EXPERIMENTAL RESEARCH ON PARAFFIN-BASED COMPOSITE PHASE CHANGE ENERGY STORAGE AND THERMAL INSULATION GYPSUM BOARDS

Ying ZHOU[1*], Jian GUAN[2], Rulong ZHOU[3], Kai CUI[4], Xuemin ZHANG[5]

Using paraffin as phase change material (PCM) and expanded graphite as carrier material, paraffin/expanded graphite composite shaped phase change material (cs-PCM) was fabricated by melt blending technique. Phase change gypsum board (PC-GB) was prepared from cs-PCM, building gypsum, fiber, water reducing agent, waterproof agent and retarder according to the calculated mixing ratio at phase change temperature 25.2 °C and latent heat 25.1 J/g, which was suitable for internal temperature adjustment in buildings. Thermal performance test results of PC-GB showed that the heat preservation and insulation effects of PC-GB were 60% and 92.3%, respectively, which were higher than those of ordinary gypsum board (GB) and indoor comfortable temperature range from 25°C to 16°C after using PC-GB remained 275% longer than that for GB. The thermal insulation as well as heat storage and release effects of PC-GB were remarkable.

Keywords: Paraffin; Expanded graphite; Phase change gypsum board; Thermal insulation; Heat storage and release

1. Introduction

Phase change energy storage refers to PCM phase changes occurring at different ambient temperatures by absorbing or releasing heat to store or release energy for ambient temperature adjustment [1,2]. Phase change energy storage building materials made by combining PCM with building materials are suitable for building envelopes [3], which can improve the heat preservation, heat insulation, heat storage and heat release capacity of building envelopes and better reduce indoor temperature fluctuation, improving living space comfort as well as energy saving and consumption. The selection principles of PCM for building envelopes mainly include: appropriate phase change temperature, large latent heat, good thermal conductivity, good phase change reversibility, low volume change, high thermal stability, no toxicity, no corrosion, etc. [4]. Cabeza et al. [5] showed

[1] Prof., College of Urban Construction, Heze University, China. Corresponding author e-mail: zhouying@hezeu.edu.cn
[2] Stud., College of Urban Construction, Heze University, China, e-mail: 1454009019@qq.com
[3] Stud., College of Urban Construction, Heze University, China, e-mail: 1977228489@qq.com
[4] Stud., College of Urban Construction, Heze University, China, e-mail: 511448613@qq.com
[5] Stud., College of Urban Construction, Heze University, China, e-mail: 980213775@qq.com

that PCMs with phase change temperatures in the range of 22-28°C could be used for heat storage in buildings to adjust the comfort in buildings. Quanying et al. [6] found that paraffin was a solid-liquid phase change material suitable for building envelopes. Huan et al. [7] prepared paraffin/expanded graphite composite shaped phase change material (cs-PCM) with high thermal conductivity for solar collectors using paraffin as the phase change material and expanded graphite as the support material. Ying et al. [8] applied expanded perlite to adsorb paraffin and fabricated paraffin/expanded perlite phase change insulation mortar with good thermal insulation and temperature adjustment effects. Zhao et al [9] employed lauric acid and paraffin as PCMs and shale ceramsite as adsorption material to prepare shale ceramsite composite shaped phase change aggregate. Jun et al. [10] applied ceramsite to adsorb paraffin for the fabrication of paraffin/ceramsite cs-PCMs and applied them as coarse aggregates to prepare composite phase change concrete with high heat storage capacity. Building gypsum has the advantages of extensive sources, simple preparation, low energy consumption, sound insulation and fire resistance and is widely applied in new wall materials [11]. Phase change gypsum board (PC-GB) is a type of energy storage building wallboard with gypsum board (GB) as matrix and mixed with PCM. It could be employed as interior wall insulation material to reduce the fluctuation range of indoor temperature and maintain indoor comfort [12]. Shengxiao et al. [13] absorbed paraffin onto light ceramsite, synthesized paraffin/ceramsite shaped heat storage material, and mixed it with gypsum to fabricate composite phase change heat storage GBs with high heat storage capacity. Becker [14] pasted PC-GB onto the inner surface of outer wall. His experimental results showed that the application of PC-GB provided favorable effects and energy saving rate could reach 57%. Weiwei et al. [15] manufactured a simple experimental device with phase change energy storage GB. Fan et al. [16] used phase change gypsum board to build a lightweight prefabricated building, and the test results show that the use of phase change gypsum board can improve indoor thermal comfort and reduce the energy consumption of air conditioning throughout the year. Experimental results revealed that phase change gypsum wallboard had high heat storage and release capacity. However, GB is prone to mildew when exposed to water, which affects its appearance and application [17] and decreases its strength. Also, this decreases its safety performance which restricts its development as building wall materials [18]. Developing waterproof GB is of practical significance. Based on the above discussion, we introduced paraffin as a phase change energy storage material into building gypsum, a traditional building material, and added some additives such as fiber and waterproof agent to prepare a waterproof PC-GB to achieve high thermal insulation as well as heat storage and release capacities.

