Energy Materials

Review

Phase change materials microcapsules reinforced with graphene oxide for energy storage technology

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Abstract

Phase change materials (PCMs) are considered one of the most promising energy storage methods owing to their beneficial effects on a larger latent heat, smaller volume change, and easier controlling than other materials. PCMs are widely used in solar energy heating, industrial waste heat utilization, energy conservation in the construction industry, and other fields. To avoid leakage, phase separation, and volatile problems of PCMs, the encapsulation technique typically uses organic polymer materials as shell structures of microcapsules. Furthermore, using inorganic materials to enhance the thermal property of phase change microcapsules is a popular approach in recent research. Especially, graphene oxide (GO) with high thermal conductivity was used as a common thermal conducting additive to improve the thermal performance of phase change microcapsules. Due to its amphiphilic property, GO combined with PCM microcapsules can achieve a variety of nanostructures for thermal energy storage. In this paper, four aspects have been summarized: configuration of PCMs, methods of combining GO with phase change microcapsules, position and content of GO, and applications of PCM/GO microcapsules. This work attempts to discuss preparation methods and heat-conducting properties of the PCM/GO microcapsules, which helps to better promote the application-targeted design and greatly improve the thermal properties of PCM microcapsules for various applications.

INTRODUCTION

With the rapid development of the global economy, the problem of energy shortage is becoming more pressing. The limited fossil energy such as coal, oil, and natural gas and environmental pollution have prompted global research teams to vigorously develop new energy and improve energy efficiency. However, many problems have been encountered in the process of development and utilization of new energy, such as the mismatch between energy supply, demand for time and space[1,2], and the low efficiency of energy conversion and utilization in industry and civil sectors. Achieving effective energy storage and conversion is of great significance for alleviating the energy crisis. Among many energy storage technologies, phase change energy storage technology can transfer part of the peak load to the off-peak load period to achieve better power management[3,4] and is considered to be one of the most promising energy storage strategies[5-7]. Although phase change energy storage technology is an important technology to improve energy utilization efficiency and protect the environment, its large-scale industrial application is limited[8,9] because of the respective shortcomings of organic and inorganic phase change materials (PCMs). Organic PCMs have high latent heat but exhibit low thermal conductivity, low melting point, and volatility[10]. Inorganic PCMs show high thermal conductivity, but there are issues such as overcooling, phase separation, corrosion, and low cycle time[11,12]. By combining inorganic materials and organic PCM, the PCM can be perfected and improved from multiple perspectives to obtain a composite PCM. It can not only have a large latent heat but also maintain a high thermal conductivity, which can further expand the application prospects of phase change energy storage[13,14]. Typical composite structure techniques include electrospinning technology, metal foam technology, and microcapsule technology[15-17], of which microencapsulation uses various polymer materials as wall materials and wraps PCMs to form phase change microcapsules. It is one of the current research hotspots in the field of phase transition through the encapsulation of the PCM, and the leakage of the liquid material can be effectively prevented[18,19].

From the present study, the PCM microcapsules mainly use organic macromolecular polymers as wall materials[20-22]; paraffin[23], polyols[24], and fatty acids[25] are used as common core materials. The low thermal conductivity of polymer materials will seriously restrict the heat transfer performance of encapsulated PCMs in practical applications. For phase change microcapsules, the shell materials with low thermal conductivity will cause most of the heat to be directly dissipated in the convection between the shell materials and the environment. The heat cannot be effectively introduced into the PCM, resulting in a low thermal response rate and slow heat storage and release rate, which directly affects the energy storage efficiency and energy storage capacity of the PCM. Many studies have found that adding high-conductivity materials, such as graphene[26], black phosphorus[27], and carbon nanotubes (CNTs)[28], can significantly improve the thermal conductivity of phase change microcapsules. Graphene oxide (GO) is the product of the chemical oxidation of graphite and has been known as an excellent nanofiller to improve tensile strength, elastic modulus, and thermal properties[29-31]. Compared with graphene, GO has many unique chemical properties, such as amphiphilicity, negatively charged nature, and multioxygen-containing groups on its sheet[32-35]. Thus, it makes GO a more favorable nanofiller that can be used to stabilize the O/W emulsion for the preparation of PCM microcapsules and also improve thermal conductivity for PCMs. GO has become one of the most commonly used fillers in the preparation of composite phase change microcapsules.

To increase the thermal conductivity of the PCMs, the traditional addition method generally adopts the random dispersion of the thermal conducting materials in the polymer matrix[36,37], whereas this will

inevitably lead to the phenomenon of agglomeration. The use of a large amount of thermal conducting materials is often required to obtain a continuous and effective thermal conduction path to achieve the desired target thermal conductivity value. Besides, a high material filling rate usually leads to problems, such as high cost, poor mechanical properties, and increased fabrication difficulty. Herein, different kinds of materials of core and shell structure of PCM microcapsules are analyzed and evaluated, and the configuration and performance and critically reviewed and compared [Figure 1]. More importantly, the methods and positions of adding GO to the PCM microcapsule for improving thermal efficiency were discussed. Finally, the applications of PCM-GO microcapsules are summarized. Therefore, it is still a huge challenge to develop new composite PCMs that can maintain thermal conductivity while minimizing the amount of filling material added to achieve significantly enhanced efficiency. This material is expected not only to open up a new way for the design and preparation of high-performance PCMs but also greatly promote the application and development of PCM microcapsules.

CONFIGURATION OF PCM MICROCAPSULES
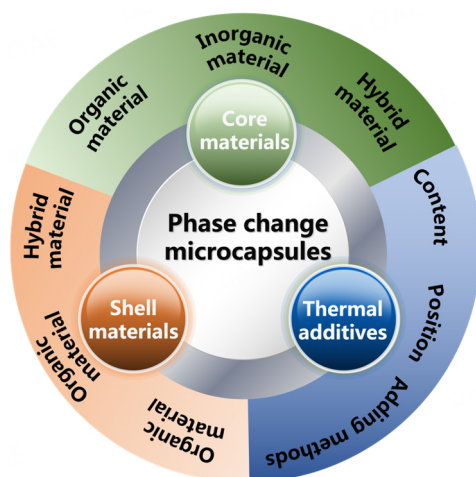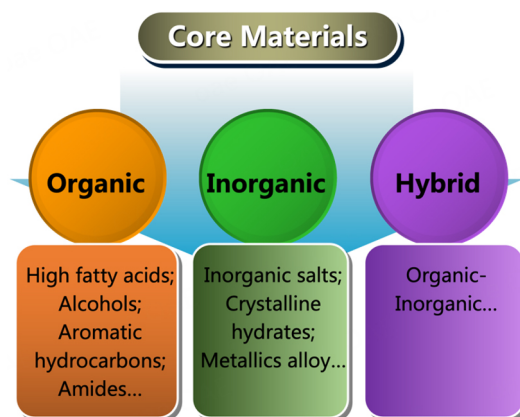
Core materials of PCM microcapsules

The PCM is used as the core material of the phase change microcapsule to prevent its leakage during the solid-liquid conversion. According to the present study, PCMs are divided into three categories: organic, inorganic, and hybrid [Figure 2].

