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$CaCl_2·6H_2O$/Expanded graphite composite as form-stable phase change materials for thermal energy storage

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Abstract In this study, $CaCl_2·6H_2O$/expanded graphite (EG) composite was prepared as a novel form-stable composite phase change material (PCM) through vacuum impregnation method. $CaCl_2·6H_2O$ used as the PCM was dispersed by surfactant and then, was absorbed into the porous structure of the EG. The surfactant was used to enhance the bonding energy between $CaCl_2·6H_2O$ and EG, which fulfilled the composites with good sealing performance and limited the leakage of the inside $CaCl_2·6H_2O$. Differential scanning calorimetry and thermal gravimetric analysis show that all the composite PCMs possess good thermal energy storage behavior and thermal stability. Thermal conductivity measurement displays that the conductivities of the samples have been significantly improved due to the highly thermal conductive EG. The thermal conductivity of the sample including 50 mass% $CaCl_2·6H_2O$ (8.796 W m^{-1} K^{-1}) is 14 times as that of pure $CaCl_2·6H_2O$ (0.596 W m^{-1} K^{-1}). Therefore, the obtained composite PCMs are promising for thermal energy storage applications.

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Keywords $CaCl_2·6H_2O$ · Expanded graphite · Phase change material · Thermal properties

Introduction

Thermal energy storage is recognized as one of the key technologies for energy supply in the future. Latent heat energy storage based on phase change material (PCM) is one of the most effective technique for thermal energy storage. This system is increasingly interesting in recent years because of the high-energy storage density and isothermal characteristics of PCM [1, 2]. Therefore, PCM has received great interest in many applications, such as industrial waste heat recovering, solar energy utilization, and active and passive cooling of electronic devices [3–9].

Phase change materials can be classified into two major categories: inorganic compounds and organic compounds. Inorganic PCMs include salts [10] or salt hydrates, metals and alloys, whereas organic PCMs are comprised of fatty acids [11], paraffin [12, 13], glycols, and alcohols [14, 15]. Inorganic salt hydrates have received great interest for application in heat storage and retrieval due to its good characteristics such as low-melting point, high-latent heat, nonflammability, and low cost. Among the salt hydrates, calcium chloride hexahydrate is very promising. Its melting temperature is 303.07 K which near the comfortable temperature of people and its fusion heat is about 190 J g^{-1}. Therefore, it is a potential PCM for energy storage applications. Besides, it is abundant and low cost. However, inorganic salt hydrates usually exhibit some intrinsic drawbacks such as phase segregation, supercooling, and poor thermal conductivity ($\sim$0.4–0.6 W m^{-1} K^{-1}). These will weaken their capability of heat storage release in practical applications. In order to eliminate these problems, various approaches have been explored over a long period, including the use of nucleating, thickening agents, and the addition of extra water to minimize supercooling and phase segregation of the inorganic PCMs. Although, the thermal performance of hydrated salts has been improved to some degree, the additives are hard to control in an accurate way and may reduce the latent heat and conversion efficiency of hydrated salts. Therefore, it is necessary to explore other more effective ways to improve the thermal properties of the hydrated salts for successful applications in thermal energy storage systems.

Recently, graphite is often used to enhance the thermal conductivity of PCMs in terms of its size, shape, and porous structure. Due to the respective structures and properties of graphite, PCMs are dispersed into the porous structure of graphite forming composites. Zhang et al. [16] prepared an expanded graphite (EG)/paraffin composite PCM by absorbing liquid paraffin into EG and the maximum sorption capacity for paraffin is 92 mass%. Sarı et al. [17] prepared palmitic acid (PA)/EG composite as form-stable PCM. The maximum mass fraction of PA retained in EG was found about 80 mass% without the leakage of PA in melted state even when it is heated over the melting point of PA. Mills et al. [18] loaded paraffin into graphite blocks made by compacting EG. The thermal conductivity of the composite was 20–130 times higher than that of pure PCM. However, these studies just use the physical binding capability of the graphite to keep the PCMs in the porous structure. Once the composites stuffer from strong squeezing, the inside PCMs may leak out due to the weak binding energy between the PCMs and graphite. Furthermore, there is little studying on the influence of the graphite on the supercooling and phase separation of inorganic salt hydrates.

