

Polyethylene Glycol–Calcium Chloride Phase Change Materials with High Thermal Conductivity and Excellent Shape Stability by Introducing Three-Dimensional Carbon/Carbon Fiber Felt

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Cite This: *ACS Omega* 2021, 6, 33033–33045



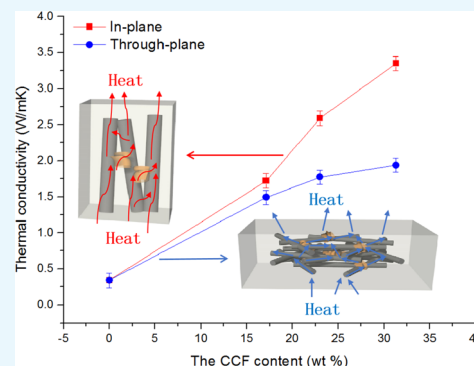
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ABSTRACT: The low thermal conductivity and poor shape stability of phase change materials (PCMs) have seriously restricted their applications in energy storage and energy saving. In this paper, poly(ethylene glycol)–calcium chloride/carbon/carbon fiber felt (PEG–CaCl₂/CCF) PCMs were fabricated by a liquid-phase impregnation–vacuum drying–hot compression molding method with carbon/carbon fiber felt as the three-dimensional (3D) thermal skeleton and PEG–CaCl₂ as the polymer PCM matrix. PCMs were heated and compressed by the compression confinement method to improve the contact area between 3D skeleton carbon fibers. The carbon fibers in PCMs presented a 3D (*X–Y–Z*) network structure and the fiber arrangement was anisotropic, which were beneficial to improve the thermal conductivity of PCMs in the fiber direction. The compression confinement can improve the contact area between the fibers in the 3D skeleton. As a result, the thermal conductivity of PEG–CaCl₂/CCF PCMs can reach 3.35 W/(m K) (in-plane) and 1.94 W/(m K) (through-plane), about 985 and 571% of that of PEG–CaCl₂, respectively. Due to the complexation of PEG and CaCl₂ and the 3D skeleton support of carbon fiber felt, PCMs have excellent shape stability. The paper may provide some suggestions for the preparation of high thermal conductivity and excellent shape stability PCMs.



INTRODUCTION

Polymer phase change materials (PCMs) can absorb heat by melting when the temperature is high and also can release heat by recrystallization when the ambient temperature is low. In the process of heat absorption or heat release, the temperature of PCMs is maintained within a certain range so as to ensure the temperature stability of the surrounding environment. Polymer PCMs can make the surrounding temperature stable so that PCMs can be used in the fields of building air conditioners, electronic cooling, building heating/cooling (indoor temperature controlling), radiant floor heating, thermal switches, clothing field, solar thermal energy storage, and so on.¹

However, the thermal conductivities of commonly used polymer PCMs are generally lower than 0.5 W/(m K) (0.13 W/(m K) for RT27, 0.17 W/(m K) for octadecane, 0.26 W/(m K) for RT25, 0.36 W/(m K) for eicosane, 0.42 W/(m K) for tetradecanol, 0.48 W/(m K) for capric acid),² which will be restricted when PCMs are used in the field of fast energy storage. Therefore, it is necessary to improve the thermal conductivity of polymer PCMs to meet the demand of rapid energy storage. At present, the thermal conductivities of PCMs are improved by adding high thermal conductivity fillers such as metal materials (silver particles,³ copper particles,⁴

aluminum particles,⁵ silver nanowires,⁶ copper nanowires⁷), ceramic materials (boron nitride,⁸ aluminum nitride,⁹ alumina,¹⁰ copper oxide¹¹), carbon materials (graphite,¹² graphene,^{13–16} carbon nanofibers,¹⁷ carbon nanotubes,¹⁸ carbon black,¹⁹ carbon fibers,²⁰ MXene²¹), and so on. The main method to obtain high thermal conductivity of PCMs is to make the filler form a high thermal conductivity path in the polymer matrix. Through some methods, the filler can form a three-dimensional (3D) network structure in the polymer matrix, thus forming a high thermal conductivity path. The heat can quickly transfer on the three-dimensional network structure so as to achieve the situation of low filler content and high thermal conductivity. At present, the methods of forming the high thermal conductivity path in polymer composites mainly include the freeze-drying orientation method,^{22,23} self-assembly molding,²⁴ metal foam method,^{25,26} carbon foam

Received: September 18, 2021

Accepted: November 16, 2021

Published: November 24, 2021



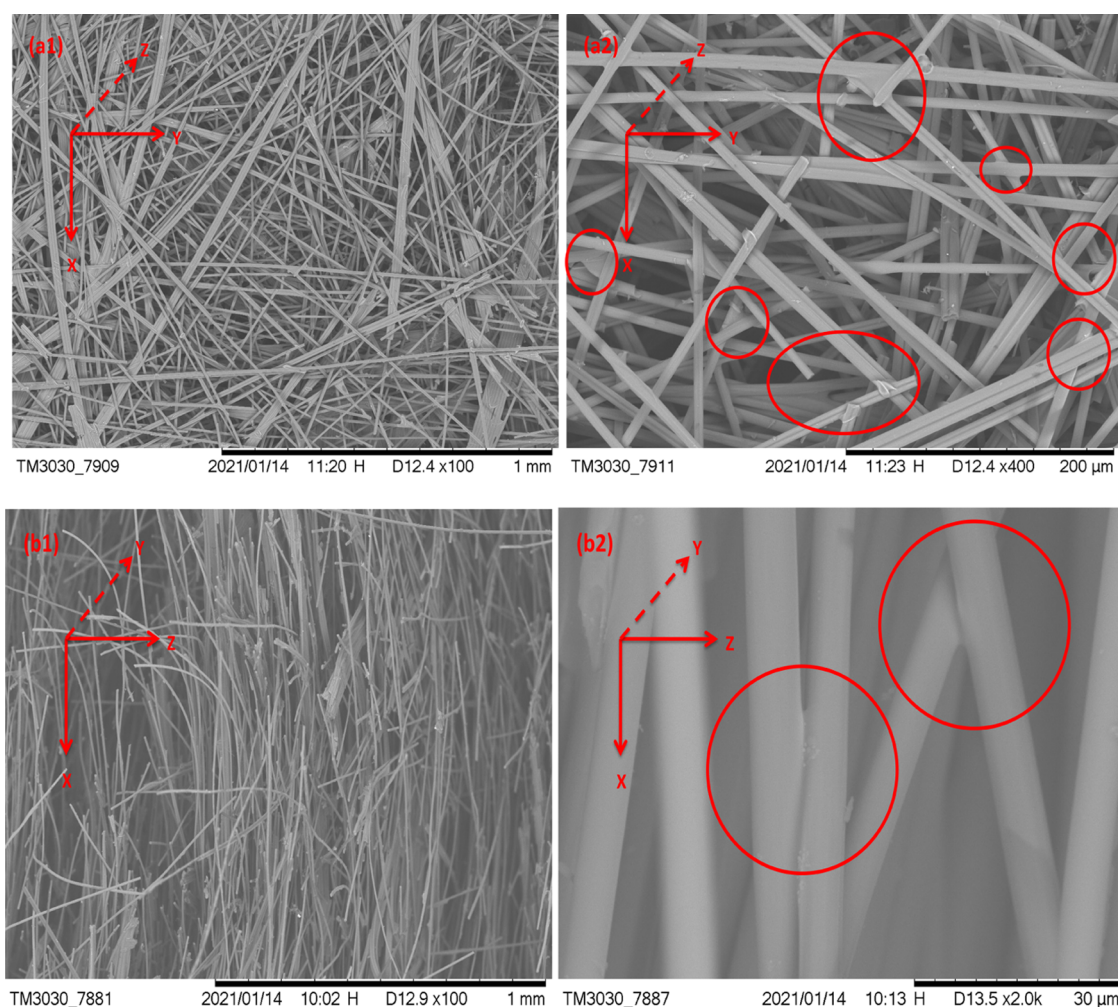


Figure 1. SEM images of carbon/carbon fiber felt: (a1) and (a2) are in the in-plane direction (X – Y plane) and (b1) and (b2) are in the through-plane direction (X – Z plane).

method,^{27,28} ceramic foam,²⁹ 3D skeleton network method,^{12,30} interfacial polyelectrolyte complex spinning,³¹ in situ reduction of metal ions,³² electrophoretic deposition method (EPD),³³ electrostatic flocking,³⁴ and so on. These methods make the thermal conductivities of polymer materials increase several times or even dozens of times, which are good methods to quickly improve the thermal conductivity. Therefore, the research of high thermal conductivity path has become a hotspot.

Because PCMs store energy by melting and absorbing heat, it is easy to produce shrinkage deformation and flow deformation after polymer material melting, which brings to difficulties in the application of PCMs. Therefore, to reduce the deformation of PCMs and improve their shape stability, the PCM matrix needs to be confined in a certain space. At present, the methods to improve the shape stability of PCMs mainly include the spherical microcapsule method,³⁵ hollow tube microcapsule method,^{36,37} nanomaterial adsorption method,^{38,39} complexation cross-linking network method,⁴⁰ chemical cross-linking network method,⁴¹ silica network confinement method,^{42,43} metal network confinement method,^{44,45} carbon network confinement method,⁴⁶ polymer network confinement method,⁴⁷ and so on.