Organic PCMs include high fatty acids, alcohols, aromatic hydrocarbons, amides, *etc.* The advantages are easy to mold, less phase separation, less corrosion, and no surfusion; the disadvantages include small density, flammability, and low thermal conductivity. Among them, paraffin is the most studied organic core material because it has a large latent heat of phase transition and a wide range of phase transition temperatures. It is a straight-chain saturated alkane, and its general formula is C_nH_{2n+2}. The form is a liquid state when the number of carbon atoms is 5 to 15, and more than 15 belongs to a solid state. Fatty acid ($CH_3(CH_2)_{2n}COOH$) is another common PCM; its phase change properties and characteristics are similar to paraffin materials, with higher phase change latent heat and smaller phase change volume change. As a class of non-paraffin organic compounds, it has superb properties than other PCMs, such as unique eutectic and eutectic characteristics, high melting enthalpy, non-flammability, low price (derived from animal fats), good thermal and chemical stability. Polyol-based PCMs refer to organic compounds formed by replacing two or more hydrogen atoms in alkane-based materials ($C_nH_{2n+2-x}(OH)_x$, x ≥ 2) with hydroxyl groups. During the phase change process, polyol-based PCMs have smaller volume changes, robust leak-proof character, and long service time. The latent heat of phase change transition is directly related to the number of hydroxyl groups, and common polyol-based PCMs include neopentyl glycol ($C_5H_{12}O_2$, NPG), trimethylolethane ($C_5H_{12}O_3$, TME), pentaerythritol ($C_5H_{12}O_4$, THME), and more. Organic PCMs are endowed with a wide selection range of phase transition temperatures and melting points [Table 1]. Typical inorganic PCMs include inorganic salts[45,46], crystalline hydrates[47,48], *etc.*, such as Na_2SO_4, $Na_2SO_4 \cdot 10H_2O$, $CaCl_2 \cdot 6H_2O$, and KOH. However, inorganic PCMs have some obvious demerits: (1) they experience a large degree of supercooling, with crystallization starting only at the crystallization temperature; (2) they are susceptible to precipitation and phase separation, which greatly restricts the development of crystalline hydrated salt PCMs. To overcome the above shortcomings, anti-supercooling agents and anti-phase separation agents are generally added in actual use to improve their phase change performance[49,50]. Most inorganic PCMs have low latent heat and will produce harmful gases to human health; therefore, their applications are limited.

Although phase change energy storage technology improves energy utilization efficiency and protects the environment, its large-scale industry application is limited due to the shortcomings of organic and inorganic PCMs. Hybrid PCMs are designed to effectivity solve the shortcomings of organic PCMs, such as

Table 1. Summary of properties of common PCMs

PCM	Melting point (°C)	Latent heat (J g^{-1})	Ref.
Hexadecane	16.70	236.00	[37]
Eicosane	36.50	237.40	[38]
Docosane	42.30	256.10	[39]
1-dodecanol	22.00 ± 0.30	191.00 ± 3.00	[40]
Stearic acid	69.40	199.00	[41]
Palmitic acid	58.00~64.00	190.00~220.00	[42]
Myristic acid	52.20	182.60	[43]
Neopentyl glycol	129.46 ± 0.14	141.91 ± 1.24	[44]

Figure 1. Overview of phase change microcapsules.

Figure 2. Core materials of phase change microcapsules.

low thermal conductivity, low melting point, and volatility, and the issues seen in inorganic PCMs, such as overcooling, phase separation, corrosion, and a low number of cycles[51-53]. By combining two or more materials, the PCMs are perfected and improved from multiple angles. A hybrid PCM can have a large phase change latent heat while maintaining a high thermal conductivity and further expand the application prospect of phase change energy storage. Among various composite structure technics, microencapsulation

uses various polymers as shell materials and wraps PCMs inside to form phase change microcapsules, which is currently the research hotspot in the field of phase transition. Through the encapsulation of PCMs, the leakage of liquid materials can be effectivity prevented. The treated PCMs have good thermal properties, a large specific surface area, and high heat storage efficiency and are not prone to leakage, corrosion, and supercooling.

Shell materials of PCM microcapsules

The shell materials of PCM microcapsules can be divided into organic, inorganic, and hybrid materials [Figure 3]. The considerations for shell material selection usually include whether it undergoes a chemical reaction with the core material, high-temperature stability, heat transfer performance, high mechanical strength, suitable permeability, and durability.

Organic materials have good thermal stability, good compactness, and a simple preparation process. The most widely used shell materials include urea-formaldehyde (UF) resin, polystyrene (PS), polymethyl methacrylate (PMMA), and poly(melamine-formaldehyde) (MF) resin, *etc*. MF resin is mostly prepared by polycondensation, and it has been used as the shell material because of its high impact strength, low price, and good stability. Yuan *et al*. designed phase change microcapsules that contain n-eicosane as core and polydopamine/poly(melamine-formaldehyde) (PDA@MF) resin as shell material via two-step polymerization[54]. The introduction of PDA efficiently improved the solar thermal conversion efficiency of phase-change microcapsules; it greatly reduces the leakage rate of the microcapsules and increases the strength of the shell structure. The inorganic shell materials have good thermal conductivity, good heat transfer properties, and high mechanical strength, but the poor airtightness and toughness limit their further applications. Common inorganic shell materials include silicon dioxide (SiO_2)[55], titanium dioxide (TiO_2)[56], calcium carbonate ($CaCO_3$)[57], zinc oxide (ZnO)[58] and so on. Liu *et al*. reported the ceramic silica microcapsules encapsulated with both stearic acid (SA) and flame retardant, which coating on the commercial polyolefin separator as a thermo-responsive composite separator[59]. Benefitting from the excellent electrolyte affinity of the ceramic shell, which effectively prevents the flame retardant from direct exposure to the electrolyte and minimizes its adverse impact on the battery performance.

Both organic and inorganic shell materials have various disadvantages in their application. For example, the generated pressure inside the microcapsules attributed to the volume expansion during the process of phase change may give rise to cracks on the surface of the inorganic shell. As one of the most widely used shell materials, PMMA is rigid and brittle, and it can easily crack during thermal cycling. However, some flexible organic shell materials, such as polyurethane (PU) and polyvinylidene fluoride (PVDF), can withstand the volume expansion of PCMs to avoid rupture and maintain the integrity of microcapsule structures. Therefore, some researchers proposed to use organic-inorganic hybrid materials as the shell to prepare phase change microcapsules with the advantages of both. Sun *et al*. reported a core-shell structured poly(ethylene glycol) silica microencapsulated phase change materials ($PEG@SiO_2$-MEPCM) was synthesized through reverse emulsion-templated *in-situ* polycondensation by optimizing the ratio of surfactant and cosurfactant achieves a high encapsulation ration (over 80.00%) with a good latent heat (130 J g^{-1})[60]. The low thermal conductivity of polymer materials will seriously restrict the heat transfer of phase change microcapsules in practical applications. Many studies have found that adding high thermal conductivity materials, such as graphite, black phosphorus, and CNTs, can greatly improve thermal conductivity[61]. Liu *et al*. investigated the effects of the combination of GO and CNTs on the morphology and thermal properties of the phase change microcapsules; the outcomes showed that the GO/CNT additive can greatly increase the thermal conductivity of the microcapsules[62]. The thermal conductivity was improved by 195.00%, with the latent heat slightly decreased, with a hybrid additive loading of 0.60 wt%[62].
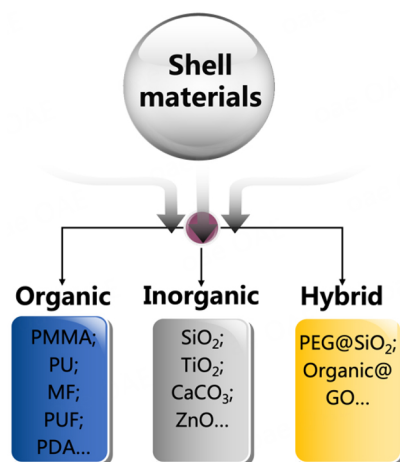
Figure 3. Shell materials of phase change microcapsules.