2. Materials and methods

2.1 Raw materials

24# paraffin (phase change temperature 23.3°C and phase change enthalpy 203.3 kJ/kg) was purchased from Fushun Tongtai Chemical Co. Ltd. Expanded graphite (EG) expanded 300 times with purity 99% and particle size 80 mesh was obtained from Qingdao Tengshengda Carbon Machinery Co. Ltd. Gypsum desulfurization was obtained from Jinan zhongxinda chemical Co., Ltd.; high-performance polycarboxylate superplasticizer 540P was purchased from Shanghai Qichen Chemical Technology Co., Ltd.; Gypsum retarder was obtained from CQ-SHJ09, Shanghai Qichen Chemical Technology Co., Ltd.; Waterproof agent was obtained from HY-SG1, Beijing Haiyan Xingye Concrete Admixture Sales Co., Ltd.; and Polypropylene fiber was purchased from PP-6 mm, Shanghai Yingjia Industrial Development Co., Ltd. Also, tap water was applied throughout the experiments.

2.2 Main instruments and equipment

Differential scanning calorimeter (Q20, TA Instruments, USA), scanning electron microscope (Apreo, Thermo Fisher Scientific Searle Technology, USA), all-in-one bending and compression machine (YAW-300C, Beijing Luda Xingwang Construction Machinery Instrument Co. Ltd.), multi-channel temperature tester (JK808, Changzhou Jinailian Electronic Technology Co. Ltd.), thermal conductivity tester (DRE-III, transient plane heat source method, Xiangtan Xiangyi Instrument Co. Ltd.), constant temperature drying oven (DHG-9073BS-III, Jintan Guowang Experimental Instrument Factory), moving stirrer (JJ-6A, Jintan Guowang Experimental Instrument Factory), electric constant-temperature water bath pot (HH-2, Jiangsu Scientific Analysis Instrument Co. Ltd.), precision electronic balance (JA2003, Shanghai Puchun Measuring Instrument Co. Ltd.), precision electronic balance (YP3002A, Shanghai Puchun Measuring Instrument Co. Ltd.), and beaker (foam box) were applied in this research.

2.3 Preparation of paraffin/EG cs-PCM

EG and paraffin were poured into a beaker, melted, blended and stirred in a water bath at about 60°C. After adsorption for 1 hour, the product was taken out and cooled to room temperature to obtain paraffin/EG cs-PCMs with different mass ratios. Table 1 summarizes the proportions of different components in different samples.

Table 1

The proportions of cs-PCMs

	S1	S2	S3	S4	S5	S6
EG	5%	10%	15%	20%	25%	30%
Paraffin	95%	90%	85%	80%	75%	70%

2.4 Preparation of PC-GB

After the addition of cs-PCM, polypropylene fiber and waterproof agent into desulfurized gypsum, mixing and stirring, the mixed solution of water, water reducer and retarder (Table 2) was added to prepare slurry which was then injected into mold. After demolding, the as-prepared PC-GB with the dimensions of 300 mm×250 mm×15 mm was obtained. Ordinary GB was prepared without adding phase change material and waterproof agent; the experimental proportions are shown in Table 3.