Therefore, in this study, $CaCl_2{\cdot}6H_2O$/EG composite was prepared as a novel form-stable composite PCM by choosing $CaCl_2{\cdot}6H_2O$ as a proper PCM, EG as a supporting material and surfactant OP-10 as a couple agent to improve the binding energy between $CaCl_2{\cdot}6H_2O$ and EG. Besides, the prepared composite PCM was characterized in terms of microstructure and morphologies using scanning electron microscope (SEM) analysis. Thermal properties and thermal reliability of prepared composite PCM were investigated by differential scanning calorimetry (DSC) and thermal gravimetric (TG) analysis. Thermal conductivity of the form-stable composite PCM was investigated by thermal constants analyzer TPS 2500 analysis.

Experimental

Materials

Expandable graphite was purchased from Qingdao Tianhe Graphite Co. Ltd. $CaCl_2{\cdot}6H_2O$ (Analytical reagent) was commercially supplied from Tianjin Fuchen Reagent Co. Ltd. OP-10 (chemical pure) was obtained from Tianjin Institute of Chemical Industry.

Preparation of EG

Firstly, the expandable graphite was dried in a vacuum oven at 353.15 K for 15 h. Then, it was heated in a microwave oven with a power of 1,500 W for 15–20 s. The EG was obtained after the microwave treatment. This heat treatment process has been proven suitable for complete expansion of the expandable graphite [19, 20]. During expansion, EG keeps the same structural layer as natural graphite flakes, but produces different sizes of pores with very large specific surface area [21].

Preparation of $CaCl_2{\cdot}6H_2O$/EG composite PCM

Firstly, amount of $CaCl_2{\cdot}6H_2O$ was mixed with several drops of deionized water, then, the mixture was put into an oven heated at 353.15 K for 2 h, so that $CaCl_2{\cdot}6H_2O$ was melted completely. Consequently, OP-10 was added into the melted mixture to form a stable emulsion by ultrasonic dispersion for 30 min. After that, EG was added into the emulsion and the mixture was put into a vacuum oven at room temperature for 30 min. Then, the composite form-stable PCM was obtained. The samples compositions are listed in Table 1.

Analysis methods

The morphologies and microstructure of the obtained composite PCMs were investigated using a SEM instrument (JSM-6360LV).

Thermal properties of the composite PCMs, such as melting and latent heats, were measured using a TA Instruments DSC Q1000 (USA). The measurements were performed at 10 °C min^{-1} in heating procedure and

Table 1 Sample identification and composition

Sample	Composition/mass%
1	$CaCl_2{\cdot}6H_2O$ 50 % + EG 50 %
2	$CaCl_2{\cdot}6H_2O$ 60 % + EG 40 %
3	$CaCl_2{\cdot}6H_2O$ 70 % + EG 30 %
4	$CaCl_2{\cdot}6H_2O$ 80 % + EG 20 %
5	$CaCl_2{\cdot}6H_2O$ 90 % + EG 10 %
6	$CaCl_2{\cdot}6H_2O$ 50 % + EG 50 % + OP-10[a]
7	$CaCl_2{\cdot}6H_2O$ 60 % + EG 40 % + OP-10[a]
8	$CaCl_2{\cdot}6H_2O$ 70 % + EG 30 % + OP-10[a]
9	$CaCl_2{\cdot}6H_2O$ 80 % + EG 20 % + OP-10[a]
10	$CaCl_2{\cdot}6H_2O$ 90 % + EG 10 % + OP-10[a]

[a] The additional content of OP-10 was about 5 mass% of the mass of $CaCl_2{\cdot}6H_2O$

5 °C min^{-1} in cooling procedure in nitrogen atmosphere. The temperature accuracy was ±0.01 °C, and the heat flow repeatability was 0.2 μW.