THE POSITION AND CONTENT OF GRAPHENE OXIDE IN PCM MICROCAPSULES

The process of storing and releasing the energy of phase change storage materials is determined by the melting point and the ambient temperature. When the temperature rises to the melting point, the PCM changes from solid to liquid. This melting process is an endothermic process in which the PCM absorbs the surrounding environmental heat and stores it. However, the shell phase with low thermal conductivity will cause most of the heat to be dissipated directly in the convection between the shell material and the outside. The heat cannot be effectively introduced into the PCM, resulting in a low thermal response rate and a slow heat storage and release rate, which directly affects the energy storage efficiency and energy storage capacity of PCMs. Since the thermal conductivity of polymer and organic PCMs has a small difference (between 0.1 and 0.2 W m^{-1} K^{-1})[63], the core-shell ratio of PCM microcapsules is mainly between 0.3 and 2.5[64]. Therefore, the selection of a suitable position and the relationship between the thermal conductivity materials and the compatible fit of the fusion phase is critical.

Shell phase of PCM/GO microcapsules

At present, distributing GO in the shell structure is the main method of composite phase change microcapsules, aiming to solve the low thermal conductivity of polymer materials. Most of the literature related to the distribution of GO in phase change microcapsules is located in the shell structure mainly due to the presence of the hydrophilic groups on the surface of GO[65,66]. The distribution positions include the surface of the shell structure, inside of the shell structure, double distribution inside, and the surface of the shell structure. Lin *et al.* prepared microencapsulated phase change materials with GO-attached (GO-MPCM) to the surface of silica by a sol-gel method and self-assembly process[67]. As compared with no GO-decorated microcapsules, the thermal conductivity of GO-MPCM was maximized to 175.00%, but the encapsulation efficiency was decreased by 21.33% [Figure 4A]. Nevertheless, Jiang *et al.* show a completely different point of view. They prepared microencapsulated phase change materials (MEPCMs) by encapsulating paraffin with GO modified the CaCO$_3$ shell [Figure 4B][19]. Compared with the MEPCMs without GO, the encapsulation efficiency of GO-modified MEPCMs was as high as 73.19%. The leakage rate was decreased by 89.60%, which indicated that the GO-modified shell played a positive role in leakage prevention [Figure 4C]. Zhang *et al.* prepared MEPCMs with high encapsulation capacity and enhanced leakage-prevention performance via *in-situ* polymerization, using paraffin and MF as core and shell material, respectively[35]. When GO was located at the core-shell interface, it successfully acted as an additional protective screen against core leakage compared with the control group. These MEPCMs showed better leakage prevention (reduced by 93.10%) [Figure 4D] and high encapsulation efficiency (93.90%). The

Figure 4. (A) Formation mechanism for the GO-MPCM[67] (Copyright 2019, Elsevier). (B) A process of preparing of MEPCMs. (C) The curve of leakage rate over time of MEPCMs with a different mass of GO (0.0, 0.5, 1.0, and 1.5 g L^{-1})[19] (Copyright 2018, American Chemical Society). (D) Paraffin leakage rate of MEPCM according to time[35] (Copyright 2017, Elsevier).

amphiphilic of GO makes it easily attach to the surface of the oil phase between the PCM core and the shell of microcapsules. As a result, it is generally used as an emulsifier for emulsion polymerization. Fan *et al.* introduced hexadecane microcapsules with GO/poly(urea-formaldehyde) (PUF) hybrid shell prepared through one-step microencapsulation, in which GO plays dual roles as a surfactant and the thermal conducting additive[68]. The hexadecane-loaded microcapsules showed excellent thermal and barrier performance; GO performed good emulsifying ability and was perfectly introduced into the shell structure of phase change microcapsules. GO has been shown to provide precursors for a Pickering emulsion polymerization via self-assembly at the liquid-liquid interface in two-phase liquid media. However, the distribution of GO between or within which two liquid phases is still related to its preparation method and its content[69].

Core phase of PCM/GO microcapsules

Some studies disperse core materials in addition to combining GO with the shell structure of phase change microcapsules to pursue the demand for microencapsulation PCMs with high thermal energy storage capacity. Chen *et al.* reported MEPCMs using MF resin as the shell material[70]. The combination of octadecylamine-grafted GO (GO-ODA) and n-octadecane as the core material was synthesized through *in-situ* polymerization [Figure 5A][70]. The alkylated GO was confirmed to be highly compatible with the core material, and the addition of GO promoted the crystallization of n-octadecane. The encapsulation efficiency of MEPCMs was over 88.00%, and the melting/freezing latent heats were 207.2 J g^{-1} and 202.5 J g^{-1}, respectively. Qian and Mao compared the thermal properties of two different GO-distributed phase change microcapsules: (1) GO was added to the inside of the core material (paraffin), which was defined as paraffin/GO@UF composite [Figure 5B]; (2) another approach was GO being coated onto the surface of shell material (UF), which defined as paraffin@UF/GO composite [Figure 5C][71]. With the increase of the GO weight percentage, the thermal conductivity of the paraffin/GO@UF composite slightly increased. However, in the paraffin@UF/GO composite, the thermal conductivity was greatly enhanced. The thermal conductivity of the paraffin/GO@UF and the paraffin@UF/GO was strengthened from 0.2236 ± 0.0003 W m^{-1} K^{-1} to 0.2517 ± 0.0003 W m^{-1} K^{-1} and 1.067 ± 0.0020 W m^{-1} K^{-1}, respectively. In the meantime, there was no obvious influence on the enthalpy or phase change temperature of these phase change microcapsules, and the encapsulation efficiency of both samples exceeded 80.00% (w/w).

Another work shows the preparation of novel SA@GO/MF superhydrophobic phase change microcapsules through condensation polymerization, in which the GO plays a positive role in preventing the paraffin leakage during the phase change process [Figure 6A][72]. With a GO volume fraction of 15 mL, the thermal conductivity of the phase change microcapsules can reach 0.435 W m^{-1} K^{-1}. More importantly, as shown in Figure 6B, the leakage prevention property of SA@GO/MF is enhanced with an increase in the GO content. The leakage prevention performance of SA@GO/MF is improved by 61.99% compared to the sample without GO addition, which contributes to the double shell structure, consisting of the GO inner shell and the MF outer shell. The studies confirmed that GO can not only improve the thermal conductivity of phase change microcapsules but also prevent the leakage of PCMs through self-assembly and layer-by-layer structure; it also can be used as a colloid stabilized in Pickering emulsion[73]. The content of GO affected the size of Pickering emulsion droplets, which decreased with increasing GO content; only 1 g L^{-1} GO was enough to stabilize the emulsion. Compared to graphene, the oxygen-containing chemical groups (such as the carboxyl group and the hydroxyl group) on the surface of GO result in amphiphilic properties, making it a useful emulsifier for stabilizing the O/W emulsion [Figure 6C].