Table 2

The experimental proportions of PC-GB

	Mass fraction
Gypsum	56%
Phase change material	11.2%
Water	28%
Water reducer	0.1%
Retarder	0.3%
Waterproof agent	2.8%
Polypropylene fiber	1.6%

Table 3

The experimental proportions of GB

	Mass fraction
Gypsum	65%
Water	32.5%
Water reducer	0.15%
Retarder	0.35%
Polypropylene fiber	2%

3. Results and analysis

3.1 Thermal stability of cs-PCM

Six types of cs-PCM were weighed and adopted as m_0. They were heated in a constant-temperature drying oven at 50 °C for 1 hour, and then, taken out to

weigh. Their weight was recorded as m_1 and the mass loss of cs-PCM was calculated as exudation rate according to the following equation:

$$\varphi = \frac{m_0 - m_1}{m_0} \times 100\% \tag{1}$$

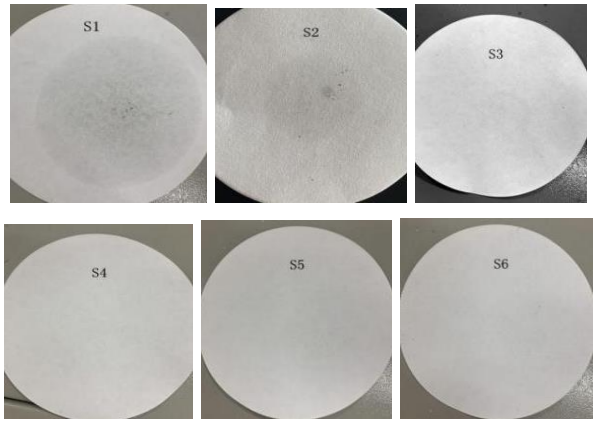


Fig. 1. The exudation of cs-PCM

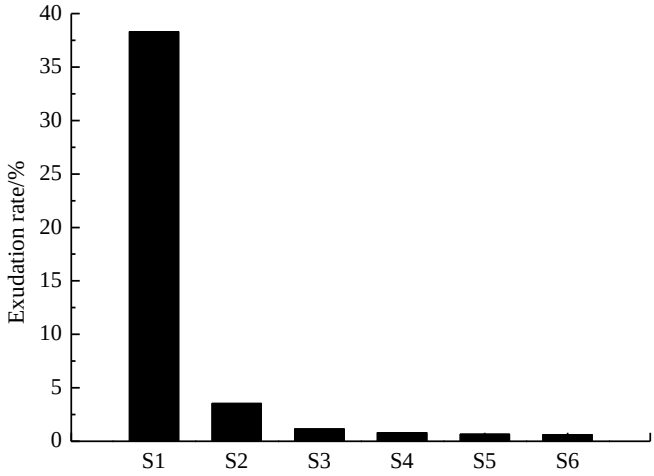


Fig. 2. The exudation rate of cs-PCM

The seepage of S1-S6 cs-PCM after heating is shown in Fig. 1 and seepage rate is shown in Fig. 2. As can be seen from Figs. 1 and 2, the mass loss of S1 was the largest, reaching 38.32%, which indicated that its thermal stability was poor, and paraffin had larger seepage. With the increase of the content of EG and decrease of the amount of paraffin, seepage and seepage rate were decreased. When the content of EG was increased to 10% and 15%, the seepage rates of S2 and S3 were 3.56% and 1.18%, respectively. When the content of EG was increased to more than 20%, the mass loss of cs-PCM was less than 1% and

tended to be stable. The seepage rates of S4, S5 and S6 were 0.82%, 0.67% and 0.64%, respectively, which indicated that S4, S5 and S6 had high thermal stability and could be used to prepare PC-GB.