The thermal stability of the composite PCMs was determined using a TG analyzer (Cahn TherMax 500). The instrument was calibrated by calcium oxalate with a measurement error of 3 %, and the analysis was performed at a temperature range of 303.15–1073.15 K at a heating rate of 10 °C min^{-1} under a Ar atmosphere.

Finally, the thermal conductivity of the composite PCMs was determined by HotDisk TPS 2500 analysis. For the thermal conductivity analysis, all the samples were made into two columns with the diameter of 32 mm and thickness of 4 mm. In this procedure, some PCMs leaked from the composite samples obtained without OP-10 due to high pressure. While this phenomenon did not happen for the samples prepared with OP-10. This indicates that the surfactant OP-10 have improved the sealing performance and mechanical strength of the composites.

Results and discussion

Microstructures of the $CaCl_2{\cdot}6H_2O$/EG composite PCMs

Figure 1 shows the SEM images of EG and the form-stable PCMs synthesized without surfactant. From Fig. 1a, it is obvious that EG has multiporous structure indicating that it is an excellent supporting material to absorb the PCM. It can be seen from Fig. 1b–f that the surface of the obtained sample becomes smoother and the microporous structure gradually decreases with the increase of the $CaCl_2{\cdot}6H_2O$ content. It implies that the $CaCl_2{\cdot}6H_2O$ is dispersed into the porous structure of EG due to the physical adsorption capacity of the pores. However, as the content of $CaCl_2{\cdot}6H_2O$ increases to 80 and 90 mass%, the surfaces of the samples are neat without porous structure. It means that the content of $CaCl_2{\cdot}6H_2O$ is too much for the composite form-stable PCMs and the excess $CaCl_2{\cdot}6H_2O$ has adhered on the surface of the EG to form the neat surface.

Figure 2 shows the SEM images of the samples synthesized with the surfactant OP-10. From these images, it can be seen that the $CaCl_2{\cdot}6H_2O$ is completely dispersed into the pores of EG and the surface of the samples is closer and smoother compared with the corresponding image of the samples shown in Fig. 1. It suggests that the surfactant improves the bonding energy between $CaCl_2{\cdot}6H_2O$ and EG due to its hydrophilic and hydrophobic groups. As a result, the surfactant improves the supporting ability of EG for the inside $CaCl_2{\cdot}6H_2O$, and the sealing performance and mechanical strength of the composites are also significantly enhanced. Nevertheless, the addition content of 80 and 90 mass% $CaCl_2{\cdot}6H_2O$ is still too much for the EG as seen from Fig. 2e, which leading to the serious accumulation at the surface of the samples. In one word, the composite

