

Experimental Study on Hybrid Organic Phase Change Materials Used for Solar Energy Storage

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Abstract: The solar energy utilization in built environment has been limited due to its low heat flux, uneven distribution in time and space and temporal difference in day and night. The phase change materials have been used to collect the fluctuant solar energy to form a stable energy source for the terminal equipment of the buildings. In this study, the hybrid organic phase change materials was prepared for the capillary radiant heating system which formed a cascade utilization of solar energy. Firstly, lauric acid and stearic acid were selected as the basic organic phase change materials and the binary equilibrium phase diagram was completed based on the method of step cooling curve according to the experimental tests data. The results showed that the phase transition temperature of the mixed acid at the lowest eutectic point was 31.2°C and the latent heat value was 264.3 kJ/kg when the mass mixing ratio was 70% for lauric acid and 30% for stearic acid. Secondly, the expanded graphite was used as an additive to enwrap the mixed acid and enhance the heat conductivity. The experimental results showed that when the mass proportion of expanded graphite in the mixed acid was 10%, the mixed acid could be completely enclosed by expanded graphite and the stability of melting and solidification was optimal. Additionally, the phase transition temperature of the hybrid phase change material was 31.5°C and the latent heat value was 217.4 kJ/kg. The novel hybrid phase change material has a lower eutectic point and a higher latent heat of phase change, so it has a large application space and is quite suitable for the cascade utilization of solar energy with capillary network heating system.

Keywords: lauric acid, stearic acid, expanded graphite, phase change material, solar energy

1. Introduction

Building energy consumption is nearly approaching 30% of the total energy consumption in recent years in China [1]. As a high quality clean and environmentally friendly energy source, solar energy has been widely used in domestic hot water and building heating [2]. However, solar energy also has the disadvantages of low heat flux, uneven distribution in time and space, and easily being influenced by weather and clouds. Moreover,

there also exists the temporal difference between the solar radiation in day and energy application in night. Phase change materials (PCMs) are of great efficiency and have the advantages of high energy storage density and isothermal properties of the energy storage process [3,4], and they have been used to collect the fluctuant solar energy to form a stable energy source for the terminal equipment of the buildings. On the other hand, since the solar radiation is relatively weak in winter, the heat storage temperature of PCMs is needed to be

Nomenclature

EG	Expanded graphite	PCM	Phase change material
LA	Lauric acid	PET	Polyethylene terephthalate
MA	Myristic acid	SA	Stearic acid
MP	Methyl palmitate		

lower, and correspondingly the capillary radiant heating system is an appropriate terminal heat equipment due to its low temperature operating property and good thermal comfort with no blowing feeling [5]. Consequently, the PCMs are appropriate for both the solar energy and the capillary radiant system to compose an energy cascade utilization system.

The research of PCMs and their application is always the front hotspots, especially in the selection of PCMs with thermal property tests, the phase diagram and the crystal growth and heat transfer properties [6]. Mao et al. analyzed the phase change heat storage process of solar energy with three PCM initial temperatures and three heat transfer fluid speeds [7]. Compared with inorganic PCMs, organic PCMs have well chemical stability and thermal stability due to the advantages of little crystallization, no supercooling and non-corrosive [4]. Generally, binary mixtures or more are often mixed to form novel PCMs with different phase transition temperature. Tan et al. [8] prepared a mixed acid PCM with lauric acid and palmitic acid by using PNIPAM gel as carrier, which had a melting range of 36.8°C–52.3°C. Saeed et al. [9] prepared a series of binary mixtures of methyl palmitate (MP) and lauric acid (LA). The results showed that the eutectic binary mixture of 60% MP and 40% LA has desirable properties of phase transition temperatures within the comfort temperature range and high latent heat capacity.

Furthermore, PCMs encapsulation and shape-stabilized composite PCMs have been developed to improve the heat-conducting property of PCMs in recent years. Pielichowska et al. [10] summarized the composite properties of PCMs with various substrates, such as polymer matrix like polyethylene and polyurethanes, and expandable graphite matrix. Sari et al. [11] studied paraffin (n-docosane)/expanded graphite composites PCM and the results showed that 10% mass fraction of EG of the composite PCM was found to have great stability. Liu et al. [12] prepared a composite PCM of lauric-myristic-stearic acid ternary eutectic mixture/expanded graphite (LA-MA-SA/EG) (12/1, w/w). The melting and freezing temperatures and the latent heats of the composite PCM were 29.1°C and 29.4°C, 137.1 kJ/kg and 131.3 kJ/kg, respectively. Chen et al. [13] prepared a ultrafine fibers of lauric-acid/polyethylene terephthalate (LA/PET) composite (1:1, w/w). The melting temperature and the latent heat of fusion of the