Most literature on GO-modified phase change microcapsules reported that water-soluble GO was incompatible with organic PCMs, making it difficult to achieve a stable dispersion within the core of the phase change microcapsules; therefore, the relevant literature on this topic is scarce. Similarly, graphite nanoplatelets were added to PCM (Crodetherm™ 60), which was successfully encapsulated within polyurea as the shell material via an interfacial reaction[74]. The results show that the phase change microcapsules prepared with 0.10 wt% graphite nanoplatelets have a latent heat of 95.5 J g^{-1} at a phase transition temperature of about 64 °C. Furthermore, a stable dispersion of 16.00 wt% of the phase change microcapsules in an aqueous solution indicated better photothermal conversion performance when the temperature rose from 17 °C to 85 °C.

So far, there are no relevant literature reports on the addition of GO to both the shell and core structure of phase change microcapsules. However, there are a few reports on the simultaneous distribution of CNTs in phase change microcapsules [Figure 7A and B]. The results show that phase change microcapsules with a dual distribution of CNTs exhibit substantially enhanced thermal transportation rates. Figure 7C indicates
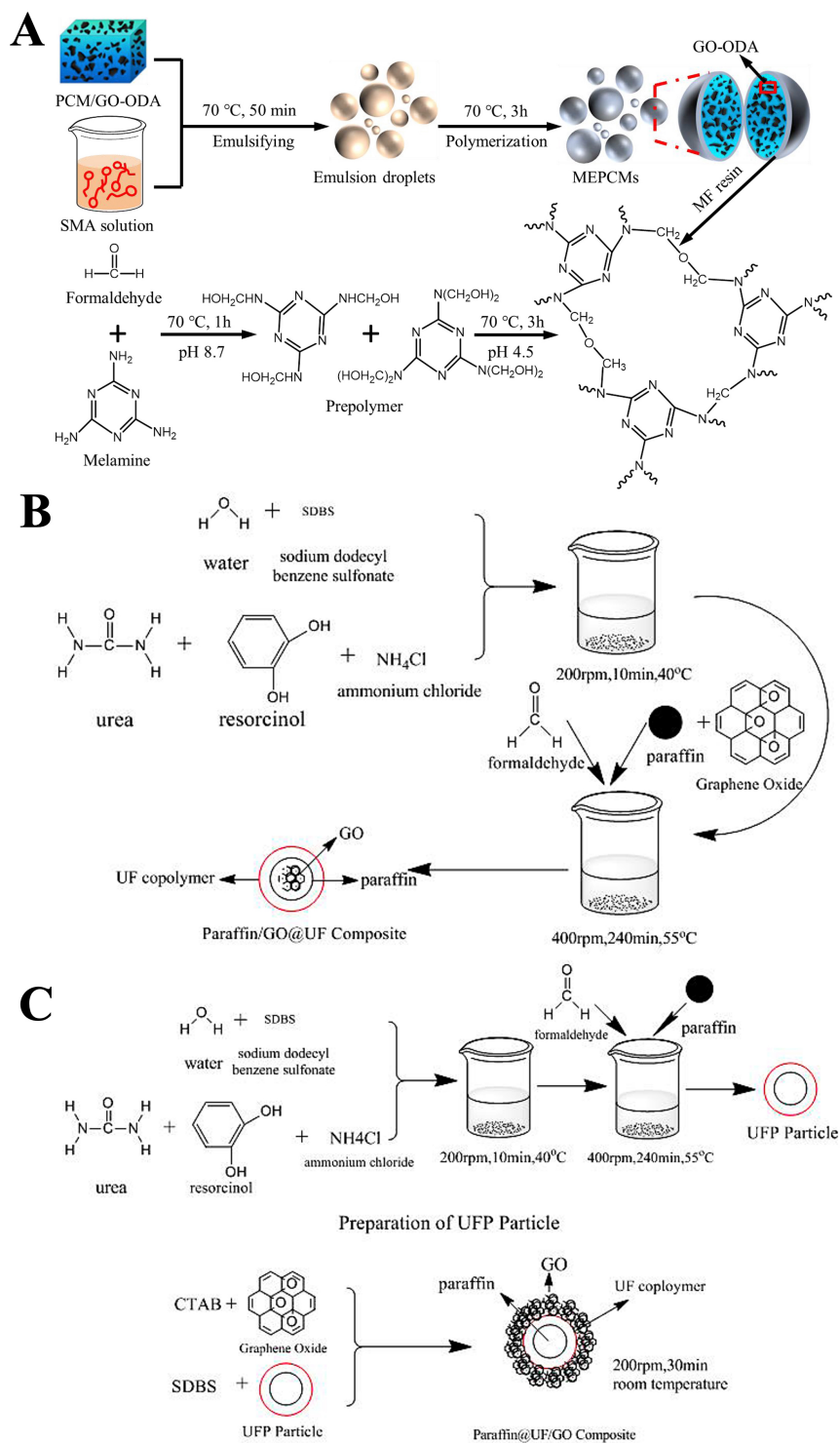
Figure 5. (A) Fabrication of GO-ODA-filled MEPCMs[70] (Copyright 2018, Elsevier). Preparation of (B) paraffin/GO@UF and (C) paraffin@UF/GO composite[71] (Copyright 2019, Informa UK limited).

the thermal conductivity of these microcapsules was increased by 71.40% compared to that of microcapsules filled with the same amount of CNTs[75].
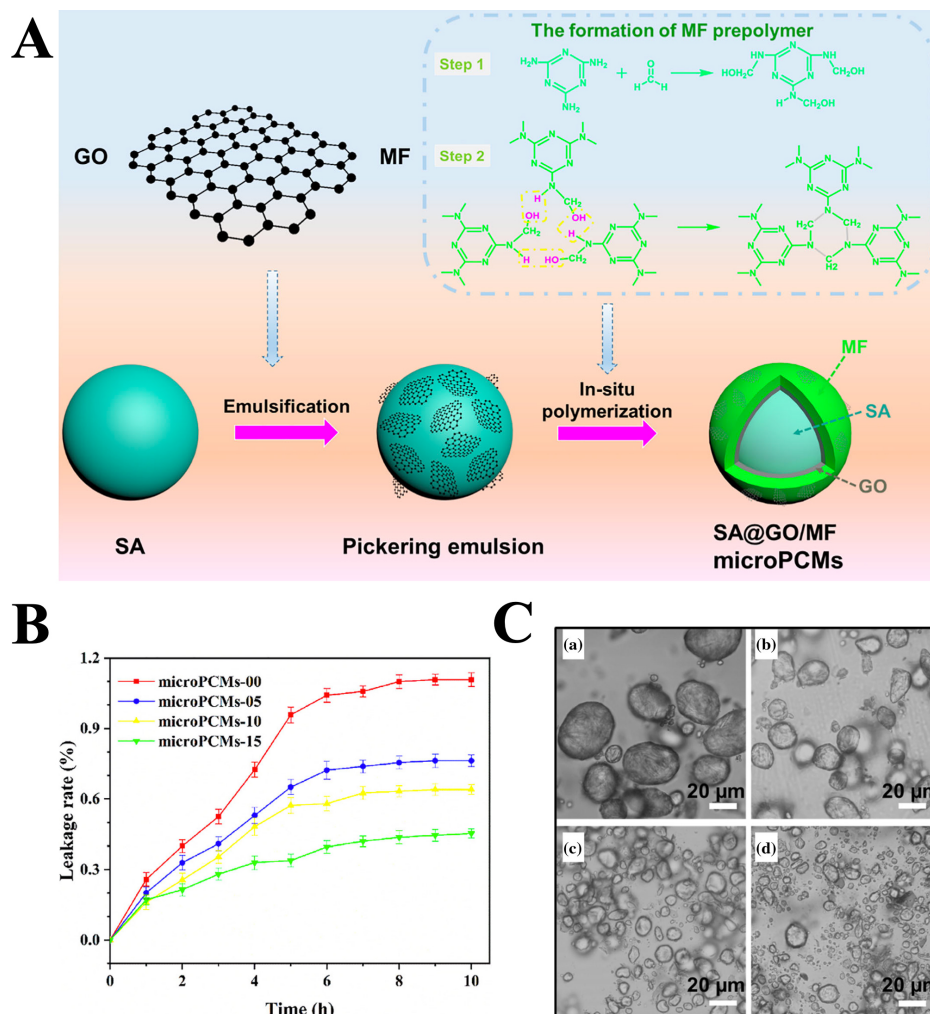
Figure 6. (A) Schematic illustration of the preparation of SA@GO/MF microcapsules. (B) Leakage rate of SA@GO/MF microcapsules in 10 h[72] (Copyright 2020, Wiley). (C) Optical images of PCM/isophorone diisocyanate (IPDI) Pickering emulsions stabilized by GO [(a) 1 g L^{-1}, (b) 2 g L^{-1}, (c) 4 g L^{-1}, (d) 8 g L^{-1}][73] (Copyright 2020, Nature).