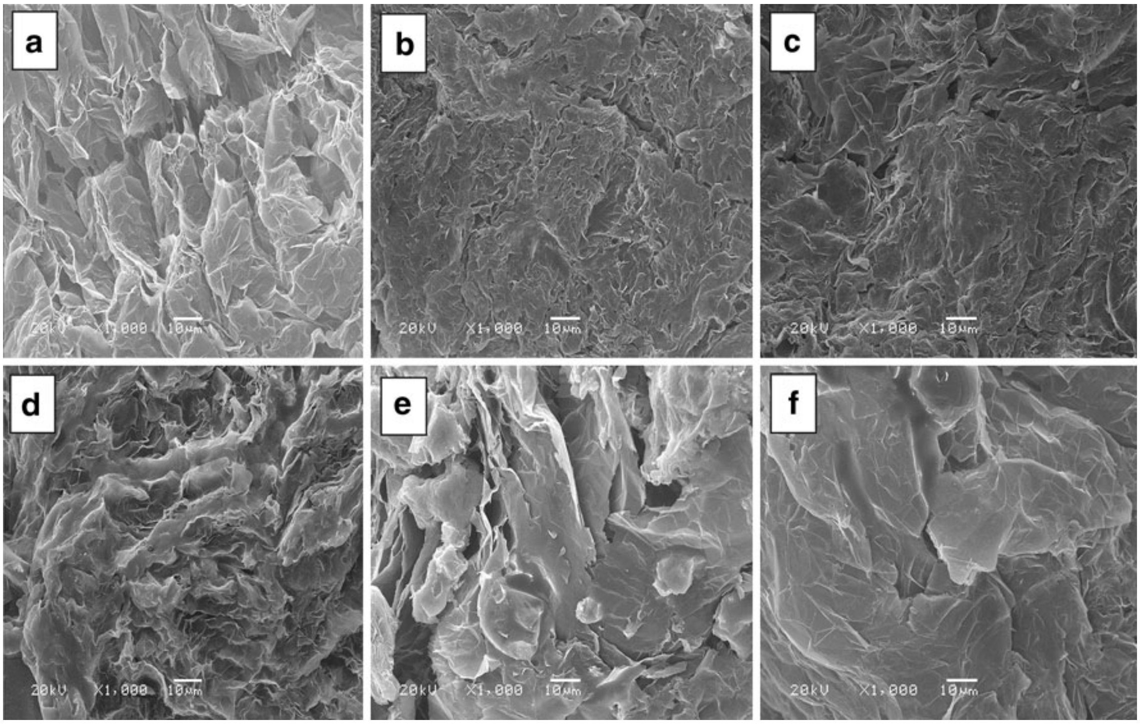

Fig. 1 SEM images of the obtained composites without OP-10 at the $CaCl_2{\cdot}6H_2O$/EG mass ratio of: **a** 0/100 mass%; **b** 50 mass%/50 mass%; **c** 60 mass%/40 mass%; **d** 70 mass%/30 mass%; **e** 80 mass%/20 mass%; and **f** 90 mass%/10 mass%