3.2 Phase change temperature and enthalpy of cs-PCM

Differential scanning calorimeter (DSC) was applied to measure the phase change temperature and enthalpy of S4, S5 and S6 under nitrogen atmosphere, temperature range of -10-60°C, and heating rate of 5°C/min. DSC results are shown in Table 4.

Table 4

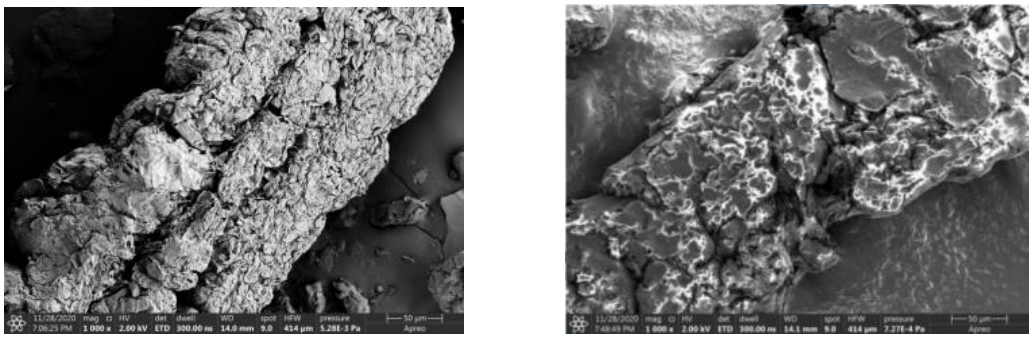
The phase change temperature and enthalpy of paraffin and cs-PCM

	Paraffin	S4	S5	S6
Phase change temperature/°C	23.3	25.1	25.2	25.2
Phase change enthalpy / $J \cdot g^{-1}$	203.3	161.5	152.8	130.4

As was seen from Table 4, phase change temperatures of S4, S5 and S6 were 25.1, 25.2 and 25.2°C, respectively, which were higher than that of pure paraffin at 23.3°C, but were still in accordance with solid-liquid phase change principle of paraffin. Phase change temperatures of S4, S5 and S6 were slightly different, indicating that when the amount of EG reached a certain level, further increase of EG had little effect on phase transition temperature. Phase change enthalpies of S4, S5 and S6 were 161.5, 152.8 and 130.4 J/g, respectively, which were slightly lower than the phase change enthalpy of paraffin 203.5 J/g. With the decrease of the amount of paraffin wax, phase change enthalpies showed a decreasing trend. This was because latent heat was mainly provided by paraffin wax and the added EG did not undergo phase change. Generally, higher latent heats resulted in better energy storage effects. Considering phase change temperature and enthalpy, 20% EG and 80% paraffin was adopted as the ideal cs-PCM to prepare PC-GB.

3.3 Morphology analysis of cs-PCM

The microscopic morphologies of EG and S4 were observed by scanning electron microscope, as shown in Fig. 3.



a. EG b. cs-PCM

Fig. 3. SEM images of EG and cs-PCM

As was seen from Fig. 3(a), EG was worm-like with honeycomb structure on the surface, giving it high adsorption capacity. Fig. 3(b) showed that honeycomb pore structure in EG was disappeared and completely filled with paraffin, which proved that EG had good adsorption effect on 80% paraffin.

3.4 DSC analysis of PC-GB

The cs-PCM obtained by mixing EG and paraffin with mass ratio of 1:4 was mixed with other experimental materials with certain test ratios to prepare PC-GB, and ordinary GB was prepared without phase change material. As shown in Fig. 4, the phase change latent heat and temperature of PC-GB were tested, and DSC curve is shown in Fig. 5.