fibers is about 45.1°C and 70.8 kJ/kg, respectively. Kong et al. [14] prepared composite PCMs by incorporating paraffin into expanded perlite through a vacuum absorption method, and the composite PCMs was used in building energy storage panels, whose related properties were studied and recognized further. Yao et al. [15] and Kong et al. [16] prepared shape-stabilized PCM with paraffin being the PCM and expanded perlite being the supporting material, and then the composite PCMs were used in indoor environment control with the form of wallboard. LA is dodecanoic acid with a melting point of 44.0°C–46.0°C, and SA is octadecanoic acid with a melting point of 56.0°C–69.6°C [17,18], both of which have high latent heat and good chemical stability under normal temperature and pressure. Moreover, the eutectic melting point of the binary mixtures of LA and SA will decrease [18] to prepare the low melting point PCMs. In this study, LA and SA were used as PCM and EG was used as additive material to prepare a hybrid PCMs. Compared with other composite PCMs, this novel hybrid PCMs has lower eutectic point, higher latent heat of phase change, and good thermal stability, which make it more suitable for solar energy storage and the cascade utilization of solar energy with capillary network heating system.

2. Experimental Process Description

2.1 Materials

The properties of the commercial PCMs provided by the manufacturer are shown in Table 1, and EG of reticulated porous structure with a wormlike shape was made by EG powder (80 mesh) with a scaly shape in high temperature heat treatment.

Table 1 Parameters of the commercial PCMs

PCM	Purity class	Melting temperature/°C	Latent heat/kJ·kg ⁻¹
Lauric Acid (LA)	AR	44.0–46.0	242.3
Stearic Acid (SA)	AR	55.0–69.6	259.9

2.2 The binary equilibrium phase diagram

In order to get the lowest eutectic melting point of the lauric acid and the stearic acid, the mixed acids composed of LA and SA with difference mass proportion were tested based on step cooling curve method. The

prepared samples were weighed by an electronic balance and then placed in the test tubes. Thermocouples with sealed rubber stoppers were inserted into the samples of the test tubes, and the samples were melted in a thermostatic water bath at 70.0°C and held for 30 minutes. Then the test tubes were quickly taken out and placed in the thermotank to be completely cooled in 10.0°C. The temperature data was recorded every 2 seconds. Moreover, the water was also tested simultaneously for reference, and the ambient temperature was also recorded. The results of the step cooling curve were shown in Fig. 1. The melting point temperature of LA was 44.4°C, and the latent heat of LA was 242.2 kJ/kg. The melting point temperature of SA was 55.9°C, and the latent heat of SA was 255.6 kJ/kg. The tested results were similar with the information provided by the manufacturer.

According to the experimental data, the binary equilibrium phase diagram of LA and SA was shown in Fig. 2. When the mass proportion of LA was 70%, and that of SA was 30%, the eutectic melting point of LA and SA reached the minimum value as 31.2°C, and the latent heat value of the mixed acid was 264.3 kJ/kg. Therefore, the mixed acid composed 70% of LA and 30% of SA was adopted as the basic phase change material. After 10 times of operation cycles, the eutectic melting point and the latent heat of mixed acid was stable. According to the experimental data, the latent heat of PCMs was measured and calculated by improvement of *T*-history method based on the step-cooling curve from our previous work in 2017 [19].

2.3 Compositing of mixed acid and EG

The PCMs need to undergo long-term repeated melting-solidification thermal processes, which can cause

deformation, delamination, creep flow and the resulting decrease in thermal conductivity, phase transition temperature shift and other defects. Therefore, the additive can fix the shape of PCMs to prevent the above defects and enhance the thermal conductivity in storage and heat transfer process. EG has a porous structure and good adsorption properties to fix shape of PCMs, and it can improve the heat transfer effect for its high thermal conductivity. Some research results showed that when the mass proportion of EG is more than 5% or within 5%–10%, it can wrap fatty acid well and had no stratification and deformation [20–22]. Therefore, in this study, EG mass content of 5%, 8%, 10%, 12% and 15% was added in the total mass of the mixed acid of 20.0 g, respectively. The experiments were carried out to test the optimal content of EG and its phase change properties.