THE METHODS OF ADDING GRAPHENE OXIDE IN PCM MICROCAPSULES

Graphene is a two-dimensional carbon material, and its internal carbon atoms are bonded by sp^2 hybrid orbitals, which connect the carbon atoms with o bonds and form large π bonds in a half-filled state[76]. This special arrangement of carbon atoms makes graphene have excellent properties, and GO is formed after oxidation, which makes it chemically active and easily modifiable to meet the different application requirements. GO has an ultra-high thermal conductivity (5,300 W m^{-1} K^{-1})[77], which is higher than sing- and double-walled CNTs. Additionally, it is compatible with non-polar solvents and exhibits excellent flexibility, making it easy to compound with other materials.

As we know, the organic-inorganic hybrid shell can combine the advantages of both materials, which can improve the sealing performance and thermal conductivity of the phase change microcapsules. At present, the traditional addition method is to directly disperse the thermal conducting materials in the shell or core material to prepare the phase change microcapsules. Using this method will lead to the aggregation and uneven distribution of thermal conducting materials in the substrate, which will greatly affect the heat conduction and heat storage performance. To improve the properties of the hybrid shell, modifications to
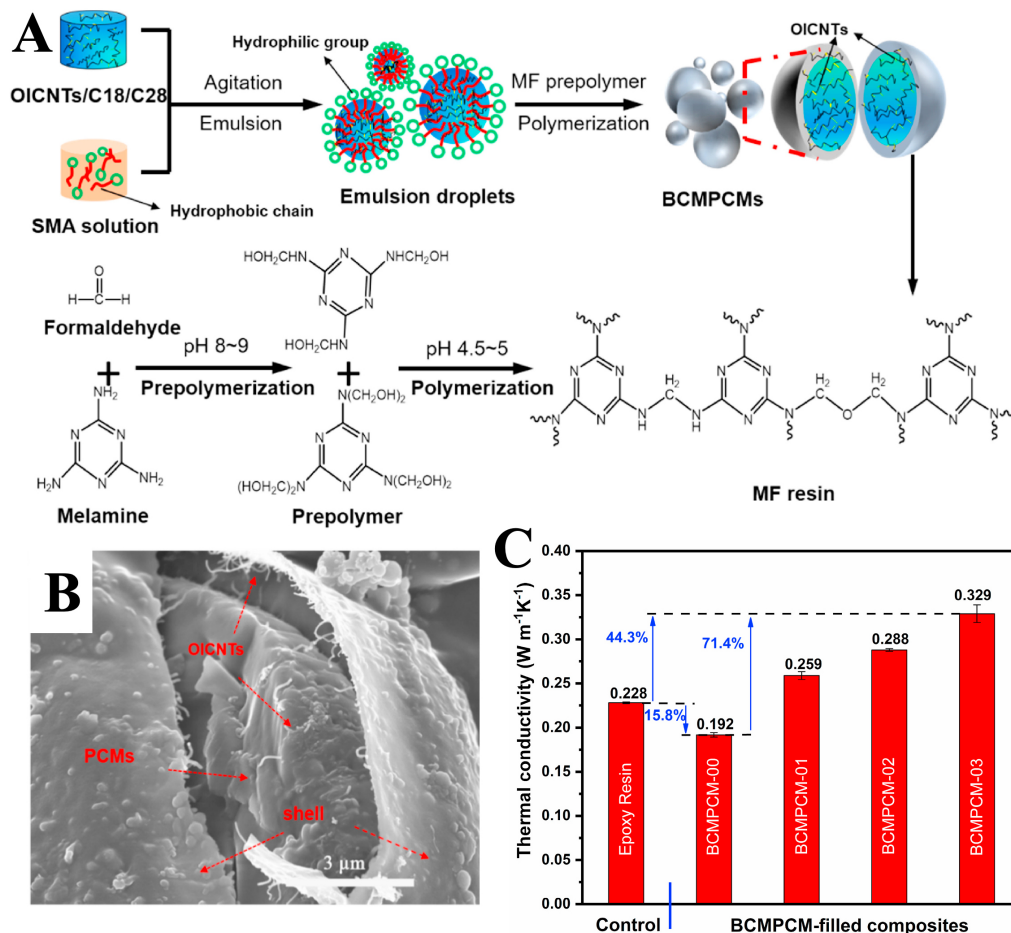
Figure 7. (A) Fabrication of PCM@CNTs microcapsules. (B) FE-SEM image of CNTs distributed in phase change microcapsules. (C) Thermal conductivity of different content of CNTs in phase change microcapsules[75] (Copyright 2020, Elsevier).

the shell and microstructure design may be necessary to obtain more stable and functional phase change microcapsules. Further research and exploration are needed to expand the application field of phase change microcapsules.