Fig. 4. GB and PC-GB

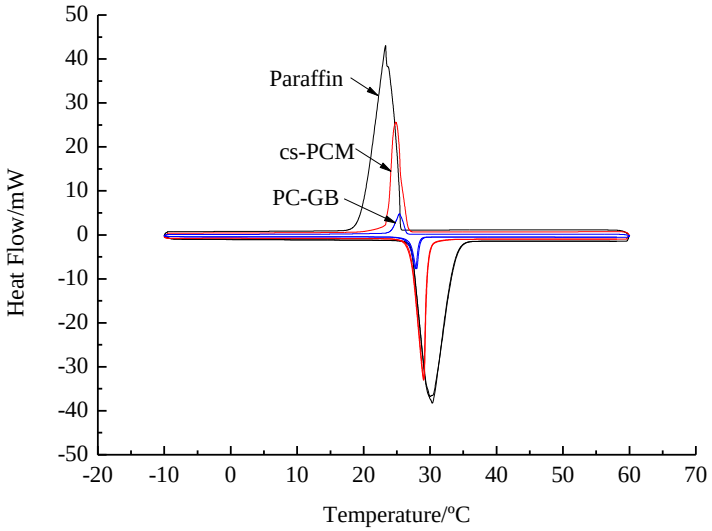


Fig. 5. DSC curves of PC-GB

Fig. 5 showed that the phase change temperature of PC-GB was 25.2°C, which was not much different from that of cs-PCM, indicating that the addition of gypsum, fiber, additives and other materials had little influence on phase change temperature. The phase change latent heat of PC-GB was 25.1 J/g, which was less than that of cs-PCM, indicating that the addition of other materials affected the heat storage of cs-PCM. Appropriate phase change temperature and large phase change latent heat of PC-GB could meet temperature adjustment needs in buildings. When PC-GB was applied for the internal insulation of building walls, high heat storage and release capacities could be obtained.

3.5 Water absorption of PC-GB

At room temperature (25±2)°C and relative humidity of 50±2%, dried PC-GB and ordinary GB were weighed. After immersing in water for 2 hours, the surface moisture of specimen was wiped off with a semi-wet towel and weighed. Water absorption rate was calculated based on the difference of dry and wet masses. The water absorption rate of ordinary GB was 21.6%, and that of PC-GB was 14.3%, which was 33.8% lower than ordinary GB. This was because the organic cs-PSM filled GB pores, which stopped water flow to a certain extent. In addition, the water blocking effect of waterproof agent reduced the water absorption rate of GB, indicating that PC-GB could be applied as waterproof GB in humid environments.

3.6 Thermal performance of PC-GB

The thermal conductivities of PC-GB and ordinary GB were tested and the obtained results are summarized in Table 5.

Table 5

Thermal performance parameters of PC-GB and GB

	Thermal conductivity /W·(m·K)$^{-1}$	Heat storage coefficient / W·(m^2·K)$^{-1}$	Specific heat capacity /J·(g·°C)$^{-1}$
GB	0.45	4.52	0.61
PC-GB	0.61	6.12	0.7

The heat storage coefficient according to the following equation:

$$S = \sqrt{\frac{2\pi\lambda c\rho}{3.6T}} \tag{2}$$

where S is the heat storage coefficient (W·(m^2·K)$^{-1}$), λ is the thermal conductivity (W·(m·K)$^{-1}$), c is the specific heat capacity (J·(g·K)$^{-1}$), ρ is the density (kg·m^{-3}), T is the temperature fluctuation period (T=24h), and π=3.14.

From Table 5, it was seen that the thermal conductivity of PC-GB was 0.61 W/(m·k), which was higher than that of ordinary GB with 0.45 W/(m·K). The thermal conductivity of PC-GB was affected after the addition of PCM, but was still small, which showed that it had good thermal insulation effect. The heat storage coefficient and specific heat capacity of ordinary GB were 4.52 W/(m^2·K) and 0.61 J/(g·°C) and those of PC-GB were 6.12 W/(m^2·K) and 0.7 J/(g·°C), respectively, which were 35.4% and 14.8% higher than those of ordinary GB, indicating that PC-GB had certain heat storage and temperature regulation effects.