To solve the two problems of low thermal conductivity and poor shape stability of polymer PCMs, the thermal

conductivity of PCMs was enhanced using carbon/carbon fiber felt (CCF) with a 3D network structure as the thermal conductivity framework in this paper. At the same time, 3D CCF can support and adsorb PCMs, which can improve the shape stability of PCMs. Then, the 3D CCF was dipped into pre-prepared PEG- CaCl_2 ethanol solution and then taken out for drying. After repeated impregnation and drying, PEG- CaCl_2 /CCF PCMs were prepared by hot pressing and complexation molding. In the process of hot pressing, CaCl_2 and PEG complexed to form a cross-linking network, which can reduce the deformation of PEG during phase transformation and ensure the shape stability of PEG. The contact area between the carbon fibers in CCF was further increased by the compression confinement method so as to further improve the thermal conduction path of the 3D CCF skeleton and hence improve the thermal conductivity of PCMs. The purpose of this paper was to improve the thermal conductivity of PCMs using the 3D carbon/carbon fiber felt network as a thermal conduction path. At the same time, 3D CCF served as a support and an adsorbent for PCMs, and PEG- CaCl_2 formed a complex structure by the complexation method so as to obtain shape-stable PCMs. Finally, PEG- CaCl_2 /CCF PCMs with high thermal conductivity and stable shape were prepared. The paper may provide some suggestions for the preparation

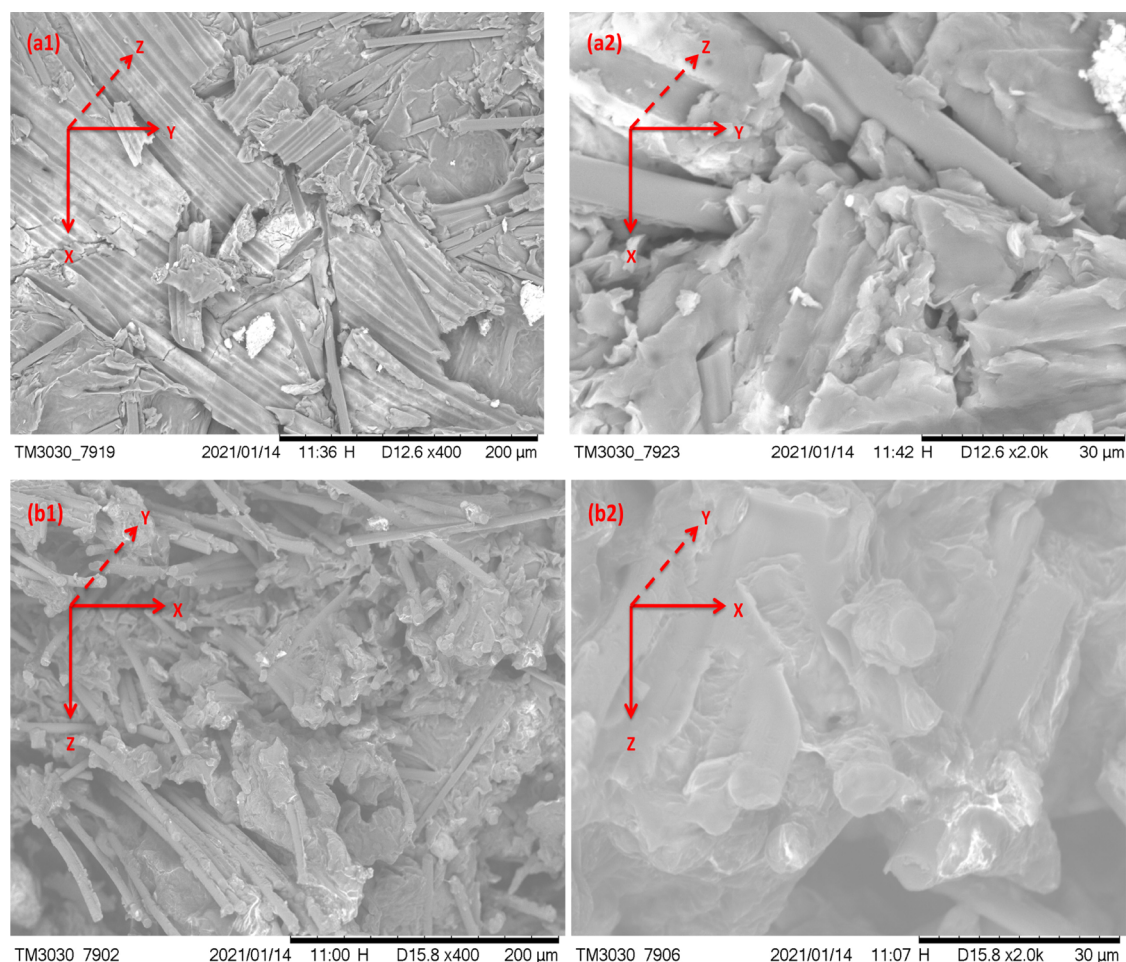


Figure 2. SEM images of PEG-CaCl₂/CCF PCMs: (a1) and (a2) are in the in-plane direction (X - Y plane) and (b1) and (b2) are in the through-plane direction (X - Z plane).

of high thermal conductivity and excellent shape stability PCMs.

RESULTS AND DISCUSSION

Morphology of CCF and PEG-CaCl₂/CCF PCMs. In the process of preparing carbon fiber felt, a kind of carbon fiber felt with a X - Y - Z three-dimensional network layer structure was formed after the carbon fibers were air laid and needle punched. In the three-dimensional network structure of carbon fiber felt, most of the axial direction of carbon fibers is in the X - Y plane, while a small part of it is in the Z -direction. The X - Y - Z structure of carbon fiber felt is loose and needs to be bonded with the carbon structure. The phenolic resin used in this paper can produce residual carbon after liquid-phase impregnation, carbonization, and graphitization. The carbon residue transforms the carbon fiber felt into a whole carbon/carbon fiber felt to form a hard carbon/carbon fiber felt structure with certain mechanical properties. The structure of materials determines their properties. CCF felt is the thermal conductive filler of PEG PCMs, so it is necessary to characterize the structure of CCF. Figure 1 indicates the SEM images of carbon/carbon fiber felt. Figure 1(a1) and (a2) shows the SEM images in the in-plane direction (X - Y plane). Figure 1(b1) and (b2) displays the SEM images in the through-plane direction (X - Z plane). From Figure 1(a1) and (a2), the carbon fibers are disorderly overlapped and some

overlapped positions stick together (in the red circle in Figure 1(a2)). The adhesion positions are caused by the residual carbon material after graphitization of the phenolic resin. These bonding points can enhance the strength of the carbon fiber felt, so that it is not easy to make the carbon fiber felt loose and to deform its shape, and the shape is not easy to deform. In other words, as a kind of bonded carbon structure, the residual carbon can maintain the stability of the whole structure of CCF. The bonded carbon can make CCF have certain mechanical strength, which plays an important role in reinforcement. At the same time, the bonded carbon can play the role of communicating with adjacent carbon fibers, making the whole carbon fiber felt into a connected whole body; that is, forming a CCF network with the three-dimensional network structure, which forms a connected network conducive to the heat conduction of phonon, and also to the propagation of heat conducting phonon. Thus, a high heat conduction path network is formed in the X - Y plane. The three-dimensional CCF network is also a connected network that is conducive to phonon transmission, and also to the propagation of heat conducting phonon, thus forming a high heat conduction path network in the X - Y plane.

It can be seen from Figure 1(b1) and (b2) that the carbon fibers are arranged in order and staggered, which is due to the uniform falling of carbon fibers layer by layer under the action of air flow during the preparation of carbon fiber felt. In addition, it can be seen that each layer of carbon fibers is

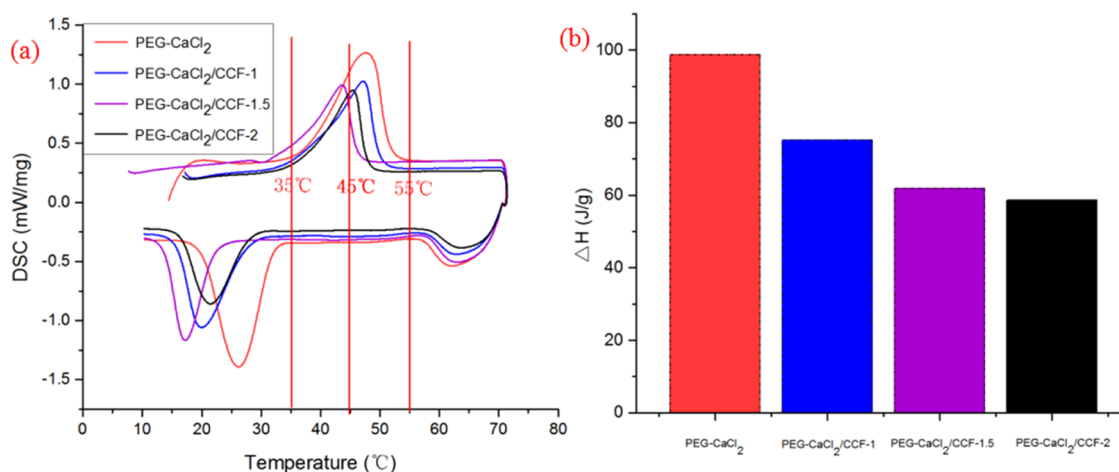


Figure 3. DSC curves of PEG-CaCl₂/CCF PCMs: (a) DSC curves and (b) ΔH .

staggered, but almost every layer is perpendicular to the cross section, and almost no carbon fiber is parallel to the cross section. In the red circles of Figure 1(b2), it can be seen that some carbon fibers in the same layer are adhered together, which is conducive to improving the strength of the carbon fiber layer. At the same time, these bonded carbon points bond to different layers of carbon fibers together, which is conducive to the heat transfer between layers. These bonded carbon points increase the fiber thermal conduction path in the Z-direction, which is beneficial to improve the thermal conductivity in the Z-direction. The thermal conductivity of carbon fiber in the axial direction is much higher than that in the vertical direction due to crystal orientation. Comparing Figure 1(b1) and (a1), it can be seen that the axial directions of carbon fibers are mostly concentrated in the X–Y plane, so the thermal conductivity in the X–Y plane will be much higher than that in the X–Z section. The results show that the carbon-bonded network can promote the thermal conductivity in both directions.