The interface plays a significant role in thermal conducting polymer composites. The interface effect is mainly reflected in three aspects: blocking effect, scattering and absorption effect, and transfer effect. Among these, the blocking effect mainly reduces the effect on the interface from the perspective of physics and force. The scattering and absorption effect means that the phonons at the interface will have vibration harmonics during the heat conduction process, resulting in serious scattering and a sharp decrease in the mean free path of the phonons. Heat flow is often hindered, causing severe heat loss, which, in turn, reduces the thermal conductivity of the polymer composite. Therefore, improving the interface of thermally conductive polymer composites and reducing the interfacial thermal resistance is the key to further improving the thermal conductivity of hybrid PCMs. As shown in Figure 8A, Zheng *et al.* controlled the interfacial adhesion between PS and sapphire samples by adjusting the rotational speed during spin coating and found that the interfacial adhesion between the two increased with an increase in rotational speed[78]. More importantly, the study also proved that the thermal conductivity of the polymer/sapphire interface increased by about three times as the rotational speed increased from 2,000 rpm to 8,000 rpm, as shown in Figure 8B. Moreover, Huxtable *et al.* measured the interfacial thermal conductivity of CNTs suspended in
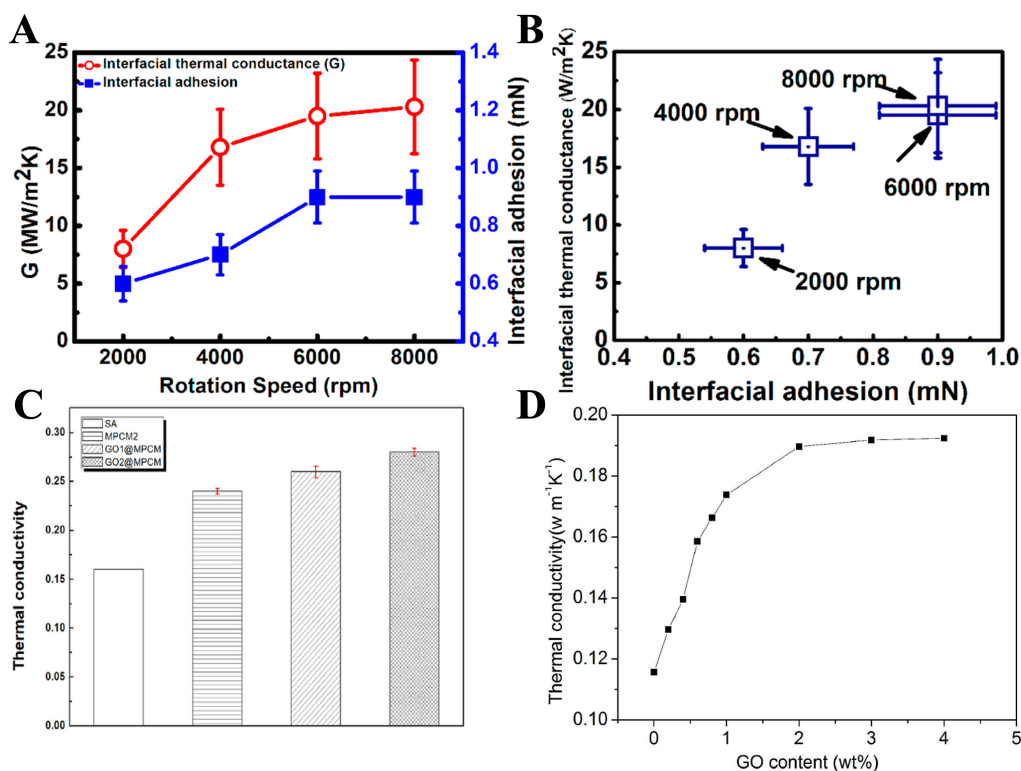
Figure 8. (A) Interfacial thermal conductance and interfacial adhesion increase with rotation speed. (B) The relationship of interfacial thermal conductance and interfacial adhesion between PS film and sapphire[78] (Copyright 2015, American Chemical Society). (C) Thermal conductivity of stearic acid (SA), microencapsulated phase change materials (MPCM2), with 20 mg GO microencapsulated phase change materials (GO1@MPCM), and 40 mg GO microencapsulated phase change materials (GO2@MPCM)[67] (Copyright 2018, Elsevier). (D)Thermal conductivity of phase change microcapsules with different content of GO[80] (Copyright 2015, Royal Society of Chemistry).

sodium dodecyl sulfate (SDS) micelles (approximately 12 MW m^{-1} K^{-1}), which indicates that the interaction between SDS molecules and CNTs occurs through van der Waals forces[79]. The van der Waals force has a minimal effect on the interfacial thermal conductivity. These studies show that establishing sufficient interfacial bonding between the thermal conducting filler and the polymer substrate can significantly reduce the interfacial thermal resistance. The thermal conductivity of the polymer composite obtained by mixing the thermal conducting material with the polymer substrate is much lower than the theoretical value. It is mainly because the interfacial force between the base and the thermal conducting filler is the van der Waals force. The interface thermal resistance has a great influence on the interface heat conduction; the weak van der Waals force will lead to low phonon-phonon coupling, and interfacial thermal conductivity cannot be effectively improved.

Physical methods of adding GO in PCM microcapsules
Table 2 shows the effect of adding GO at different contents and locations through physical methods on the enhancement of thermal conductivity of phase change microcapsule. The statistical results indicate that, when excluding the interference of the thermal conductivity of the capsule shell materials themselves, the thermal conductivity of thermal conducting additives in the shell structure is better than its distribution on the surface. Conversely, the worst scenario is the distribution of GO in the core structure. These results can be attributed to the fact that the GO embedded in the shell structure can form a continuous thermal matrix between the outer shell and the core. The core material is well connected with the external environment through the GO material, thus significantly improving its thermal conductivity. However, it does not mean

Table 2. Phase change microcapsules with GO added by physical methods

Microcapsules	GO content	Thermal conductivity (W m^{-1} K^{-1})	GO addition position	Ref.
Paraffin@CaCO$_3$	1.00 wt%	0.879	Both inside and outside the shell	[19]
Stearic acid/SiO$_2$	40 mg	0.280	External surface	[67]
Paraffin@UF/GO	10.00 wt%	1.067 ± 0.002	External surface	[71]
Stearic acid/MF	15 mL	0.435	Between the shell and core	[72]
MF/GO	4.00 wt%	0.192	Embedded in shell	[80]
Paraffin@SiO$_2$/GO	1.80 wt%	1.162	External surface	[81]
TiO$_2$@Paraffin	2.00 wt%	0.291	External surface	[82]
Paraffin@PbWO$_4$	1.5 mg mL^{-1}	0.735	Between the double shell	[83]
Paraffin@Regenerated Chitin-PU	0.10 wt%	0.345	Between the shell and core	[84]
N-dodecanol/melamine	0.60 wt%	0.279	Embedded in shell	[85]
FGO/PMMA-NanoPCMs	0.10 wt%	0.109	External surface	[86]
GO/SiO$_2$@Solar salt	3.00 wt%	0.676	External surface	[87]
Wax@PDVB@GO@PDMS	1.01 wt%	0.410	External surface	[88]
Paraffin@EC/MC/GO	5 mL	0.587	Embedded in shell	[89]
Paraffin@TiO$_2$/GO	2.0 mg mL^{-1}	0.950	External surface	[90]
Paraffin@GO	10.00 wt%	10.500	External surface	[91]
Paraffin@GO	0.20 wt%	0.645	External surface	[92]

that the more thermal conducting additives are added to the structure of the capsule shell, the higher thermal conductivity will obtain, which is not proportional to the mass of the thermal conducting additive being beyond a certain range. When the content of GO in the SA/SiO$_2$ microcapsules shell structure doubled, its thermal conductivity only increased by 12.50%, while the encapsulation efficiency dropped by 5.71% [Figure 8C][67]. Figure 8D also shows that when the content is less than 2.00 wt%, the thermal conductivity grows greatly with the increase of GO mass. However, after the mass of GO in the shell structure exceeds 2.00 wt%, the thermal conductivity of the phase change microcapsules gradually slows down and tends to saturate[82]. This can be attributed to the fact that the content of GO increased to 4.00 wt%, and the polymer substrate network became saturated. Excess GO is easily separated from the shell structure surface of phase change microcapsules. This is because the increase of GO content in the shell structure cannot exceed the electrostatic adhesion ability of O/W emulsion droplets in the *in-situ* polymerization.