3.7 Heat storage/release capacity of PC-GB

Thermocouples were placed on the surfaces of PC-GB and ordinary GB and the two GBs were placed in an environment with constant temperature of 16°C. Then, the board to be tested was placed in a 38°C constant temperature box to simulate and analyze the thermal insulation performance of GB. Temperature was recorded every 10 seconds and the heating curve of GB is shown in Fig. 6. After heating process was over, the two GB types were placed at a constant temperature of 16°C to simulate thermal insulation performance. The cooling curve of GBs is shown in Fig. 7.

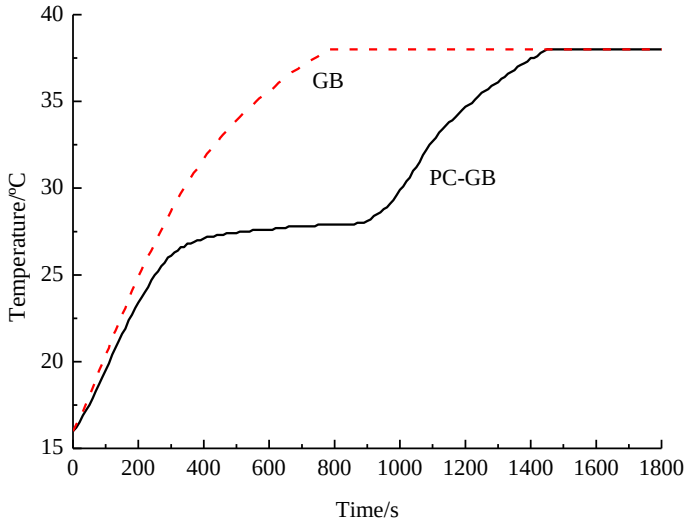


Fig. 6. Endothermic curves of PC-GB and GB

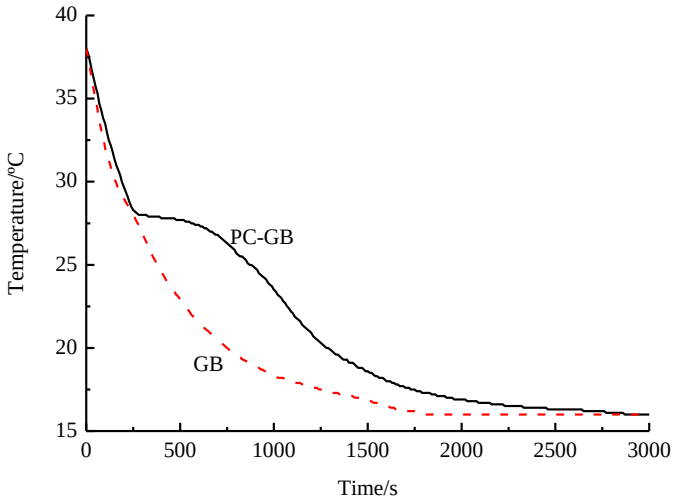


Fig. 7. Exothermic curves of PC-GB and GB

As it was seen from Fig. 6, when the temperatures of the two GB types were lower than 26°C, heating rate was the same. When temperature reached 26°C-28°C, the temperature curve of PC-GB was relatively gentle with an obvious temperature lag phenomenon compared with the curve of ordinary GB. At this time, cs-PCM underwent solid-liquid phase change in PC-GB, absorbing a great amount of heat and delaying the heating rate of PC-GB surface. After phase change process was finished, the temperature of the two GB types was balanced with ambient temperature. Then, it takes about 13 minutes for ordinary GB and about 25 minutes for PC-GB to increase temperature from 16°C to 38°C, which

showed that the thermal insulation effect of PC-GB was 92.3% higher than that of ordinary GB. It was seen from the cooling curve of Fig. 7 that when the temperatures of GBs were higher than 28°C, their cooling rates were basically the same. The temperature of ordinary GB started to decrease at 28°C, while the cooling curve of PC-GB was relatively gentle. At this time, cs-PCM underwent phase change, giving off a great amount of heat. It takes about 30 minutes for the ordinary GB and about 48 minutes for the PC-GB to cool down to 16°C, which showed that the thermal insulation effect of PC-GB was 60% higher than that of ordinary GB. Temperature rise and drop of PC-GB were slower than those of ordinary GB, which was due to the addition of paraffin/EG cs-PCM. This additive made PC-GB undergo solid-liquid phase change near phase change temperature to absorb or release heat, thus delaying heating and cooling of PC-GB surface.