The samples were prepared as follows. The mixed acid was heated in a water bath at 70.0°C until the solid-state mixed acid was completely dissolved, then stirred and shook it until the liquid mixed acid was well mixed. Simultaneously, EG was added slowly to the liquid-state mixed acid and kept stirring for one hour. Finally, the mixture was completely cooled in a cold water bath to form a mixed acid/EG hybrid phase change heat storage material.

The parameters of samples with different mass proportion of EG were shown in Table 2. Among them, No.1 to No.5 were the first set tests with the mixed acid of 20.0g to research the composite rules, and 10 cycles for each sample was operated to observe the saturated adsorption capacity of EG to mixed acids and to verify the thermal stability. Moreover, in order to observe the saturated adsorption of EG to mixed acid more clearly, No.6 to No.10 were the another set of tests with greater total quality of the composite acid as a contrast group.

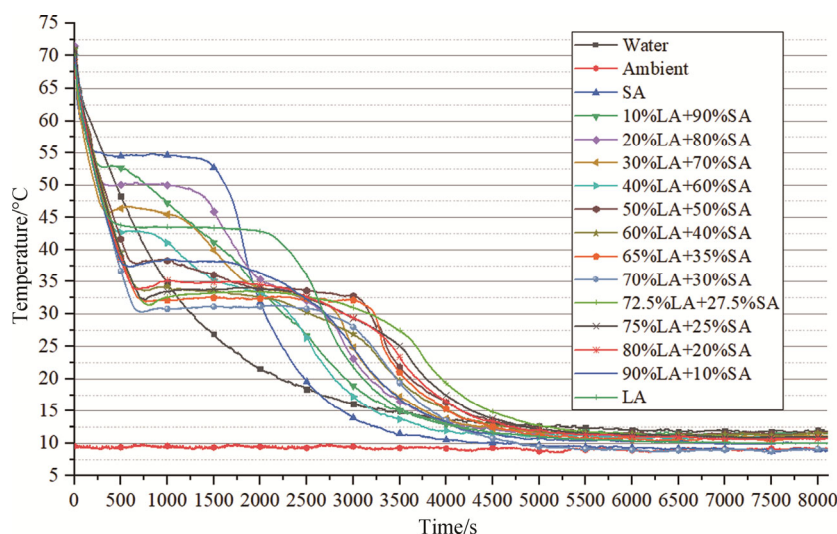


Fig. 1 Step cooling curve of the mixed acid

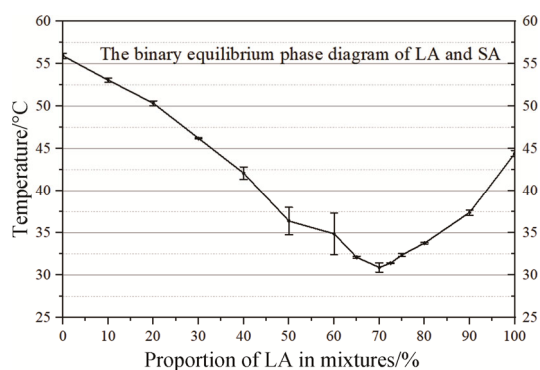


Fig. 2 Binary equilibrium phase diagram of lauric acid-stearic acid mixture

Table 2 The sample parameters of expanded graphite with different mass content

Sample No.	mass content	mixed acid/g	lauric acid/g	stearic acid/g	expanded graphite/g
1	5%	9.500	6.650	2.850	0.500
2	8%	9.200	6.440	2.760	0.800
3	10%	7.200	5.040	2.160	0.800
4	12%	5.900	4.130	1.770	0.800
5	15%	4.500	3.150	1.350	0.800
6	3%	38.80	27.16	11.64	1.20
7	4%	38.40	26.88	11.52	1.60
8	5%	28.50	19.95	8.55	1.50
9	10%	14.40	10.08	4.32	1.60
10	10%	43.20	30.24	12.96	4.80

2.4 Experimental error analysis

In the experimental set-up, the main instruments affecting the experimental results were as follows. The thermostatic water bath 501A, with a temperature fluctuation of less than $\pm 0.1^\circ\text{C}$. The incubator SPX-250BX, with a temperature fluctuation of less than

$\pm 0.1^\circ\text{C}$. 14 T-type thermocouple sensors TT-T-36, with the precision of $\pm 0.5^\circ\text{C}$. The 14 T-type thermocouple sensors were calibrated by least square fitting before tests, and the correlation coefficient of each thermocouple calibration curve was greater than 0.9999. Finally, Standard deviation method was used for the experimental error according to the tests data, as Fig. 2 and Fig. 6 shown.