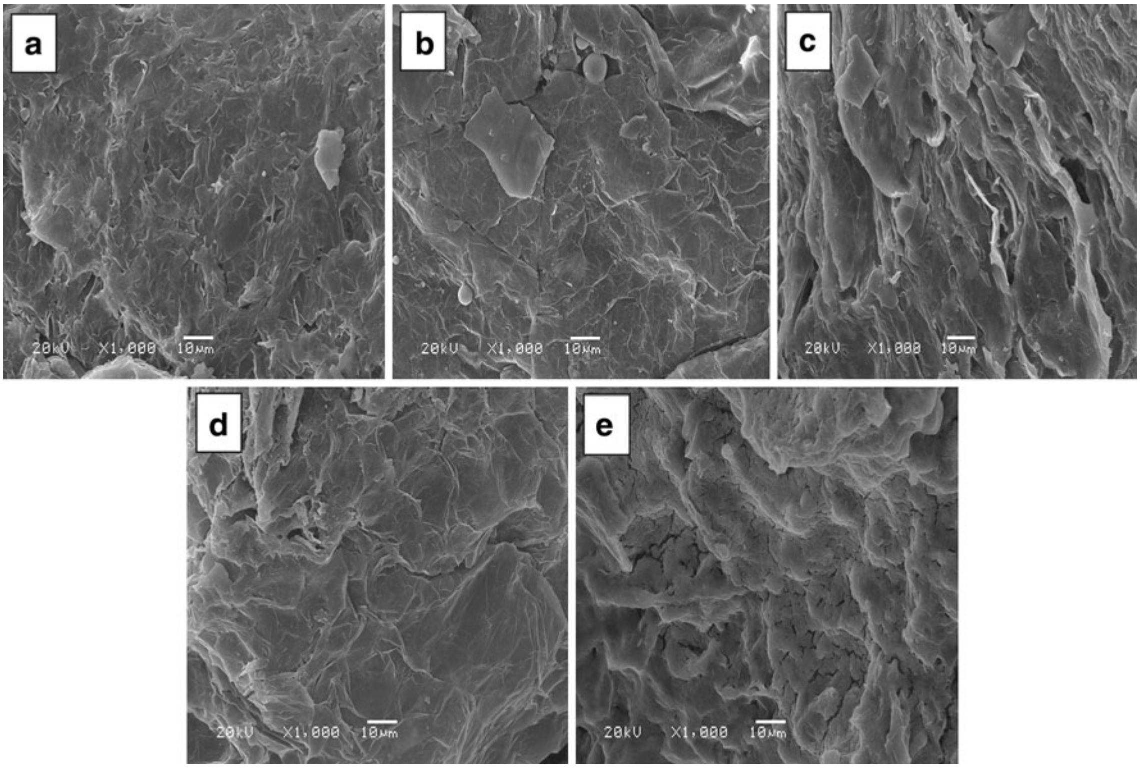

Fig. 2 SEM images of the obtained composites with OP-10 at the $CaCl_2 \cdot 6H_2O$/EG,mass ratio of: **a** 50 mass%/50 mass%; **b** 60 mass%/40 mass%; **c** 70 mass%/30 mass%; **d** 80 mass%/20 mass%; and **e** 90 mass%/10 mass%

form-stable PCMs were prepared by using EG as the supporting material and surfactant OP-10 as the couple agent which has endowed the samples with good microstructure and sealing performance.

Thermal stability of the $CaCl_2 \cdot 6H_2O$/EG composite PCMs

Thermal gravimetric curves of $CaCl_2 \cdot 6H_2O$/EG synthesized without OP-10 are shown in Fig. 3, and the corresponding data deduced from the TG curves are listed in Table 2. As can be seen from the curves and Table 2, the mass loss of $CaCl_2 \cdot 6H_2O$/EG composites starts at 323.15 K and ends at 423.15–473.15 K due to the degradation of crystal water in $CaCl_2 \cdot 6H_2O$. With the increase of the $CaCl_2 \cdot 6H_2O$ content, the ended temperature raises. It implies that the thermal stability of the composite PCMs is improved by the impregnated $CaCl_2 \cdot 6H_2O$. It is significant that the mass loss of the composites strongly depends on the content of $CaCl_2 \cdot 6H_2O$ as seen in Fig. 3. It can been seen that the mass loss increases from 29.05 to 51.56 % for the samples impregnated with different contents of $CaCl_2 \cdot 6H_2O$.

Thermal gravimetric curves of $CaCl_2 \cdot 6H_2O$/EG with OP-10 are shown in Fig. 4. As can be seen from the curves and Table 2, the mass loss have two stages, the first stage corresponding to the degradation of $CaCl_2 \cdot 6H_2O$ starts at 323.15 K and ends at 423.15–473.15 K, which is in agreement with the degradation of the obtained composites without OP-10. It suggests that the incorporation of OP-10 maintains the good thermal stability of the composite PCMs. The second stage is due to the degradation of OP-10, which starts at 623.15 K and ends at 673.15 K. It can also been seen that the mass loss percent of the $CaCl_2 \cdot 6H_2O$ is 31.08–51.56 %, and the mass loss percent in stage two is 4.36–9.97 %. These mass loss percents are consistent with the calculated value of the crystal water in $CaCl_2 \cdot 6H_2O$ loss. These results indicate that the incorporation of OP-10 improves the related thermal stability of the composites.

Phase change behavior of the $CaCl_2 \cdot 6H_2O$/EG composite PCMs

Figure 5 shows the DSC curves of the sample synthesized without OP-10, and the corresponding data deduced from the DSC curves are listed in Table 2. As can be seen from Table 2, the melting temperature of the samples with 50, 60, 70, 80, and 90 mass% $CaCl_2 \cdot 6H_2O$ are 303.07, 303.68, 305.28, 304.37, and 309.92 K, respectively. It is significant that the phase change temperatures are quite close to each other. And the corresponding latent heats for the samples are 86.48, 95.97, 123.8, 146.6, and 160.9 J g^{-1}, respectively.