It can be seen from Figure 1 that the bonded carbon has a bonding effect on carbon fibers in both the X–Y plane and the X–Z plane, and carbon and carbon fibers form a connected 3D heat conduction network. When the 3D network is combined with phase change materials, high thermal conductivity PCMs will be formed. At the same time, because carbon and carbon fiber form a three-dimensional network, it will inevitably hinder the flow of PCMs, so the deformation resistance of the formed PCMs will be improved.

The structure of the materials determines their properties. Therefore, it is highly necessary to characterize the microstructure of PEG-CaCl₂/CCF PCMs. Especially, it is necessary to observe the interface between the resin matrix and the filler in PCMs. The interface adhesion will directly affect the properties of PCMs. Figure 2 illustrates the SEM images of PEG-CaCl₂/CCF PCMs. As seen from Figure 2, the interface between the carbon fibers and PEG-CaCl₂ in the high thermal conductivity framework is closely combined, and there are no obvious pores and defects, which indicates that the liquid-phase impregnation–vacuum drying–molding method is a very feasible method for preparing PCMs. The heat transfer of PEG-CaCl₂/CCF PCMs is mainly through the high thermal conductivity carbon/carbon fiber skeleton, but there will still be a part of heat transfer through the phase change material. The close interface structure is conducive to phonon transfer

so as to further improve the thermal conductivity of PEG-CaCl₂/CCF PCMs.

Heat Storage Performance of PEG-CaCl₂/CCF PCMs.

PCMs can store heat energy by melting and release heat energy by crystallization. In the process of melting, polymer PCMs will absorb heat and change from solid to liquid. In the endothermic process, the energy is mainly used to destroy the crystalline structure of polymer PCMs, while the temperature of PCMs is not changed much, which is mainly kept near the melting point. The heat required for crystallization and melting of PCMs is the energy stored in polymer PCMs.

When the ambient temperature decreases, polymer PCMs change from the liquid state to the solid state and from the molten state to the crystalline state. In the crystallization process, polymer PCMs will release the heat absorbed by melting, which is an exothermic process. In the process of exothermic crystallization, the temperature of polymer PCMs remains near the crystallization temperature. Polymer PCMs store and release heat energy through repeated endothermic and exothermic processes. However, the temperature of polymer PCMs can be kept near the melting point and crystallization point, which can keep the ambient temperature stable. Using this feature, PCMs can be used in the field of battery heat storage and protection. When the temperature of the battery is too high due to the heat emitted by the battery, PCMs wrapped outside the battery can absorb the heat and ensure the battery at a constant temperature through phase change. Figure 3 illustrates the DSC curves of PEG-CaCl₂/CCF PCMs. Table 1 shows the phase change temperature and latent heat of PEG-CaCl₂/CCF PCMs. From Figure 3a and Table 1, it can be found that with the increase of compression ratio, the melting point of PCMs changes from 47.7 °C (PEG-CaCl₂) to 47.2 °C (PEG-CaCl₂/CCF-1), 43.7 °C (PEG-CaCl₂/CCF-1.5), and 45.5 °C (PEG-CaCl₂/CCF-2), which are all kept at about 45 °C. The melting temperature ranges from 35 to 55 °C. When the temperature of the battery is higher than 40 °C, it is easy to be dangerous, so in the process of charging or discharging, if the temperature exceeds 40 °C, the PEG-CaCl₂/CCF PCMs can quickly absorb heat and keep it at about 40 °C so as to ensure the safety of the battery. This is the significance of polymer PCMs used in the field of battery applications.

From Figure 3b, with the increase of compression ratio, the melting heat of PEG-CaCl₂/CCF PCMs gradually decreases

Table 1. Phase Change Temperature and Latent Heat of PEG-CaCl₂/CCF PCMs

	crystallization temperature— $T_{C-onset}$ (°C)	crystallization peak temperature— T_{CP} (°C)	melting temperature— $T_{M-onset}$ (°C)	melting peak temperature— T_{MP} (°C)	ΔH (J/g)
PEG-CaCl ₂	31.9	26.2	38.1	47.7	98.65
PEG-CaCl ₂ /CCF-1	27.6	20.0	38.4	47.2	75.20
PEG-CaCl ₂ /CCF-1.5	22.2	17.2	35.6	43.7	61.86
PEG-CaCl ₂ /CCF-2	27.8	21.5	37.6	45.5	58.67

from 98.65 J/g (PEG-CaCl₂) to 75.20 J/g (PEG-CaCl₂/CCF-1), 61.86 J/g (PEG-CaCl₂/CCF-1.5), and 58.67 J/g (PEG-CaCl₂/CCF-2). The melting heat of phase change is related to the content of the phase change material. The content of carbon fiber gradually increases with the increase of compression ratio, but the content of the phase change material gradually decreases, so the latent heat of PEG-CaCl₂/CCF PCMs gradually decreases with the increase of compression ratio. Therefore, on the one hand, the increase of carbon fiber in PEG-CaCl₂/CCF PCMs improves the thermal conductivity of PCMs, but on the other hand, the increase of carbon fiber reduces the latent heat of PCMs. Therefore, the increase of thermal conductivity and latent heat of PCMs are contradictory, which should be considered comprehensively.

Thermal Conductivity of PEG-CaCl₂/CCF PCMs. Due to the low thermal conductivity of polymer PCMs (PEG, 0.47 W/m K), the application of polymer PCMs in the field of rapid energy storage is limited. Therefore, it is necessary to improve the thermal conductivity of polymer PCMs by modification. In this study, the thermal conductivity of PEG-CaCl₂/CCF PCMs with the 3D CCF network was studied by the hot-disk method. The thermal conductivity of PEG-CaCl₂/CCF PCMs is described in Figure 4.

It can be seen from Figure 4a,b that with the increase of compression ratio, the in-plane thermal conductivity of PCMs gradually increases from 1.72 W/(m K) (PEG-CaCl₂/CCF-1) to 2.59 W/(m K) (PEG-CaCl₂/CCF-1.5) and 3.35 W/(m K) (PEG-CaCl₂/CCF-2), which are 506, 712, and 985% of that of pure PEG-CaCl₂ (0.34 W/(m K)), respectively, indicating that the compression confinement effect is beneficial to improve the thermal conductivity of PCMs. The improvement of in-plane thermal conductivity can be attributed to the following reasons. (1) The in-plane orientation structure of CCF in PEG-CaCl₂/CCF PCMs improves the in-plane thermal conduction path of PCMs. Carbon fiber is a kind of one-dimensional anisotropic material prepared by the process of spinning, drawing, orientation, high-temperature carbonization, and graphitization. Because of the crystal orientation in the production process, the axial thermal conductivity of the carbon fiber is much higher than that in other directions. The carbon fibers in the carbon fiber felt are mainly distributed in the X–Y plane, so the composite prepared by the carbon fiber felt has higher in-plane thermal conductivity. In addition, the carbon fibers used in this paper are all long fibers with a length of about 120 mm. The thickness of the testing composite is less than 20 mm, so it can be considered that the heat is transmitted in the axial direction of the straight path through carbon fiber. This is equivalent to the fact that there is no interface in the transmission path; that is, there is no interface thermal resistance, thus improving the thermal conductivity of the PEG-CaCl₂/CCF composite. (2) The compression confinement increases the content of carbon fibers per unit volume. The increase of carbon fiber content means that the thermal conduction skeleton in PCMs increases. The thermal conduction skeleton is the main heat transfer path, so the thermal conduction path increases and the thermal conductivity of PCMs increases with the increase of compression ratio. (3) Compression confinement increases the contact probability between carbon fibers. The carbon fiber network is bonded together by carbon particles, and the contact probability increases with the increase of the number of carbon fibers. Compression confinement widens the side

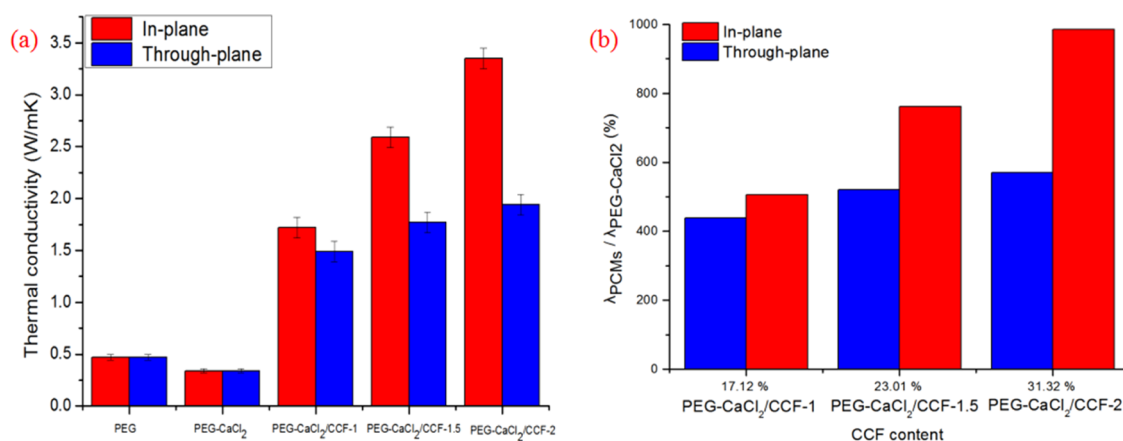


Figure 4. Thermal conductivity of PEG-CaCl₂/CCF PCMs: (a) in-plane ($\lambda_{\text{in-plane}}$) and out-plane ($\lambda_{\text{through-plane}}$) thermal conductivities at 25 °C and (b) $\lambda_{\text{PCMs}}/\lambda_{\text{PEG-CaCl}_2}$.