3. Results and Discussion

In the first set tests of No.1 to No.5 shown in Table 2, the samples were tested 10 times of melting-solidification cycles, respectively. There was a little white mixed acid crystals appeared at the top and the bottom of the beaker in sample No.1, and a little white crystals appeared at the top of the beaker in sample No.2. Moreover, in No.1 and No.2, both mixed acid showed a certain deformation, shown in Fig. 3. It can be deduced that the expanded graphite was not enough to adsorb or wrap up the mixed acid completely in No.1 and No.2. Additionally, in No.3, No.4 and No.5, samples were basically unchanged and no white crystal and deformation appeared. Therefore, it could be considered that the expanded graphite reached the maximum saturated adsorption amount at the mass ratio of 10%.

According to the tests results, after repeating the tests of No.3, No.4 and No.5 for 10 times, no delamination, no deformation and no white mixed acid appeared. Moreover, they were easily to mash into powder. Then heating the samples again, and no liquid leakage appeared when squeezed lightly on the paper. When squeezed heavily, only a little liquid leakage appeared in No.3 and no liquid leakage in No.4 and No.5, as shown in Fig. 4. Therefore, it can be concluded that the mixed acid can be completely adsorbed by EG with long-term thermal stability when the mass content of expanded graphite is 10%.

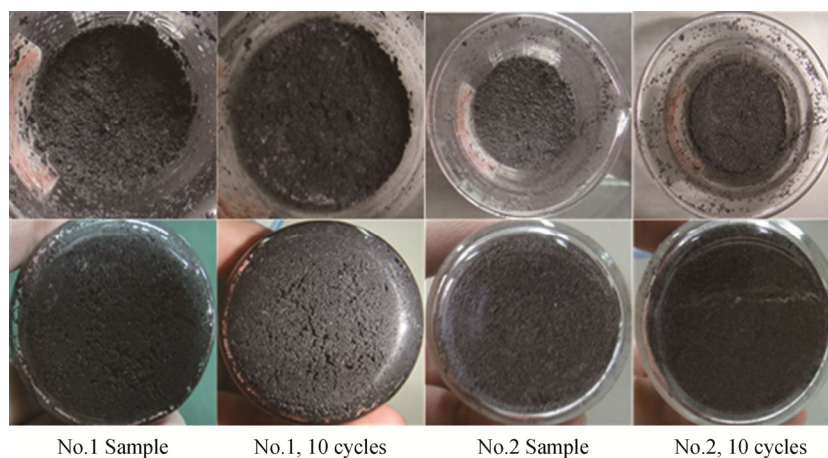


Fig. 3 Comparison of samples No.1 and No.2 before and after the cycles

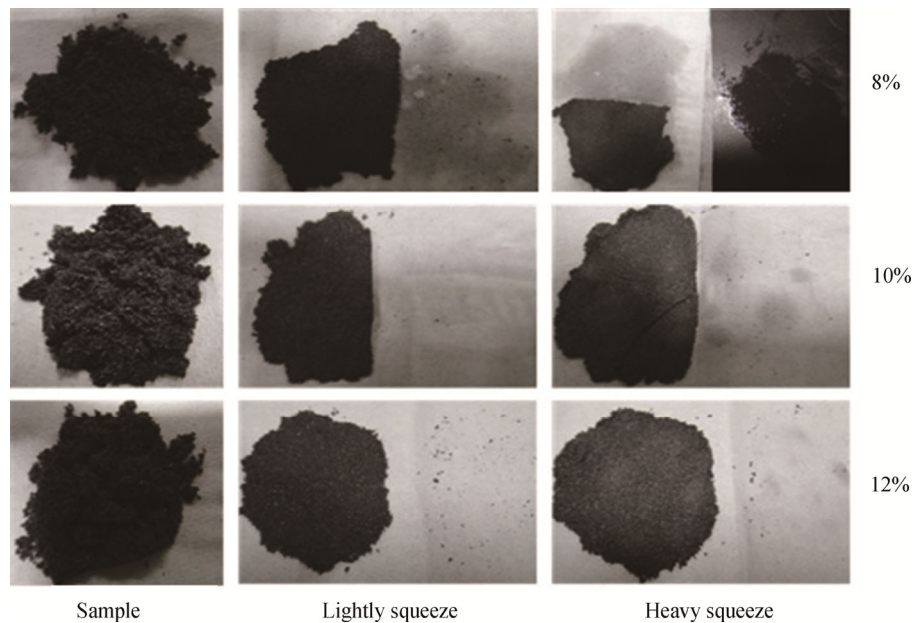


Fig. 4 Squeeze effects of No.3, No.4 and No.5

The mixed acid with 10 wt.% EG was re-prepared and the melting-solidification experiments were carried out to obtain the step cooling curves in different cycles, which are shown in Fig. 5.

