et al., 2020b](#); [Wang et al., 2020c](#)), and SBS ([Huang et al., 2021b](#); [Sun et al., 2018](#)), are also capable of constructing a crosslinked network to encapsulate PCMs for the preparation of flexible composite PCMs. [Wu et al. \(2019d\)](#) prepared thermally induced flexible composite PCMs by infiltrating paraffin into OBC thermoplastic elastic supporting skeleton. Actually, other additives with specific functions could be also introduced into the thermoplastic elastic crosslinked network, such as CNTs, MXene, BN. OBC could form a contiguous 3D network composed of soft blocks and hard blocks to stabilize PCMs. Paraffin in the soft blocks would melt and generate amorphous phases with chain mobility upon heated above the melting point of paraffin. At this moment, composite PCMs were transformed into flexible block and could be deformed under external force accompanied by the distance changing between hard blocks and a loss of entropy. It was noted that the distance and entropy were restored to the original state when the external force was released, thus stimulating the shape to return to the original shape. In addition, composite PCMs with higher EG mass fraction exhibited a quicker heating and cooling rate than that of lower EG mass fraction ([Figure 13C](#)).

It should be noted that chemical grafting strategy is an excellent and promising method to synthesize flexible composite PCMs. [Yin et al. \(2021\)](#) prepared flexible PCMs film consisting of cyclodextrin (CD) “wheels” and poly (ethylene oxide) (PEO) “axles” by a polyrotaxanes (PLR) grafting method. The Young’s modulus, tensile strength, and elongation at break of flexible PCMs film with 80 wt% α -CD loading was 1755.3 MPa, 24.3 MPa, and 451%, respectively, which were 2.56, 2.25, and 1.66 times of original PEO. PCMs film could be twisted, folded, and stretched. Moreover, PCMs film exhibited outstanding shape-fixing and recovery ratios of about 90% and 99%, respectively. The reinforcement and toughening of PLR may be attributed to

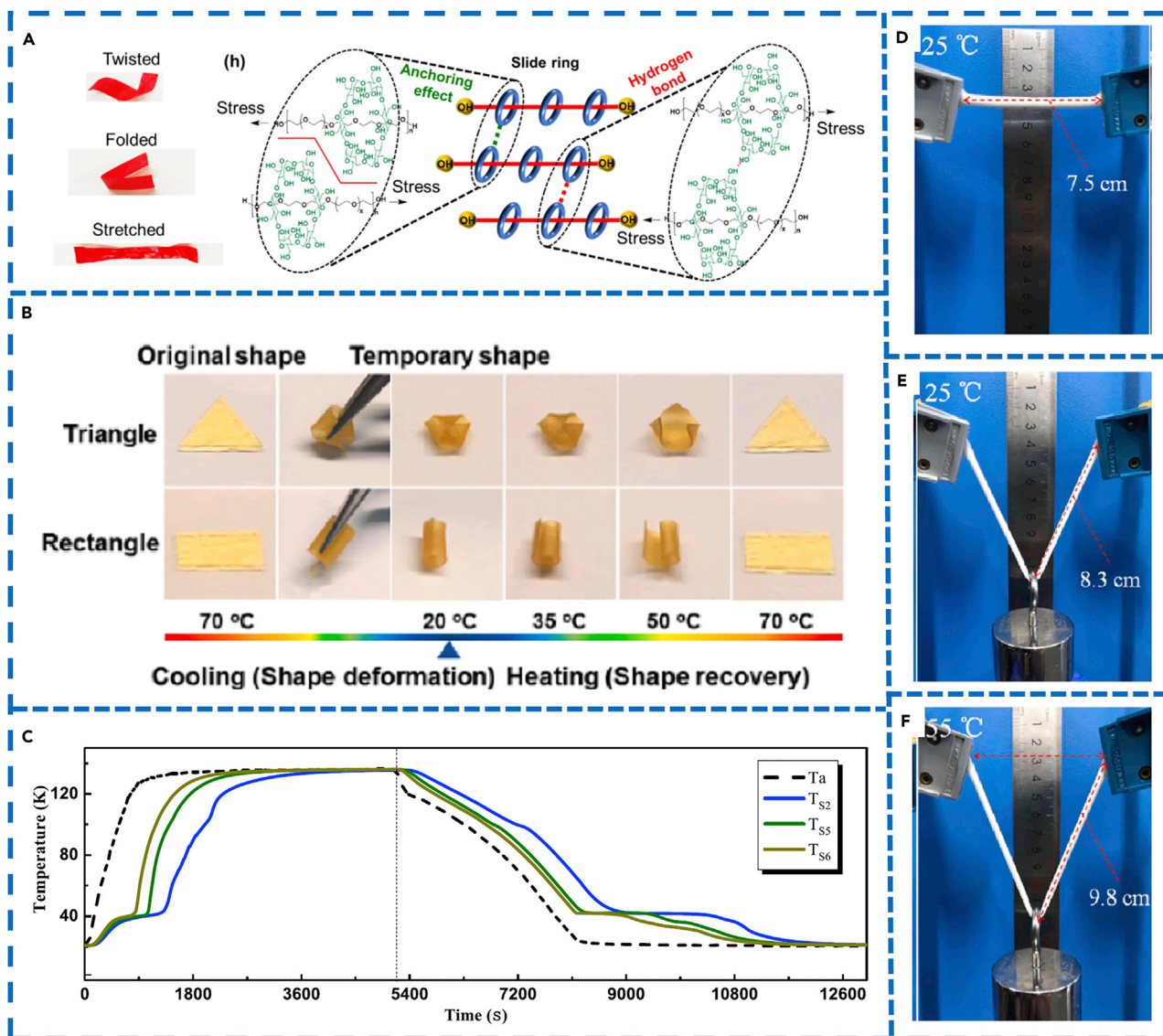


Figure 13. Other 3D-based flexible composite PCMs

(A) Mechanical enhancement mechanism. Adapted from Yin et al. (Yin et al., 2021) with permission; copyright 2021, Elsevier.