branch heat conduction path; that is, the increase of the number of side branches in the heat conduction path can also improve the thermal conductivity of PEG-CaCl₂/CCF PCMs. Therefore, the increase of thermal conductivity of PEG-CaCl₂/CCF PCMs is due to the inherent high thermal conductivity of the carbon fiber and the oriented structure of carbon fibers in the X–Y–Z carbon/carbon fiber felt. With the increase of compression ratio, the proportion of CCF content in the PEG-CaCl₂ matrix increases, and the contact surface between carbon fibers also increases, so the heat conduction path is further widened, which is more conducive to phonon heat transfer, thus further improving the in-plane thermal conductivity of PEG-CaCl₂/CCF PCMs.

As seen from Figure 4a,b, with the increase of compression ratio, the through-plane thermal conductivity of PEG/CCF PCMs gradually increases from 1.49 W/(m K) (PEG-CaCl₂/CCF-1) to 1.77 W/(m K) (PEG-CaCl₂/CCF-1.5) and 1.94 W/(m K) (PEG-CaCl₂/CCF-2), which are 438, 521, and 571% of that of pure PEG-CaCl₂ (0.34 W/(m K)), respectively, indicating that the compression confinement is beneficial to improve the thermal conductivity of PCMs in the Z-direction. Under the effect of compression, the contact probability of carbon fibers between adjacent carbon fiber layers increases, and more heat conduction paths are formed, and thus the thermal conductivity is further improved. Because the thermal conductivity of the carbon fiber and carbon is higher than that of the polymer material, in addition to the increase of thermal conduction path, it is also related to the increase of the proportion of carbon fiber and carbon in the thermal conduction path caused by compression.

However, comparing the in-plane thermal conductivity with the through-plane thermal conductivity, it can be found that the in-plane thermal conductivity is much higher than the through-plane thermal conductivity, which is determined by the structure of the carbon/carbon fiber 3D skeleton. From the above SEM images, it can be seen that the carbon fibers are mainly laid in the X–Y plane, the axial direction of carbon fibers is mainly distributed in the X–Y plane, the fibers are connected together by bonding carbon to form an X–Y plane network, and the thermal conductivities of PCMs are the same in all directions in the X–Y plane. In the Z-direction, if the heat is to be transferred, it needs to be transferred through contact points between the carbon fibers in different layers, and the thermal conductivity is also low in the direction

perpendicular to the fiber axis, so the thermal conductivity in the Z-direction is far lower than that in the X–Y plane. Therefore, we can make full use of the high thermal conductivity in the X–Y plane to provide help for the rapid heat storage of PCMs.

In this paper, CCF with the 3D structure was used to prepare PCMs with high thermal conductivity. The designed carbon-bonded carbon fiber 3D skeleton structure has a superior thermal conduction path. Therefore, it is necessary to compare the thermal conductivity of PCMs prepared by other preparation methods to show the advantages of the structure designed in this paper. Figure 5 indicates the thermal

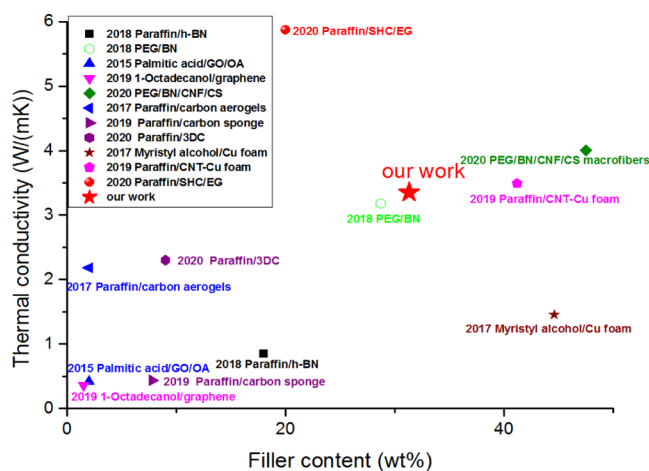
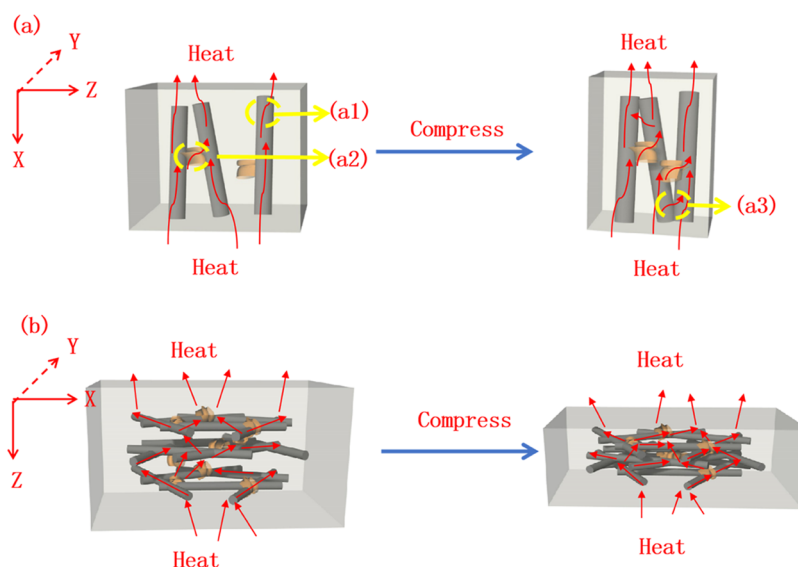


Figure 5. Thermal conductivities of different kinds of PCMs.

conductivity of different kinds of PCMs. The data in Figure 5 can be summarized in Table 2. Table 2 shows the detailed comparisons of the thermal conductivity of different kinds of PCMs. As seen from Figure 5 and Table 2, the properties of PCMs prepared by different preparation methods such as the freeze-drying orientation method, self-assembly method, interfacial polyelectrolyte complex spinning method, 3D-carbon foam, 3D Cu foam, and porous silica method are compared with each other. The following conclusions can be found through comparison. (a) When the filler content was less than 30 wt %, PCMs prepared in this paper have higher thermal conductivity. The thermal conductivity of PCMs was significantly higher than that of PCMs prepared by the freeze-

Table 2. Detailed Comparisons of the Thermal Conductivities of Different kinds of PCMs

year	method	materials	filler content	λ (W/(m K))	reference
2018	freeze-drying orientation	paraffin/h-BN	18 wt % h-BN	0.85	22
2018	freeze-drying orientation	PEG/BN	28.7 wt % BN	3.18	23
2015	self-assembly	palmitic acid/GO/OA	2 wt % GO	0.419	48
2019	self-assembly	1-octadecanol/graphene	1.5 wt % graphene	0.358	49
2020	interfacial polyelectrolyte complex spinning	PEG/BN/CNF/CS macrofibers	47.5 wt % BN-OH	4.005	31
2017	3D carbon aerogel	paraffin/carbon aerogels	2 wt % carbon aerogels	2.182	50
2019	3D carbon foam	paraffin@carbon sponge	7.8 wt % carbon	0.434	28
2020	3D graphene foam	paraffin/3DC	9 wt % 3D graphene	2.3	27
2017	Cu foam	myristyl alcohol/Cu foam	46.6 wt % Cu foam	1.452	25
2019	carbon nanotube–Cu foam	paraffin/CNT-Cu foam	41.2 wt % Cu, 0.68 wt % CNT	3.49	26
2020	porous silica	paraffin/SHC/EG	10 wt % EG + 10 wt % SHC	5.87	12
2021	carbon/carbon fiber network	PEG-CaCl ₂ /CCF	31.32 wt % CCF	3.35	our work

Figure 6. Mechanism of heat conduction in PEG-CaCl₂/CCF PCMs: (a) X–Y direction (in-plane) and (b) Z-direction (through-plane).

drying method^{24,26} and the self-assembly method.^{48,49} (b) When the content was less than 30 wt %, Yanwei Zhang et al.¹² prepared paraffin/SHC/EG PCMs using SHC/EG with the network structure, and the thermal conductivity reached 5.87 W/(m K) (10 wt % EG + 10 wt % SHC), showing the advantage of high thermal conductivity. (c) When the filler content was higher than 30%, the thermal conductivity of the CCF PCMs was even higher than that of some copper foam PCMs. Xiang Huang et al.²⁵ fabricated myristyl alcohol/metal foam PCMs by the vacuum melting infiltration method and the thermal conductivity of PCMs with 46.6 wt % Cu foam was 1.452 W/(m K). (d) The higher the filler content, the better the thermal conductivity of PCMs. At the same time, combined with certain methods, higher thermal conductivity can be further obtained. Hui Fang et al.³¹ manufactured the PEG/BN/CNF/CS macrofiber composite by the interfacial polyelectrolyte complex spinning method. The thermal conductivity of PCMs can reach 4.005 W/(m K) (47.5 wt % BN-OH). Wei Zhu et al.²⁶ fabricated paraffin/CNT-Cu foam PCMs with the conductivity of 3.49 W/(m K) (41.2 wt % Cu, 0.68 wt % CNT).