Chemical methods of adding GO in PCM microcapsules

The transfer effect is to act as a bridge between the polymer substrate and the thermal conducting additive through the interface to ensure continuity[93], and it is also the key to improving the thermal conductivity of the phase change microcapsules. To achieve efficient conduction of heat flow in phase change microcapsules, a continuous and effective thermal conductive path is established in the substrate via the thermal conducting additive. Due to the enormous thermal resistance of the polymer matrix, heat flow will follow the path formed by the contact of the thermal conducting additive, which has the lowest thermal resistance. However, randomly dispersing of thermal conducting additives in the polymer matrix by physical addition to improve the thermal conductivity of the phase change microcapsules will lead to the inevitable aggregation of thermal conducting additives.

To greatly increase the thermal conductivity of the interface, researchers began to try to build chemical bonds between the polymer matrix and the thermal conducting additives. They tried to use the heat-carrying phonons formed on the chemical bonds to improve the thermal conductivity of the phase change

microcapsules. Zhou *et al.* prepared paraffin@modified GO microcapsules by an emulsion method, and GO was modified by 3-aminopropyltriethoxysilane (3-ATPS)[94]. The 3-ATPS is not only used to decrease the hydrophilic of GO but also improve the connection strength among paraffin (core material), hydroxypropyl cellulose (APC, shell material), and GO. The results showed that the phase change microcapsules with chemically modified GO had both a high thermal conductivity (1.662 W m^{-1} K^{-1}) and a high latent heat (88.7 J g^{-1}).

Liang *et al.* reported the use of functionalized GO-modified PMMA as the shell structure and n-octadecane and n-butyl stearate as binary core phase change microcapsules (FGO/PMMA-NanoPCMs) through emulsion polymerization[86]. GO was successfully modified by methacryloxy trimethoxyl silane (KH-570) to reduce its hydrophilicity, given the high inherent hydrophilicity of GO and its poor compatibility with PMMA [Figure 9A]. As shown in Figure 9B and C, the GO and FGO aqueous suspensions were clear yellow-brown and turbid, respectively, showing that long carbon chains were grafted onto the GO surface after treatment with KH-570, leading to a decrease in hydrophilicity. Compared to the control group (without FGO), the thermal conductivity of FGO/PMMA-NanoPCMs increased with an increase in the content of GO. Only 0.03 wt% FGO can increase by 90.18% in thermal conductivity, which means that few quantities of FGO can significantly improve the thermal conductivity of PMMA NanoPCMs, as shown in Figure 9D.

From the above research, it can be seen that the formation of chemical bonds between substrates and thermal conducting additives is an effective strategy to enhance the interaction between the two and greatly improve thermal conductivity because the resonance frequency is generated by stronger chemical bonds, which can effectively couple heat-carrying phonons between different materials, making heat transfer easier.

APPLICATIONS OF PCM/GRAPHENE OXIDE MICROCAPSULES

The PCM/GO microcapsules provide a reliable approach for the blending of PCMs with polymers and other functional materials, effectively addressing the drawbacks of organic and inorganic PCMs while also expanding the application fields of PCM. Due to their large storage capacity and thermal stability of the thermal storage process, phase change microcapsules have attracted great attention, extending their use to fields such as energy storage, buildings, textiles, battery thermal management, and more. Table 3 displays a set of applications of the PCM/GO microcapsules. Through the addition of GO, a high thermal conducting additive, the high latent heat characteristics of PCMs are preserved while their thermal conductivity is greatly increased. Therefore, phase change microcapsules are widely used in the field of energy storage. By selecting different polymer shell materials and functionalizing them, different properties can be imparted to phase change microcapsules, which can be used in a variety of applications, such as microwave-absorbing materials, military thermal camouflage materials, building material additives, and smart temperature-regulating fabrics.

Ruan *et al.* found that the encapsulated PCMs and functionalized GO-modified PMMA hybrid shell (FGO/PMMA-NanoPCMs) had a higher latent heat (77.72 J g^{-1}) and encapsulation efficiency (74.22%) due to the loading FGO on nanocapsules[88]. Compared to no FGO addition (NanoPCMs), the cotton fabric with FGO/PMMA-NanoPCMs had higher heat storage and thermoregulation performance. Therefore, FGO/PMMA-NanoPCMs will be considered a promising candidate in the application of intelligent temperature-regulation fabric. Shang *et al.* used graphene micropopcorns (GMPs) as an efficient additive for multifunctional composite materials. These GMPs were fabricated through the thermal treatment of spray-dried GO powder[97]. Subsequently, GMPs/paraffin composites were used as microwave-absorbing materials, exhibiting superior performance compared to most previously reported graphene-based

Table 3. Applications of PCM/GO microcapsules

Shell materials	Core materials	Latent heat (J g^{-1})	Applications	Ref.
SiO$_2$	Stearic acid	-	Thermal management	[59]
GO/PbWO$_4$	Paraffin	120.50	Wearable personal protection	[83]
PMMA	N-octadecane, n-butyl stearate	77.72	Textile	[88]
Long chain alkanes	Docosane	240.80	Heat dissipation	[95]
GO	Paraffin	232.40	Energy storage	[96]
GO	Paraffin	224.70	Microwave absorption	[97]
SiO$_2$	Solar salt	71.89	Energy storage	[87]
GO	Paraffin, expanded graphite	158.50	Energy storage	[98]
1,1-diphenylethylene capped hydrolyzed poly(glycidyl methacrylate) (PPVB)	Wax	158.44 ± 0.89	Thermal camouflage, stealth	[88]
MUF	Paraffin	32.50	Gypsum building	[99]
TiO$_2$	Paraffin	142.50	Energy storage	[100]
Ethylene propylene diene monomer (EPDM)	Paraffin	97.00	Thermal management	[101]
Ethylcellulose, methylcellulose	Paraffin	152.20	Energy storage	[89]
[2-(methacryloxy)ethyl]trimethylammonium chloride/decyltrimethylammonium chloride	N-hexadecane	184.70	Energy storage	[102]
TiO$_2$/GO	Paraffin	74.99	Energy storage	[90]
GO	Hexadecanol	232.75	Energy storage	[103]
GO	Paraffin	199.5	Intelligent sensing	[91]
GO	Paraffin	-	Photothermal conversion	[92]
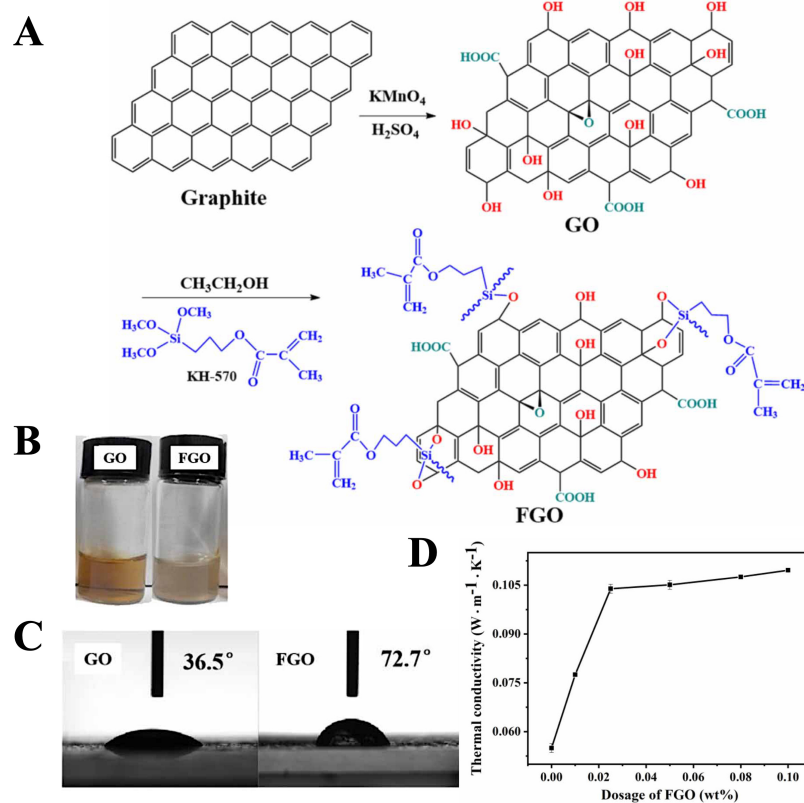
Figure 9. (A) Scheme of modified GO (FGO). (B) Photographs of GO and FGO. (C) The contact angle of GO and FGO. (D) Effect of FGO addition on thermal conductivity of FGO/PMMA-NanoPCMs[86] (Copyright 2020, IOP Publishing).