According to the experimental tests data and the step cooling curves shown in Fig. 5, the phase transition temperature of the hybrid material is 31.5°C, which is basically the same as that of pure mixed acid, and the latent heat value of phase change of the hybrid material is 217.4 kJ/kg, which is slightly lower than the that of the pure mixed acid. Additionally, 10 cycles of melting-solidification experiments were carried out to verify the the phase transition temperature and the latent heat value of the hybrid material, as shown in Fig. 6. The results showed that the phase transition temperature and the latent heat value of the hybrid material remained basically unchanged, indicating that the hybrid material has good thermal stability.

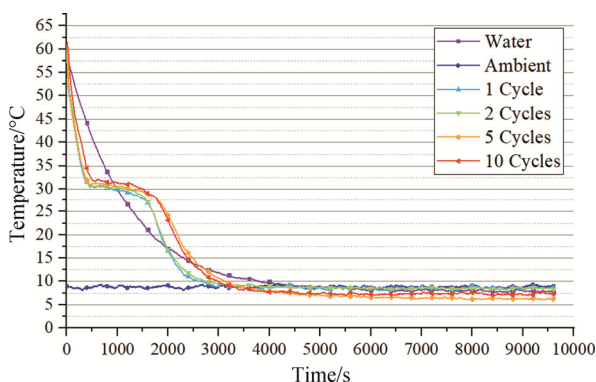


Fig. 5 Step cooling curves of hybrid material in different cycles

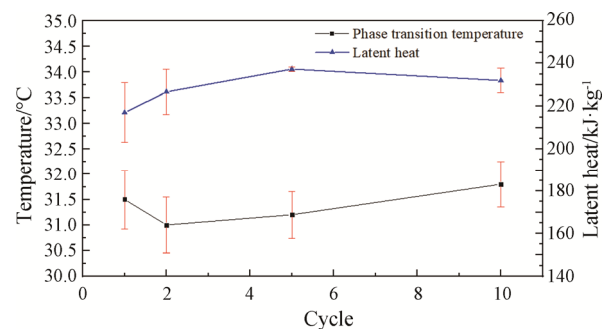


Fig. 6 The phase transition temperature and latent heat of the hybrid material

4. Conclusion

In this study, the hybrid organic PCM composed of LA, SA and EG was prepared for solar heat storage requirements. According to the binary equilibrium phase diagram and the experimental data, the lowest eutectic point of LA-MA mixture was obtained based on step cooling curve method. The results showed that the phase transition temperature of the mixed acid at the lowest eutectic point was 31.2°C and the latent heat value was 264.3 kJ/kg when the mixing mass ratio was 70% for lauric acid and 30% for stearic acid. The optimal mass content of expanded graphite in the hybrid phase change thermal storage material was 10% to wrap up the mixed acid completely. Moreover, melting-solidification cycle experiments were carried out with the hybrid material containing 10% ratio of expanded graphite. The result showed that the phase transition temperature was 31.5°C, and the latent heat value was 217.4 kJ/kg. Therefore, this

kind of hybrid organic phase change material is suitable for solar energy storage and for the cascade utilization of solar energy.