Based on the above analysis, the thermal conductivity of PCMs can be improved by constructing the 3D CCF framework, which has certain advantages compared with other methods, but it is not completely higher than that of

PCMs prepared by other methods. However, the CCF prepared in this paper can be prepared on a large scale, and its size can now be prepared to 2000 mm × 2000 mm × 50 mm, which can be used for large-scale industrial applications.

Heat Conduction Mechanism of PEG-CaCl₂/CCF PCMs. Both in-plane thermal conductivity and through-plane thermal conductivity of PEG-CaCl₂/CCF PCMs increase with the increase of compression ratio. The in-plane thermal conductivity of the same PEG-CaCl₂/CCF PCMs is much higher than the through-plane thermal conductivity, so it is necessary to analyze the heat conduction mechanism of PEG-CaCl₂/CCF PCMs. The mechanism of heat conduction in the PEG-CaCl₂/CCF PCMs is illustrated in Figure 6. Heat transfer in materials includes heat convection, heat radiation, and heat conduction.^{51,52} The structure of materials determines these properties. The composite materials include the matrix resin, filler, and interface. In PEG-CaCl₂/CCF PCMs, the SEM images in the above figure show that the PEG matrix resin and carbon fibers are closely combined, and there are almost no pores, so it is difficult to transfer heat through heat convection. When the object is in the environment above absolute zero, there will be radiation phenomenon. However, in composite materials, the heat transferred by thermal radiation is very little, and it is not the main way of heat transfer in most cases. In most cases, heat is transmitted by means of heat conduction

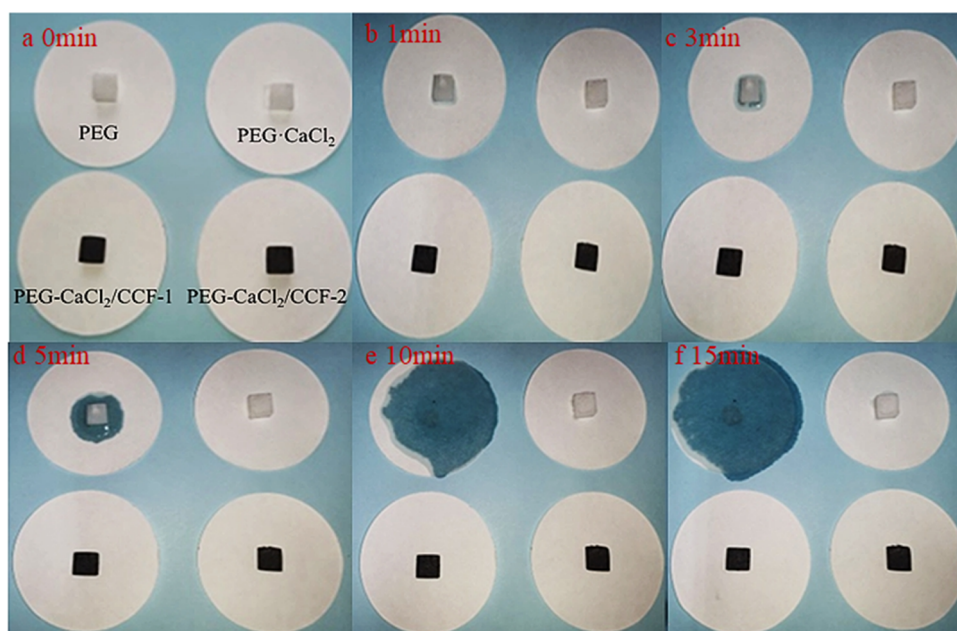


Figure 7. Leakage diagram of PEG-CaCl₂/CCF PCMs.

composite materials. The objects transfer heat through the motion of phonons (simple harmonic vibrations of molecules or crystals) or electrons. Therefore, the thermal conductivity of composites can be improved if the phonon conduction path can be formed or widened, or the interface defects between the matrix material and the filler can be reduced. In PEG-CaCl₂/CCF PCMs, CCF is a three-dimensional network structure with the X–Y–Z structure. Due to its unique structural design, CCF has an anisotropic structure, so its heat conduction mechanism in different directions is different. In Figure 6a, heat conduction propagates along the fiber axis, which is a straight path through the rapid propagation process. In Figure 6b, heat conduction is a zigzag process. In Figure 6a, three ways can be used to increase and widen the heat conduction path in composite materials so as to improve the heat transfer and then the thermal conductivity of composite materials. (a1) The first way is to increase the heat transfer through the axial orientation of carbon fiber with high thermal conductivity, that is, the heat transfer through the axial direction of carbon fiber in the X–Y plane. (a2) In the 3D thermal conductive CCF network, the carbon dots bonded with carbon fibers can also increase the side branch thermal conduction path so as to improve the thermal conductivity of PCM composites. (a3) The third way is to increase the carbon fiber contact probability after compression so as to increase the side branch heat conduction path and also to improve the thermal conductivity. After compression, the content of carbon fiber per unit volume will also increase, and the axial heat conduction path and other side branch heat conduction paths of carbon fiber will increase; then, the thermal conductivity of PCM composites will increase. The CCF has formed a percolation structure in the resin matrix, so it is very conducive to heat transfer.^{53,54}

Comparing Figure 6a,b, it can be found that the heat transfer path in the X–Y plane is fast, which is mainly linear and supplemented by various side branches. The heat transfer route in the Z-direction is zigzag. In the process of heat transfer, a lot of heat will change along the fiber axis, which reduces the efficiency of heat transfer. In addition, in the Z-direction, the

carbon fibers are stacked by layers of X–Y carbon fibers, and there are few contact points between the carbon fibers, which makes the heat conduction path longer and the thermal conductivity lower. In the Z-direction, due to the nanofiber axial heat transfer, the path becomes longer due to fewer contact points. There are fewer paths between carbon fibers in the different layers, and the interface thermal resistance between carbon fibers is larger, which makes the thermal conductivity in the Z-direction (through-plane) lower than that in the X–Y direction (in-plane).

Shape Stability of PEG-CaCl₂/CCF PCMs. Polymer PCMs can absorb heat from the surrounding environment, and then melt; thus, the crystallization of PCMs is destroyed. PCMs will change from solid to liquid and the volume will also expand. In the process of phase change, if the shape of PCM is not limited, it is very easy to leak, expand, or shrink. At present, from the Introduction section, the methods to improve the shape stability of PCMs mainly include the spherical microcapsule method, hollow tube microcapsule method, nanomaterial adsorption method, complexation cross-linking network method, chemical cross-linking network method, metal network confinement method, carbon network confinement method, polymer foam network confinement method, and so on. The method used in this paper was to form a cross-linking network through the complex reaction of PEG and CaCl₂ so as to limit the deformation of the PEG material. Figure 7 indicates the leakage diagram of PEG-CaCl₂/CCF PCMs. It can be seen from Figure 7 that when PEG is placed on the heating platform of 80 °C (much higher than the PEG phase transition temperature), PEG begins to melt in 1 min (Figure 7b) and then melts in a large area (Figure 7c,d) with the increase of time. When heated for 10 min, PEG is completely melted (Figure 7e). There is only a little leakage of PEG-CaCl₂ due to the cross-linking network structure (15 min, Figure 7f). However, PEG-CaCl₂/CCF PCMs have no obvious leakage and their shapes remain intact, which is mainly attributed to the complex cross-linking network structure of PEG and CaCl₂ and the network structure adsorption and network barrier of CCF. (1) PEG reacts with CaCl₂ to form

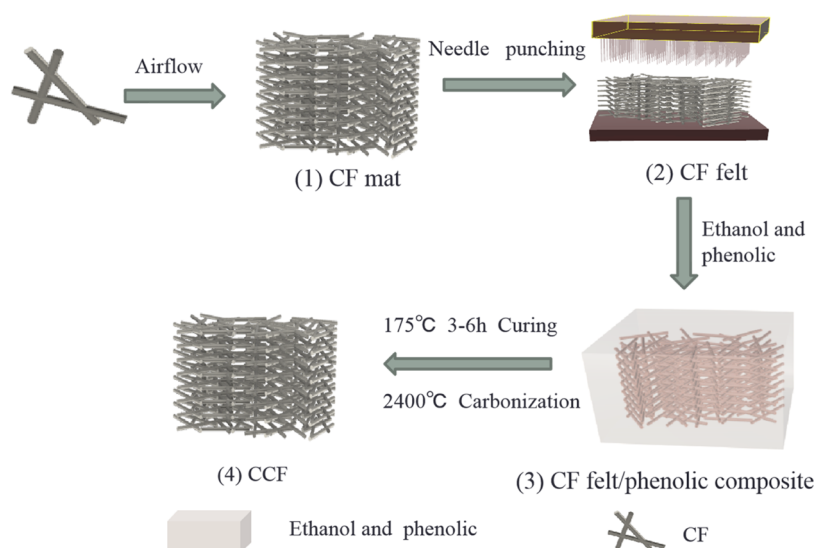


Figure 8. Schematic diagram of the preparation process of carbon/carbon fiber felt.