materials. However, due to their low tap density (6-8 mg cm^{-2}), the additive content achieved a record-low level (2.50 wt%) while exhibiting a high specific surface area (947 m^2 g^{-1}). Lin *et al.* introduced GO platelet-patched PCM microcapsules (wax@PDVB@GO) in a GO and amphiphilic macromolecule PDVB synergistic stable system[67]. The addition of GO has boosted the thermal conductivity, encapsulation efficiency, and encapsulation ratio of phase change microcapsules. Thanks to the high selectivity of the GO platelet-patched microcapsules and their ability to regulate thermal radiance, infrared thermography has indicated that they are an excellent method for active thermal camouflage and stealth applications. This composite is a promising material for active thermal camouflage and stealth applications. Besides, the photothermal property of GO enabled the prepared composites to achieve photothermal responsiveness, which can significantly expand the application of phase change microcapsules in biomedical therapeutics.

The majority of phase change microcapsules are used as energy storage materials for the photothermal conversion of solar energy or thermal energy storage of devices. The combination of paraffin@mixed cellulose and GO microcapsules was proposed by Zhang *et al.*, as shown in Figure 10. The melting temperature and latent heat were 49.7 °C and 152.2 J g^{-1}, respectively [Figure 10B][89]. There is no chemical reaction process during the self-assembly preparation of the phase change microcapsules; therefore, the thermal properties of these microcapsules are close to the pure paraffin. The encapsulation efficiency was 85.40%, and it can maintain the phase change property after experiencing l00 cycles [Figure 10C]. The results showed that these phase change microcapsules have great potential in solar heat utilization systems. Ji *et al.* used a Pickering emulsion templating to microencapsulated hexadecaol with GO shell (MEPCMs) for preparing a novel composite PCM for thermal energy storage[103]. The results indicated that the MEPCMs with 6 wt% GO had high thermal storage capabilities, excellent shape stability, and reinforced thermal stability, as the existence of GO shell can protect PCM from leakage.

CONCLUSIONS AND REMARKS

The configuration of phase change microcapsules added with GO was reviewed, and the effects of the position and content of GO in the microcapsules structure on the thermal properties of phase change microcapsules, such as latent heat and thermal conductivity, were studied and compared. The most common fabrication method for PCM/GO microcapsules is *in-situ* polymerization, and the thermal conductivity of phase change microcapsules has been greatly improved after embedding GO in the capsule shell structure. Due to the amphiphilic nature of GO, it can be used as an emulsifier or stabilizer for Pickering emulsion, and the addition of GO also decreases the leakage rate of phase change microcapsules. However, adding GO in phase change microcapsules can slightly decrease latent heat because it will lead to a lower core-shell ratio. Moreover, this paper also reviews the method of adding GO in phase change microcapsules, which is divided into two types, physical and chemical methods. The results show that the formation of chemical bonds between polymer matrix and thermal conducting materials is one of the effective strategies to enhance the interaction between the two and greatly improve thermal conductivity. Finally, the applications of PCM/GO microcapsules in energy storage, building, thermal management, textile, and military were presented with conductivity.

At present, most of the research studies mainly concentrate on the enhancement of the thermal conductivity of PCM/GO microcapsules. Nevertheless, the other properties, such as latent heat, morphology, encapsulation efficiency, and photothermal conversion of PCM/GO microcapsules, were poor. Thus, it is necessary to utilize the merits of different synthesis methods for PCM/GO microcapsules to exploit high-quality phase change microcapsules. The majority of the properties of PCM/GO microcapsules are largely dependent on the reagents and synthesis processes used. By controlling these factors, the properties of phase change microcapsules can be further optimized. In addition, it is important to investigate the interaction
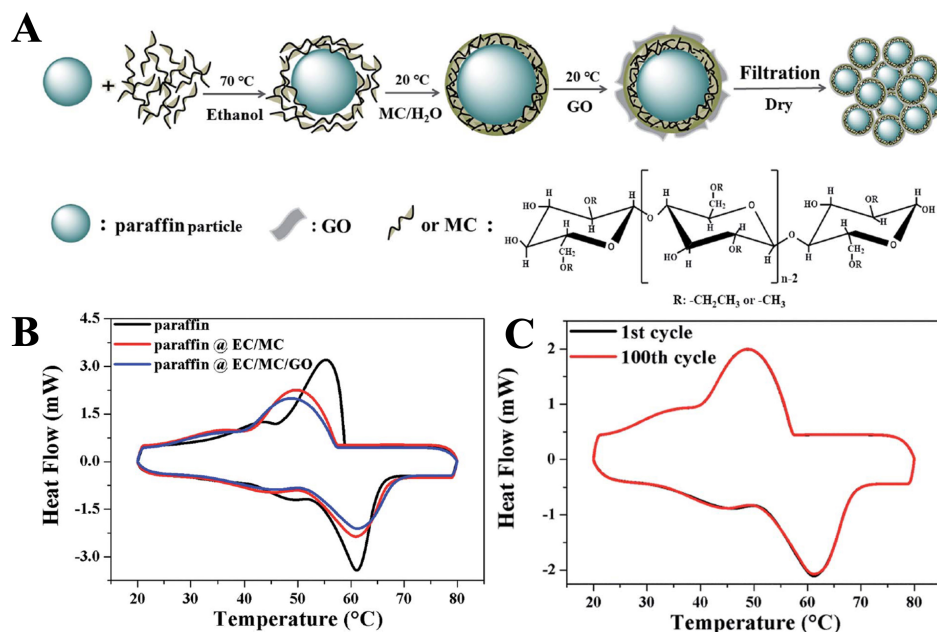
Figure 10. (A) Scheme of the preparation of paraffin/mixed cellulose GO microcapsules. (B) DSC curve of paraffin, paraffin/mixed cellulose microcapsules, and paraffin/mixed cellulose GO microcapsules. (C) DSC curve of the paraffin/mixed cellulose GO microcapsules before and after 100 cycles[89] (Copyright 2018, Royal Society of Chemistry).

mechanism between thermal conducting additives, polymers, and PCMs. It is still a huge challenge to develop new PCM microcapsules that can maintain thermal conductivity and minimize the content of filling materials added to gain reinforced thermal efficiency. We believe that the construction of a three-dimensional thermal network is the ultimate solution to increase the thermal conductivity of composite phase change microcapsules. Additionally, previous studies have demonstrated that GO can be integrated into phase change microcapsules at various positions, but two-phase and multiphase distributions are rarely studied. Therefore, adjusting and modifying the simultaneous distribution of GO in the capsule shell and core structure may become a key area of research in the future.

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