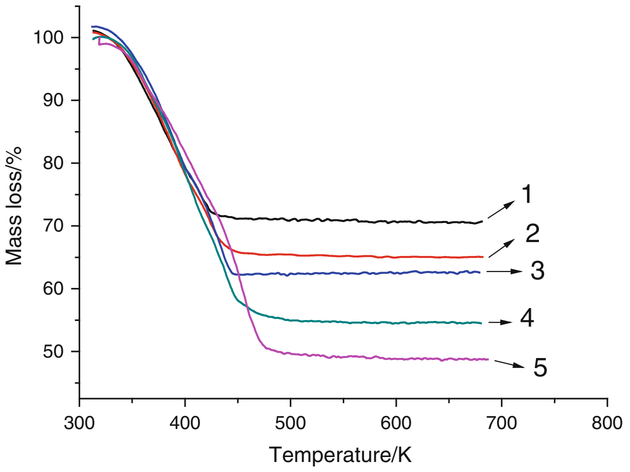

Fig. 3 TG curves of $CaCl_2·6H_2O$/EG composites without OP-10

Table 2 Thermal properties of the obtained composite PCMs

Sample	Mass loss/%		Melting temperature/K	Heat of fusion/ J g^{-1}
	Stage-one	Stage-two		
1	29.05	–	303.07	86.48
2	35.61	–	303.68	95.97
3	39.54	–	305.28	123.80
4	45.51	–	304.37	146.60
5	51.56	–	309.92	160.90
6	31.08	9.97	301.03	49.10
7	36.60	4.73	304.49	145.00
8	45.01	7.03	303.81	95.68
9	48.33	4.36	304.68	139.60
10	50.53	5.00	302.63	98.30

Moreover, the latent heat of the samples increases with the increase of the $CaCl_2·6H_2O$ content, and the sample incorporated with 90 mass% $CaCl_2·6H_2O$ has the best thermal storage capacity. Figure 6 shows the DSC curves of samples prepared with OP-10. As can be seen from Table 2, the melting temperature of the samples incorporated with OP-10 are 301.03, 304.49, 303.81, 304.68, and 302.63 K, respectively. Their latent heats are 49.10, 145.0, 95.68, 139.6, and 98.30 J g^{-1}, respectively. It is obvious that the latent heat of the sample with 60 mass% $CaCl_2·6H_2O$ and OP-10 is higher than the sample without OP-10. This result means that the PCMs were homogeneously dispersed by the surfactant OP-10 forming a stable emulsion, so that the PCMs were absorbed completely by the supporting materials. As a result, the sample with 60 mass% $CaCl_2·6H_2O$ and OP-10 has better thermal storage property.

In a word, from Figs. 5 and 6, we can make a conclusion that the latent heat of the sample increases with the increase of the $CaCl_2·6H_2O$ content due to the good phase