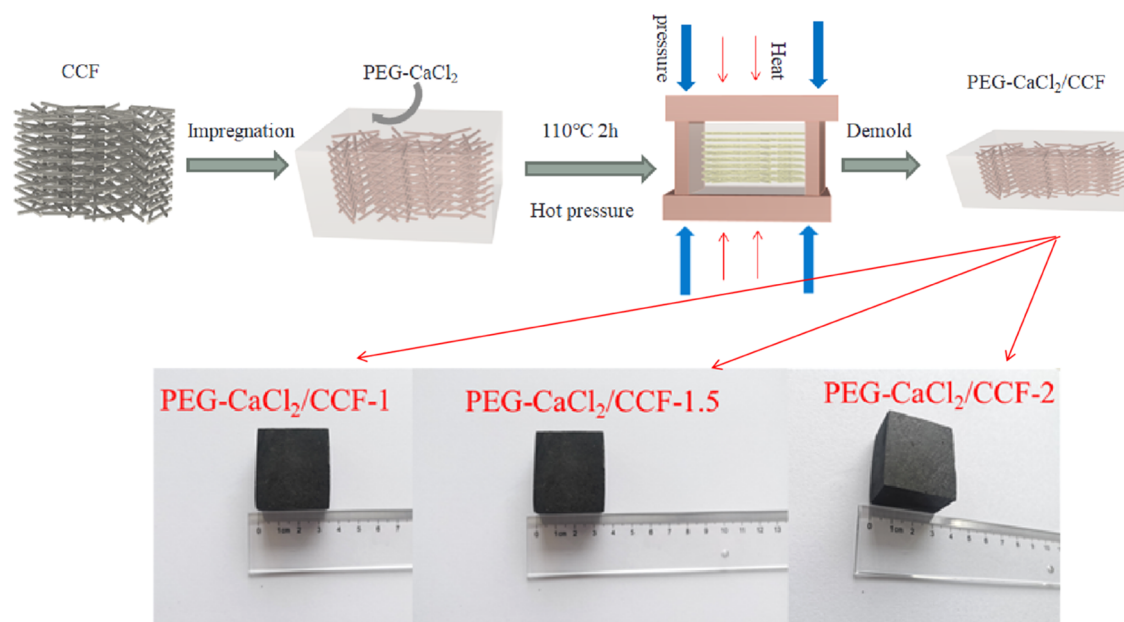


Figure 9. Preparation process of PEG-CaCl₂/CCF PCMs.

the cross-linking structure.⁵⁵ At this time, PEG is equivalent to forming a large three-dimensional network structure, and almost all PEG molecules become a part of this network; that is, PEG is forbidden in the macromolecular structure of PEG-CaCl₂, thus ensuring the shape stability of PCMs. (2) The three-dimensional carbon/carbon fiber network structure in PCMs can prevent their leakage through surface adsorption, and also has a certain fixation effect on PCMs so as to further improve their shape stability. At the same time, the special three-dimensional carbon/carbon fiber network structure formed by one-dimensional carbon fiber and carbon can prevent the flow of phase change molecules through the network structure, and can also play a role in fixing the phase change material, making the phase change material maintain shape stability. In conclusion, the PEG and CaCl₂ complex cross-linking network structure can make PEG form macromolecules, fundamentally eliminating the flow of PEG molecules. The adsorption and network barrier of the CCF

network structure further play a role in fixing PEG molecules, thus making PEG PCMs have high stability.

EXPERIMENTAL SECTION

Materials. Carbon fibers (SYT45 12K) were purchased by Zhongfu Shenyang Carbon Fiber Co., Ltd., China. Phenolic resin (PF-5408) was supplied from Jinan Shengquan Group Co., Ltd., China. PEG (PEG1500), CaCl₂ (AR), and ethanol (AR) were obtained from Sinopharm Chemical Reagent Co., Ltd., China.

Preparation of CCF. Carbon/carbon fiber felt was prepared by the methods of air flow netting–needle punching–liquid-phase impregnation–high-temperature carbonization and graphitization.⁵⁶ The schematic diagram of the preparation process of carbon/carbon fiber felt is described in Figure 8. The preparation process of carbon/carbon fiber felt includes the following steps. (1) The loose carbon fiber felt was prepared by air flow netting. The carbon fibers with an

average length of 120 mm were put into the cage, opened, and then spread on the conveyor belt by air adsorption. (2) Carbon fiber felt with certain strength was prepared by the needle-punching method. In the carbon fiber felt formed by air flow adsorption, the carbon fibers were in physical contact and could move freely and destroy the original stacking structure in the X - Y plane. To enhance the mechanical stability, the carbon fiber felt was needled by a vertically arranged needle array. Through the needling process, the metal needle with bifurcation in the Z -direction turned about 1% of the carbon fibers in the X - Y plane into the Z -direction. At this time, most of the carbon fibers were evenly distributed in the X - Y plane, and the Z -direction fibers, which account for about 1% of the total carbon fibers, can restrain the carbon fiber movement in the X - Y plane so as to enhance the structural stability and mechanical strength of the carbon fiber felt. Carbon fiber felt with the X - Y - Z structure was prepared by the methods of air flow netting and needle punching. The area density of the carbon fiber felt was about 700 g/m² and the thickness was 10 mm. (3) The carbon fiber felt/phenolic resin composite was prepared by liquid impregnation and compression curing. At room temperature, the phenolic resin was added to the ethanol solution and stirred for 0.5 h. The solid content of phenolic solution was 35 wt %. The carbon fiber felt with the X - Y - Z structure was completely immersed in the phenolic solution. The mass ratio of carbon fiber felt to phenolic resin solution was 1:1.25. The impregnated carbon fiber felt was transferred to an oven at 80 °C for 2 h to volatilize ethanol. (4) Then, the dried carbon fiber felt/phenolic resin composite was heated and cured in a metal mold at 175 °C for 5 h. The carbon/carbon fiber composite was prepared by carbonization and graphitization of the carbon fiber felt/phenolic resin composite at a high temperature. The carbon fiber felt/phenolic resin composite was transferred to a high-temperature furnace and heated to 2400 °C to graphitize. In this furnace, the phenolic resin was decomposed into carbon and graphitized at a high temperature. After cooling to atmospheric temperature, the anisotropic carbon/carbon fiber felt was obtained.

Preparation of PEG-CaCl₂/CCF PCMs. The preparation process of PEG-CaCl₂/CCF PCMs is shown in Figure 9. First, PEG and CaCl₂ (molar ratio 2:1) were dissolved in ethanol with the concentration of 20% at 80 °C. CCFs (3.8 cm × 3.8 cm, 2 cm, 3 cm, 4 cm in thickness) were dipped into the above solution, and the soaking time was 10 min in vacuum at room temperature. CCFs were removed from the solution and dried in an oven (80 °C for 24 h). CCFs were impregnated and dried several times until the weight of CCFs could not be increased by impregnation. Second, the impregnated PEG-CaCl₂/CCF composites were put into a mold (4 cm × 4 cm × 2 cm) for pressing and complexing. The pressing temperature and time were 110 °C and 2 h, respectively. PEG-CaCl₂/CCF PCMs were obtained by cooling demoulding and processing. The composition of PEG-CaCl₂/CCF PCMs is illustrated in Table 3.

Table 3. Composition of PEG-CaCl₂/CCF PCMs

samples	CF/C (wt %)	CaCl ₂ (wt %)
PEG-CaCl ₂	0	12.89
PEG-CaCl ₂ /CF-1	17.12	10.68
PEG-CaCl ₂ /CF-1.5	23.01	9.92
PEG-CaCl ₂ /CF-2	31.32	8.85

Characterization. The micromorphology of the carbon/carbon fiber felt and PEG-CaCl₂/CCF PCMs was characterized by field emission scanning electron microscopy (SEM) of S-2150 (Hitachi Corp., Japan). The specimens were fractured in liquid nitrogen to show cross section. To get high-definition pictures, the cross section of the specimens was sprayed with gold.

The macromorphology of carbon/carbon fiber felt and PCMs was captured by a Sony α6000L digital camera.

Thermal conductivities of PCMs at 25 °C were measured by a hot-disk thermal constant analyzer (TPS500, Hot Disk, Sweden). The size of the sample was about 15 mm × 15 mm × 15 mm. The thermal conductivity in the Z -direction was marked as $\lambda_{\text{through-plane}}$. The thermal conductivity in the X - Y plane was marked as $\lambda_{\text{in-plane}}$. The probe heating power was about 200 mW. The data was read in about 20 s.

The melting heat and crystallization heat of PCMs were measured by differential scanning calorimetry (DSC, Netzsch 200 F3, Germany). The melting heat and crystallization heat of PCMs were measured in the range of 10–70–10 °C at the speed of 5 °C/min in nitrogen atmosphere.

PCMs were placed on a hot plate at 80 °C to characterize the resin leakage.

CONCLUSIONS

PEG-CaCl₂/CCF PCMs were successfully prepared by the liquid-phase impregnation–vacuum drying–hot compression molding method with carbon/carbon fiber felt as the 3D thermal skeleton and PEG-CaCl₂ as the polymer phase change material matrix. PEG-CaCl₂/CCF PCMs have high thermal conductivity and excellent shape stability due to the high heat transfer of the 3D CCF skeleton and the complexation of PEG and CaCl₂. The following conclusions can be obtained.