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References

- [1] Yi J., Research report on annual development of China's building energy efficiency. China Architecture & Building Press, 2018. (in Chinese)
- [2] Xu W., Zheng R., Lu B., Research report on application development of solar energy in China. China Architecture & Building Press, 2009. (in Chinese)
- [3] Pomianowski M., Heiselberg P., Zhang Y.P., Review of thermal energy storage technologies based on PCM application in buildings. *Energy and Buildings*, 2013, 67: 56–69.
- [4] Sharma A., Tyagi V.V., Chen C.R., Buddhi D., Review on thermal energy storage with phase change materials and applications. *Renewable & Sustainable Energy Reviews*, 2009, 13(2): 318–345.
- [5] Mikeska T., Svendsen S., Dynamic behavior of radiant cooling system based on capillary tubes in walls made of high performance concrete. *Energy and Buildings*, 2015, 108: 92–100.
- [6] Zalba B., Marin J.M., Cabeza L.F., Mehling H., Review on thermal energy storage with phase change: materials, heat transfer analysis and applications. *Applied Thermal Engineering*, 2003, 23(3): 251–283.
- [7] Mao Q.J., Chen H.Z., Yang Y.Z., Energy storage performance of a PCM in the solar storage tank. *Journal of Thermal Science*, 2019, 28(2): 195–203.
- [8] Tan H.J., Pan C.Y., Yu D., et al., Preparation and analysis of a heat storage phase change composite material taking PNIPAM as carrier. *Journal of Functional Materials*, 2008, 39(12): 2015–2017+21. (in Chinese)
- [9] Saeed R.M., Schlegel J.P., Castano C., Sawafta R., Kuturu V., Preparation and thermal performance of methyl palmitate and lauric acid eutectic mixture as phase change material (PCM). *Journal of Energy Storage*, 2017, 13: 418–424.
- [10] Pieliowska K., Pieliowski K., Phase change materials for thermal energy storage. *Progress in Materials Science*, 2014, 65: 67–123.
- [11] Sari A., Karaipekli A., Thermal conductivity and latent heat thermal energy storage characteristics of paraffin/expanded graphite composite as phase change material. *Applied Thermal Engineering*, 2007, 27(8): 1271–1277.
- [12] Liu C., Yuan Y., Zhang N., Cao X., Yang X., A novel PCM of lauric–myristic–stearic acid/expanded graphite composite for thermal energy storage. *Materials Letters*, 2014, 120: 43–46.
- [13] Chen C.Z., Wang L.G., Huang Y., A novel shape-stabilized PCM: Electrospun ultrafine fibers based on lauric acid/polyethylene terephthalate composite. *Materials Letters*, 2008, 62(20): 3515–3517.
- [14] Kong X.F., Zhong Y.L., Rong X., Min C.H., Qi C.Y., Building energy storage panel based on paraffin/expanded perlite: Preparation and thermal performance study. *Materials*, 2016, 9(2): 70. DOI: 10.3390/ma9020070.
- [15] Yao C.Q., Kong X.F., Li Y.T., Du Y.X., Qi C.Y., Numerical and experimental research of cold storage for a novel expanded perlite-based shape-stabilized phase change material wallboard used in building. *Energy Conversion and Management*, 2018, 155: 20–31.
- [16] Kong X.F., Yao C.Q., Jie P.F., Liu Y., Qi C.Y., Rong X., Development and thermal performance of an expanded perlite-based phase change material wallboard for passive cooling in building. *Energy and Buildings*, 2017, 152: 547–557.
- [17] San A., Kaygusuz K., Some fatty acids used for latent heat storage: thermal stability and corrosion of metals with respect to thermal cycling. *Renewable Energy*, 2003, 28(6): 939–948.
- [18] Su D., Jia Y., Alva G., Tang F., Fang G., Preparation and thermal properties of n–octadecane/stearic acid eutectic mixtures with hexagonal boron nitride as phase change materials for thermal energy storage. *Energy and Buildings*, 2016, 131: 35–41.
- [19] Wang Z.S., Yang L.S., Hu X.W., Luo X.L., Gu Z.L., Improvement and experimental study of the T-history method. *Journal of Refrigeration (In Chinese)*, 2017, 38(6): 34–38+45. (in Chinese)
- [20] Li C.C., Zhang B., Xie B.S., Zhao X.B., Chen J., Chen Z.S., et al. Stearic acid/expanded graphite as a composite phase change thermal energy storage material for tankless solar water heater. *Sustainable Cities and Society*, 2019, 44: 458–464.
- [21] Ma G.X., Sun J.H., Zhang Y., Jing Y., Jia Y.Z., Preparation and thermal properties of stearic acid–benzamide eutectic mixture/expanded graphite composites as phase change materials for thermal energy storage. *Powder Technology*, 2019, 342: 131–140.
- [22] Zhang D., Chen M.Z., Wu S.P., Riara M., Wan J.M., Li Y.Y., Thermal and rheological performance of asphalt binders modified with expanded graphite/polyethylene glycol composite phase change material (EP-CPCM). *Construction and Building Materials*, 2019, 194: 83–91.