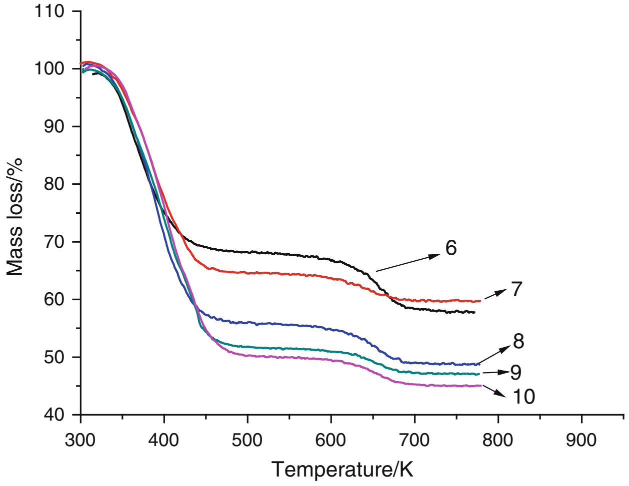

Fig. 4 TG curves of $CaCl_2·6H_2O$/EG composites with OP-10

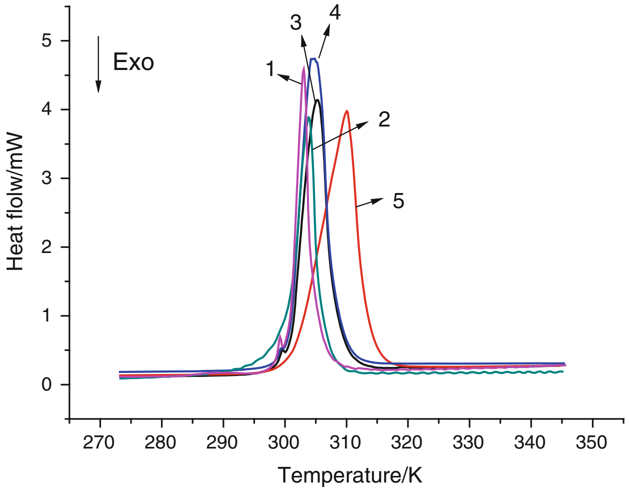

Fig. 5 DSC curve of $CaCl_2·6H_2O$/EG composites without OP-10

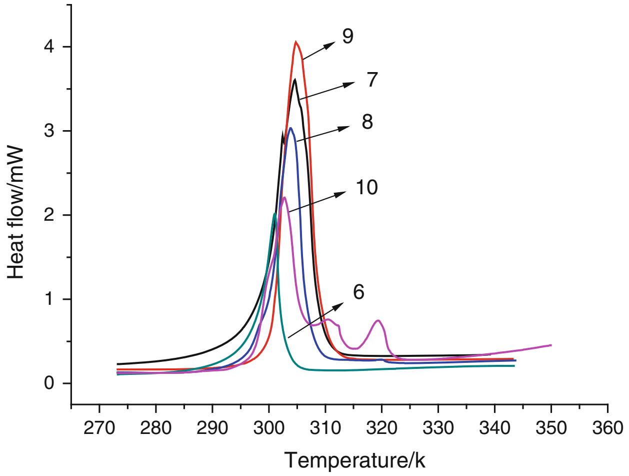

Fig. 6 DSC curve of $CaCl_2·6H_2O$/EG composites with OP-10

Table 3 Thermal characteristics of some composite PCMs in literature

Material/mass/%	Thermal conductivity/ W m^{-1} K^{-1}	Melting point/ K	Latent heat, Melting/ J g^{-1}	Reference
PEG (45 %)/diatomite (45 %)/EG (10 %)	0.67	300.85	82.22	[22]
Paraffin(60 %)/HDPE(15 %)/(APP/PER/ MA)25 %	0.34	324.85	81.50	[23]
Paraffin(72 %)/SiO_2(20.8 %)/EG(7.2 %)	0.25	300.87	104.4	[24]
LA(60 %)/EP(30 %)/EG(10 %)	0.13	316.95	86.70	[25]
PA(80 %)/EG (20 %)	0.60	334.03	148.36	[15]
Paraffin55/EP45/EG5	0.067	315.42	87.40	[26]

Table 4 Thermal conductivities of the prepared $CaCl_2{\cdot}6H_2O$/EG composite PCMs

Sample	Thermal conductivity/W m^{-1} K^{-1}							Average value
	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	
EG	13.861	14.174	14.382	14.564	14.685	13.884	13.911	14.209
$CaCl_2{\cdot}6H_2O$	0.615	0.565	0.568	0.622	0.622	0.617	0.563	0.596
1	8.806	8.819	8.822	8.832	8.785	8.781	8.737	8.796
2	7.711	7.707	7.700	7.731	7.635	7.558	7.545	7.655
3	7.464	7.587	7.557	7.548	7.646	7.623	7.526	7.564
4	7.081	7.060	7.041	6.904	6.945	6.893	6.878	6.972
5	6.754	6.750	6.762	6.774	6.757	6.793	6.766	6.765
6	4.097	4.005	3.965	3.992	4.009	4.016	4.035	4.017
7	3.807	3.825	3.817	3.582	3.575	3.386	3.557	3.650
8	3.422	3.452	3.440	3.451	3.464	3.523	3.548	3.471
9	3.482	3.463	3.406	3.415	3.420	3.453	3.538	3.454
10	3.505	3.350	3.447	3.375	3.452	3.415	3.515	3.437