- (1) The carbon fibers in the 3D CCF skeleton are isotropic in the X - Y plane. However, there are very few carbon fibers in the Z -direction, which can only be bonded by carbon particles, so the in-plane thermal conductivity of PEG-CaCl₂/CCF-2 (3.35 W/(m K)) is higher than the through-plane thermal conductivity (1.94 W/(m K)).
- (2) The compression confinement can improve the contact area between the fibers in the 3D skeleton. The contact surface between fibers increases with the increasing compression ratio, so the thermal conduction path also increases, and then the thermal conductivity increases with the increasing compression ratio, both in-plane and through-plane.
- (3) The oxygen in PEG can react with calcium in CaCl₂ to form a complex network between PEG molecules. The complex network can reduce the leakage of PEG and then increase the shape ability of PCMs. At the same time, the CCF 3D skeleton has a certain adsorption effect and network blocking effect on PCMs, which is also conducive to improving the shape ability of PCMs.
- (4) The melting point and enthalpy of PCMs reach 45.5 °C and 58.67 J/g, respectively. The content of CCF in PCMs increases with the increasing compression ratio, and then the content of PEG decreases, so the melting heat decreases accordingly. Therefore, the improvement of thermal conductivity loses part of the heat storage capacity. Hence, when improving the thermal conductivity of PCMs, thermal conductivity and melting heat should be considered comprehensively.

The paper may provide some suggestions for the preparation of high thermal conductivity and excellent shape stability PCMs.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the China Postdoctoral Science Foundation (2017M611757) and the National Natural Science Foundation of China (51573201 and 51803119).

REFERENCES

- (1) Eanest Jebasingh, B.; Valan Arasu, A. A comprehensive review on latent heat and thermal conductivity of nanoparticle dispersed phase change material for low-temperature applications. *Energy Storage Mater.* **2020**, *24*, 52–74.
- (2) Qureshi, Z. A.; Ali, H. M.; Khushnood, S. Recent advances on thermal conductivity enhancement of phase change materials for energy storage system: A review. *Int. J. Heat Mass Transfer* **2018**, *127*, 838–856.
- (3) Zhan, W.; Zhao, Y.; Yuan, Y.; Yi, H.; Song, S. Development of 2D-Mt/SA/AgNPs microencapsulation phase change materials for solar energy storage with enhancement of thermal conductivity and latent heat capacity. *Sol. Energy Mater. Sol. Cells* **2019**, *201*, No. 110090.
- (4) Gao, J.; Tang, X.; Chen, Y.; Liu, Y. Shape-stabilized phase change material with enhanced thermal conductivity fabricated based on biomimetic polymerization and in situ reduction of Cu ions. *Int. J. Energy Res.* **2021**, *45*, 2058–2069.
- (5) Singh, R.; Sadeghi, S.; Shabani, B. Thermal Conductivity Enhancement of Phase Change Materials for Low-Temperature Thermal Energy Storage Applications. *Energies* **2019**, *12*, 75.
- (6) Zeng, J. L.; Cao, Z.; Yang, D. W.; Sun, L. X.; Zhang, L. Thermal conductivity enhancement of Ag nanowires on an organic phase change material. *J. Therm. Anal. Calorim.* **2010**, *101*, 385–389.
- (7) Angayarkanni, S. A.; Philip, J. Thermal conductivity measurements in phase change materials under freezing in presence of nanoinclusions. *J. Appl. Phys.* **2015**, *118*, No. 094306.
- (8) Lei, C.; Wu, K.; Wu, L.; Liu, W.; Du, R.; Chen, F.; Fu, Q. Phase change material with anisotropically high thermal conductivity and excellent shape stability due to its robust cellulose/BNNSs skeleton. *J. Mater. Chem. A* **2019**, *7*, 19364–19373.
- (9) Wang, W.; Yang, X.; Fang, Y.; Ding, J.; Yan, J. Enhanced thermal conductivity and thermal performance of form-stable composite phase change materials by using beta-Aluminum nitride. *Appl. Energy* **2009**, *86*, 1196–1200.
- (10) Mishra, A. K.; Lahiri, B. B.; Solomon, V.; Philip, J. Nano-inclusion aided thermal conductivity enhancement in palmitic acid/di-methyl formamide phase change material for latent heat thermal energy storage. *Thermochim. Acta* **2019**, *678*, No. 178309.
- (11) George, M.; Pandey, A. K.; Abd Rahim, N.; Tyagi, V. V.; Shahabuddin, S.; Saidur, R. A novel polyaniline (PANI)/paraffin wax nano composite phase change material: Superior transition heat storage capacity, thermal conductivity and thermal reliability. *Sol. Energy* **2020**, *204*, 448–458.
- (12) Zhang, Y.; Sun, K.; Kou, Y.; Wang, S.; Shi, Q. A facile strategy of constructing composite form-stable phase change materials with superior high thermal conductivity using silicagel industrial wastes. *Sol. Energy* **2020**, *207*, 51–58.
- (13) Cao, R.; Wang, Y.; Chen, S.; Han, N.; Liu, H.; Zhang, X. Multiresponsive Shape-Stabilized Hexadecyl Acrylate-Grafted Graphene as a Phase Change Material with Enhanced Thermal and Electrical Conductivities. *ACS Appl. Mater. Interfaces* **2019**, *11*, 8982–8991.
- (14) Yuan, P.; Zhang, P.; Liang, T.; Zhai, S.; Yang, D. Effects of functionalization on energy storage properties and thermal conductivity of graphene/n-octadecane composite phase change materials. *J. Mater. Sci.* **2019**, *54*, 1488–1501.
- (15) Goli, P.; Legedza, S.; Dhar, A.; Salgado, R.; Renteria, J.; Balandin, A. A. Graphene-enhanced hybrid phase change materials for thermal management of Li-ion batteries. *J. Power Sources* **2014**, *248*, 37–43.
- (16) Renteria, J. D.; Nika, D. L.; Balandin, A. A. Graphene Thermal Properties: Applications in Thermal Management and Energy Storage. *Appl. Sci.* **2014**, *4*, 525–547.
- (17) Qu, Y.; Wang, S.; Zhou, D.; Tian, Y. Experimental study on thermal conductivity of paraffin-based shape-stabilized phase change material with hybrid carbon nano-additives. *Renewable Energy* **2020**, *146*, 2637–2645.
- (18) Ranjbar, S.; Masoumi, H.; Khoshkhou, R. H.; Mirfendereski, M. Experimental investigation of stability and thermal conductivity of phase change materials containing pristine and functionalized multi-walled carbon nanotubes. *J. Therm. Anal. Calorim.* **2020**, *140*, 2505–2518.
- (19) Mishra, A. K.; Lahiri, B. B.; Philip, J. Carbon black nano particle loaded lauric acid-based form-stable phase change material with

enhanced thermal conductivity and photo-thermal conversion for thermal energy storage. *Energy* **2020**, *191*, No. 116572.

(20) Zhu, X.; Han, L.; Yang, F.; Jiang, J.; Jia, X. Lightweight mesoporous carbon fibers with interconnected graphitic walls for supports of form-stable phase change materials with enhanced thermal conductivity. *Sol. Energy Mater. Sol. Cells* **2020**, *208*, No. 110361.

(21) Aslfattahi, N.; Saidur, R.; Arifuzzaman, A.; Sadri, R.; Bimbo, N.; Sabri, M. F. M.; Maughan, P. A.; Bouscarrat, L.; Dawson, R. J.; Said, S. M.; Goh, B. T.; Sidik, N. A. C. Experimental investigation of energy storage properties and thermal conductivity of a novel organic phase change material/MXene as a new class of nanocomposites. *J. Energy Storage* **2020**, *27*, No. 101115.

(22) Qian, Z.; Shen, H.; Fang, X.; Fan, L.; Zhao, N.; Xu, J. Phase change materials of paraffin in h-BN porous scaffolds with enhanced thermal conductivity and form stability. *Energy Build.* **2018**, *158*, 1184–1188.

(23) Yang, J.; Tang, L.-S.; Bai, L.; Bao, R.-Y.; Liu, Z.; Xie, B.-H.; Yang, M.-B.; Wei, Y. Photodriven Shape-Stabilized Phase Change Materials with Optimized Thermal Conductivity by Tailoring the Microstructure of Hierarchically Ordered Hybrid Porous Scaffolds. *ACS Sustainable Chem. Eng.* **2018**, *6*, 6761–6770.

(24) Yin, H.; Gao, S.; Liao, C.; Li, C.; Cai, Z.; Xu, Y.; Liu, J. Self-assembly of 3D-graphite block infiltrated phase change materials with increased thermal conductivity. *J. Cleaner Prod.* **2019**, *235*, 359–368.

(25) Huang, X.; Lin, Y.; Alva, G.; Fang, G. Thermal properties and thermal conductivity enhancement of composite phase change materials using myristyl alcohol/metal foam for solar thermal storage. *Sol. Energy Mater. Sol. Cells* **2017**, *170*, 68–76.

(26) Zhu, W.; Hu, N.; Wei, Q.; Zhang, L.; Li, H.; Luo, J.; Lin, C.-T.; Ma, L.; Zhou, K.; Yu, Z. Carbon nanotube-Cu foam hybrid reinforcements in composite phase change materials with enhanced thermal conductivity. *Mater. Design* **2019**, *172*, No. 107709.

(27) Li, W. H.; Lai-Iskandar, S.; Tan, D.; Simonini, L.; Dudon, J.-P.; Leong, F. N.; Tay, R. Y.; Tsang, S. H.; Joshi, S. C.; Teo, E. H. T. Thermal Conductivity Enhancement and Shape Stabilization of Phase-Change Materials Using Three-Dimensional Graphene and Graphene Powder. *Energy Fuels* **2020**, *34*, 2435–2444.