(B) Photographs of reversible shape deformation and recovery behaviors of composite PCMs. Adapted from Huang et al. (Huang et al., 2021c) with permission; copyright 2021, Elsevier.

(C) Temperature-time curves of composite PCMs. Adapted from Wu et al. (Wu et al., 2019d) with permission; copyright 2019, Elsevier.

(D–F) Photographs of the composite during stretching. Adapted from Zhang et al. (Zhang et al., 2021) with permission; copyright 2021, Elsevier.

the hydrogen bonding and riveting among α -CD, and the crystallization of PEO and α -CD in PLR (Choi et al., 2017). In the network, α -CD units played a role of physical entanglement and slide rings guaranteed the free slip of PEO molecular, thus effectively avoiding stress concentration. In addition, PEO and α -CD crystal could form a physical crosslinking point in PLR, which could also enhance the mechanical behaviors (Figure 13A). Strikingly, flexible PCMs film showed a tunable phase change enthalpy of 57.1–104.3 J/g by varying the α -CD content, which was sustainable for thermal energy storage and temperature regulation of flexible electronic devices.

In brief, the 3D flexible spatial network composed of one or more different constituents/substances usually have more free space and junctions, which makes the composite PCMs easier to stretch and move. The composite PCMs not only exhibit flexibility, but also broadened advanced applications of PCMs.

CONCLUSIONS AND FUTURE PROSPECTS

Multifunctional PCMs have been widely explored for advanced latent heat storage systems. Extensive utilization of PCMs in thermal regulation can efficiently heat or cool human body, building and electric battery etc. Nevertheless, liquid leakage, intrinsic rigidity and easy brittle failure are the long-standing bottlenecks of conventional PCMs, which seriously hinder their widespread applications. Facing low-carbon and green strategic demands, therefore, great efforts have been invested in flexible thermal regulation systems based on shape-stabilized composite PCMs, and advanced applications have been explored to satisfy diverse thermal regulation requirements. Importantly, flexible composite PCMs can effectively overcome the long-standing bottlenecks mentioned above, and can guarantee superior mutual contact with integrated devices, thereby providing great application potential. In this review, we provide a comprehensive overview of preparation strategies, flexibility enhancement, flexible mechanisms, thermal performance and the state-of-the-art applications of flexible PCMs-based thermal regulation systems from the perspective of material chemistry.

Compared with conventional composite PCMs, flexible shape-stabilized composite PCMs exhibit remarkable advantages, including excellent flexibility, lightweight, intelligence, and wearability. Based on the flexibility mechanisms, we focused on two preparation strategies: physically encapsulating PCMs into flexible supporting materials, and chemically grafting PCMs onto the supporting materials. In regard to flexible composite PCMs, we creatively divided them into 1D (cellulose, CNTs and other 1D materials), 2D (graphene, BN and MXene) and 3D (EG, sponge and other 3D materials) flexible composite PCMs according to the structural dimensionality. Benefiting from significant thermal performances, shape evolution and adaptability, flexible composite PCMs exhibit remarkable achievements in air-conditioning, thermal regulation of human body, electronic devices and batteries, thermal therapy, shape memory and solar/electro-thermal energy conversion.

Although numerous important advancements have been made in flexible shape-stabilized composite PCMs for thermal regulation systems, more efforts and challenges are still required to further investigate and conquer in the future. 1) Currently, there is a serious conflict between the flexibility and thermal storage capacity of composite PCMs. Further research should focus on how to balance the flexibility and thermal storage capacity of composite PCMs. 2) High-performance flexible composite PCMs with higher thermal conductivity should be further developed for better thermal regulation. 3) The development of new flexible wearable and self-repairing energy storage devices based on PCMs integrated with other advanced functions is a promising research direction. 4) The flexibility mechanisms of flexible shape-stabilized composite PCMs need more systematic explanations for better practical applications. 5) To realize the practical application of flexible PCMs in complex and harsh conditions, stable flexibility and durability should be guaranteed under different conditions. Further researches should focus on the stability and durability of flexible PCMs. 6) Specific evaluation criteria, assessment index, and test standards of flexible PCMs (such as bending and twisting angle, tensile length, fatigue test, etc.) should be established in further research. In addition, flexible characterization techniques need further development, such as extension test, pre-stretching and nanoindentation techniques. 7) Exploring low-cost, large-scale and refined production technology of flexible PCMs is a very valuable research direction, although the road is very long and bumpy. 8) The potential and emerging applications of flexible PCMs should be further developed such as thermo-electric conversion, nanogenerator, electromagnetic shielding, etc.

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AUTHOR CONTRIBUTIONS

Conceptualization: X. C. and P. C.; Visualization: P. C. and Z. T.; Writing-Original Draft: P. C. and Z. T.; Writing-Review & Editing: P. C., Z. T. and X. C.; Copyright: Y. G., P. L. and C. L.; Funding Acquisition: X. C.; Supervision: X. C.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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