change behavior of $CaCl_2{\cdot}6H_2O$ in the composite PCM. From Table 2, we can see that samples 7 and 9 have bigger heat of fusion than 6, 8, and 10. It seems both 60 mass% $CaCl_2{\cdot}6H_2O$ and 90 mass% $CaCl_2{\cdot}6H_2O$ show optimum properties, but considering that porous structure of sample 9 has broken (we can see it in Fig. 2e) and agglomerated in macroscopic structure (it exceeds the mix adsorption of EG), 60 mass% $CaCl_2{\cdot}6H_2O$ has better thermal storage capacity and may be regarded as the optimum proportion. Nevertheless, all the prepared $CaCl_2{\cdot}6H_2O$/EG composites have suitable phase change temperature and high-latent heat as seen from Table 3.

Thermal conductivity of $CaCl_2{\cdot}6H_2O$/EG composite PCMs

Thermal conductivity of $CaCl_2{\cdot}6H_2O$/EG composites were measured by using thermal constant analyzer, and the results are presented in Table 4. It is significant that pure EG possesses high-thermal conductivity as shown in Table 4. And the thermal conductivity of all the samples has been highly improved compared with that of the pure $CaCl_2{\cdot}6H_2O$. Moreover, with the increase in the mass of $CaCl_2{\cdot}6H_2O$, the thermal conductivity of composites is decreased due to the low-thermal conductivity of $CaCl_2{\cdot}6H_2O$. It indicated that the improvement of the thermal conductivity is mainly attributed to the high-thermal conductivity of EG. The standard deviation for seven reduplicate thermal conductivity experiments of samples 1, 2, 3, 4, 5, 6, 7, 8, and 9, are 0.033, 0.077, 0.061, 0.086, 0.015, 0.041, 0.169, 0.046, 0.046, and 0.062, respectively. It shows good reproducibility. As the mass percent of $CaCl_2{\cdot}6H_2O$ is 50 mass%, the thermal conductivity of this sample reaches 8.796 W m^{-1} K^{-1} which is about 14 times as that of the pure $CaCl_2{\cdot}6H_2O$. Additionally, although the thermal conductivity of the sample prepared with OP-10 is lower than those of the samples obtained without OP-10, their thermal conductivities are also significantly enhanced. Therefore, these results indicate that the obtained composite form-stable PCMs possess good thermal conductivities for thermal energy storage.

Conclusions

In this study, $CaCl_2 \cdot 6H_2O$/EG composites were successfully prepared as a novel form-stable PCM. SEM images show that $CaCl_2 \cdot 6H_2O$ was absorbed into the porous structure of EG. DSC analysis displays that the composite PCMs possess excellent thermal energy storage property. TG analysis shows that the composite PCMs have a good thermal stability. Furthermore, the samples prepared with OP-10 maintain the thermal stability and thermal energy storage property of the PCMs. Besides, the surfactant OP-10 has improved the sealing performance and mechanical strength of the composites. Thermal conductivity of the composite PCM has been significantly enhanced due to the highly thermal conductive EG. And the thermal conductivity of the sample with 50 mass% $CaCl_2 \cdot 6H_2O$ ($8.796\ W\ m^{-1}\ K^{-1}$) is 14 times as that of pure $CaCl_2 \cdot 6H_2O$ ($0.596\ W\ m^{-1}\ K^{-1}$). Based on these results, it can be concluded that $CaCl_2 \cdot 6H_2O$/expanded graphite composite can be considered as a promising PCM for thermal energy storage applications due to its good thermal properties.

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