(28) Sheng, N.; Nomura, T.; Zhu, C.; Habazaki, H.; Akiyama, T. Cotton-derived carbon sponge as support for form-stabilized composite phase change materials with enhanced thermal conductivity. *Sol. Energy Mater. Sol. Cells* **2019**, *192*, 8–15.

(29) Li, Y.; Li, J.; Feng, W.; Wang, X.; Nian, H. Design and Preparation of the Phase Change Materials Paraffin/Porous Al₂O₃@Graphite Foams with Enhanced Heat Storage Capacity and Thermal Conductivity. *ACS Sustainable Chem. Eng.* **2017**, *5*, 7594–7603.

(30) Jiang, Z.; Ouyang, T.; Yang, Y.; Chen, L.; Fan, X.; Chen, Y.; Li, W.; Fei, Y. Thermal conductivity enhancement of phase change materials with form-stable carbon bonded carbon fiber network. *Mater. Des.* **2018**, *143*, 177–184.

(31) Fang, H.; Lin, J.; Zhang, L.; Chen, A.; Wu, F.; Geng, L.; Peng, X. Fibrous form-stable phase change materials with high thermal conductivity fabricated by interfacial polyelectrolyte complex spinning. *Carbohydr. Polym.* **2020**, *249*, No. 116836.

(32) Chen, Y.; Ding, H.; Gao, J.; Tang, X.; Liu, Y.; Yang, M. A novel strategy for enhancing the thermal conductivity of shape-stable phase change materials via carbon-based in situ reduction of metal ions. *J. Cleaner Prod.* **2020**, *243*, No. 118627.

(33) Li, L. Z.; Liu, W. B.; Yang, F.; Jiao, W. C.; Hao, L. F.; Wang, R. G. Interfacial reinforcement of hybrid composite by electrophoretic deposition for vertically aligned carbon nanotubes on carbon fiber. *Compos. Sci. Technol.* **2020**, *187*, No. 107946.

(34) Lu, S. W.; Li, B. H.; Ma, K. M.; Wang, S.; Liu, X. M.; Ma, Z.; Lin, L. Y.; Zhou, G. N.; Zhang, D. X. Flexible MXene/EPDM rubber with excellent thermal conductivity and electromagnetic interference performance. *Appl. Phys. A* **2020**, *126*, 513.

(35) Ding, Z.; He, F.; Li, Y.; Jiang, Z.; Yan, H.; He, R.; Fan, J.; Zhang, K.; Yang, W. Novel Shape-Stabilized Phase Change Materials Based on Paraffin/EPDM@Graphene with High Thermal Conductivity and Low Leakage Rate. *Energy Fuels* **2020**, *34*, 5024–5031.

(36) Song, S.; Zhao, T.; Zhu, W.; Qiu, F.; Wang, Y.; Dong, L. Natural Microtubule-Encapsulated Phase-Change Material with Simultaneously High Latent Heat Capacity and Enhanced Thermal Conductivity. *ACS Appl. Mater. Interfaces* **2019**, *11*, 20828–20837.

(37) Luo, D.; Wei, F.; Shao, H.; Xiang, L.; Yang, J.; Cui, Z.; Qin, S.; Yu, J. Shape stabilization, thermal energy storage behavior and thermal conductivity enhancement of flexible paraffin/MWCNTs/PP hollow fiber membrane composite phase change materials. *J. Mater. Sci.* **2018**, *53*, 15500–15513.

(38) Feng, D.; Li, P.; Feng, Y.; Yan, Y.; Zhang, X. Using mesoporous carbon to pack polyethylene glycol as a shape-stabilized phase change material with excellent energy storage capacity and thermal conductivity. *Microporous Mesoporous Mater.* **2021**, *310*, No. 110631.

(39) Zhang, J.; Wang, Z.; Li, X.; Wu, X. Novel composite phase change materials with enhancement of light-thermal conversion, thermal conductivity and thermal storage capacity. *Sol. Energy* **2020**, *196*, 419–426.

(40) Zhang, H.; Sun, Q.; Yuan, Y.; Zhang, Z.; Cao, X. A novel form-stable phase change composite with excellent thermal and electrical conductivities. *Chem. Eng. J.* **2018**, *336*, 342–351.

(41) Sundararajan, S.; Samui, A. B.; Kulkarni, P. S. Crosslinked polymer networks of poly(ethylene glycol) (PEG) and hydroxyl terminated poly(dimethyl siloxane) (HTPDMS) as polymeric phase change material for thermal energy storage. *Sol. Energy* **2019**, *181*, 187–194.

(42) Zhang, X.; Huang, Z.; Ma, B.; Wen, R.; Zhang, M.; Huang, Y.; Fang, M.; Liu, Y.-g.; Wu, X. Polyethylene glycol/Cu/SiO₂ form stable composite phase change materials: preparation, characterization, and thermal conductivity enhancement. *RSC Adv.* **2016**, *6*, 58740–58748.

(43) Tang, B.; Wu, C.; Qiu, M.; Zhang, X.; Zhang, S. PEG/SiO₂-Al₂O₃ hybrid form-stable phase change materials with enhanced thermal conductivity. *Mater. Chem. Phys.* **2014**, *144*, 162–167.

(44) Grosu, Y.; Zhao, Y.; Giacomello, A.; Meloni, S.; Dauvergne, J.-L.; Nikulin, A.; Palomo, E.; Ding, Y.; Faik, A. Hierarchical macro-nanoporous metals for leakage-free high-thermal conductivity shape-stabilized phase change materials. *Appl. Energy* **2020**, *269*, No. 115088.

(45) Wang, J. J.; Huang, X. B.; Gao, H. Y.; Li, A.; Wang, C. Construction of CNT@Cr-MIL-101-NH₂ hybrid composite for shape-stabilized phase change materials with enhanced thermal conductivity. *Chem. Eng. J.* **2018**, *350*, 164–172.

(46) Yin, H. B.; Gao, S. Y.; Liao, C. C.; Li, C. M.; Cai, Z. D.; Xu, Y. J.; Liu, J. Self-assembly of 3D-graphite block infiltrated phase change materials with increased thermal conductivity. *J. Cleaner Prod.* **2019**, *235*, 359–368.

(47) Amaral, C.; Vicente, R.; Ferreira, V. M.; Silva, T. Polyurethane foams with microencapsulated phase change material: Comparative analysis of thermal conductivity characterization approaches. *Energy Build.* **2017**, *153*, 392–402.

(48) Akhiani, A. R.; Mehrali, M.; Tahan Latibari, S.; Mehrali, M.; Mahlia, T. M. I.; Sadeghinezhad, E.; Metselaar, H. S. C. One-Step Preparation of Form-Stable Phase Change Material through Self-Assembly of Fatty Acid and Graphene. *J. Phys. Chem. C* **2015**, *119*, 22787–22796.

(49) Wang, X. L.; Cheng, X. M.; Li, Y. Y.; Li, G.; Xu, J. Self-assembly of three-dimensional 1-octadecanol/graphene thermal storage materials. *Sol. Energy* **2019**, *179*, 128–134.

(50) Tian, B. Q.; Yang, W. B.; He, F. F.; Xie, C. Q.; Zhang, K.; Fan, J. H.; Wu, J. Y. Paraffin/carbon aerogel phase change materials with high enthalpy and thermal conductivity. *Fullerenes, Nanotubes, Carbon Nanostruct.* **2017**, *25*, 512–518.

(51) Baxter, R. I.; Rawlings, R. D.; Iwashita, N.; Sawada, Y. Effect of chemical vapor infiltration on erosion and thermal properties of porous carbon/carbon composite thermal insulation. *Carbon* **2000**, *38*, 441–449.

(52) Liu, X. X.; Wang, T. T.; Zhuang, M. Y.; Xin, B. J.; Liu, W. Investigation of the Thermal Transfer Behavior of Single Layer Woven Fabrics at Different Temperatures. *J. Eng. Fibers Fabr.* **2016**, *11*, No. 155892501601100.

(53) Kargar, F.; Barani, Z.; Salgado, R.; Debnath, B.; Lewis, J. S.; Aytan, E.; Lake, R. K.; Balandin, A. A. Thermal Percolation Threshold and Thermal Properties of Composites with High Loading of Graphene and Boron Nitride Fillers. *ACS Appl. Mater. Interfaces* **2018**, *10*, 37555–37565.

(54) Lewis, J. S.; Barani, Z.; Magana, A. S.; Kargar, F.; Balandin, A. A. Thermal and electrical conductivity control in hybrid composites with graphene and boron nitride fillers. *Mater. Res. Express* **2019**, *6*, No. 085325.

(55) Zheng, L. Y.; Zhang, X. L.; Hua, W. S.; Wu, X. F.; Mao, F. The Effect of Hydroxylated Multi-Walled Carbon Nanotubes on the Properties of Peg-Cacl(2) Form-Stable Phase Change Materials. *Energies* **2021**, *14*, 1403.

(56) Wu, X. F.; Tang, B.; Chen, J.; Shan, L. M.; Gao, Y.; Yang, K.; Wang, Y.; Sun, K.; Fan, R. H.; Yu, J. H. Epoxy composites with high cross-plane thermal conductivity by constructing all-carbon multi-dimensional carbon fiber/graphite networks. *Compos. Sci. Technol.* **2021**, *203*, No. 108610.