3.8 Experimental model analysis of PC-GB

According to Weigao [19], an incubator with length× width× height× thickness of 340 mm×220 mm×180 mm×30mm was made. Ordinary GB and PC-GB were placed at box cover and the joint of GB and thermal insulation box cover was sealed with adhesive tape to obtain phase change model box to simulate phase change building and test thermal insulation, heat storage and release effects of GB. The thermocouples of temperature inspection instrument were placed outside and inside the box. The thermocouples inside the box were hung at the center of model box. The experimental model was put in a 60°C oven. When the temperature of the inner space of the experimental model reached 38°C, the model was taken out and placed in ambient temperature to monitor temperature changes in box. The cooling curve is shown in Fig. 8.

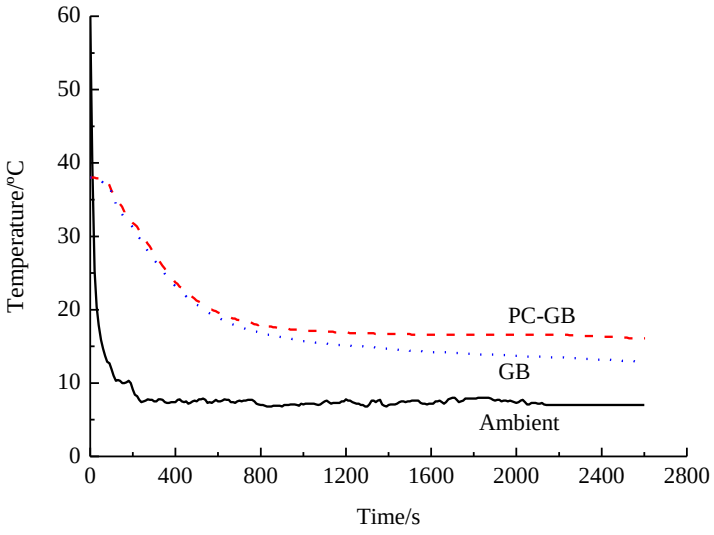


Fig. 8. Temperature change in the experimental model box

The application of PC-GB in building walls has a certain energy-saving effect. The relationship between comfort temperature duration and energy saving in energy-saving systems could be analyzed with standard temperature damping ratio γ [20].

$$\gamma = \frac{T_2 - T_1}{T_1} \times 100\% \tag{3}$$

Where γ is standard temperature damping rate, T_1 is the time required for temperature in ordinary GB experimental model box to decrease from 25 to 16°C (minutes), and T_2 is the time required for temperature in the experimental model box of PC-GB to decrease from 25 to 16°C (minutes).

From Fig. 8, it was seen that temperature decrease from 25 to 16°C took 10 minutes for ordinary GB experimental model box and 37.5 minutes for PC-GB experimental model box. According to Eq. (1), standard temperature damping rate was γ = (375-10)/10× 100% = 275%, which meant that the duration of indoor comfortable temperature was increased by 275% after using PC-GB. The board could reduce the opening time of heating equipment and save electric energy in winter.

4. Conclusion

(1) At the mass ratio of EG to paraffin of 1:4, the cs-PCM obtained by melt blending had good thermal stability, suitable phase change temperature of 25.1°C and large latent heat of 161.2 J/g. Therefore, it could be applied to prepare PC-GB.

(2) The PC-GB prepared according to test proportion had phase change temperature of 25.2°C, phase change latent heat of 25.1 J/g, thermal conductivity of 0.61 W/(m·K), thermal storage coefficient of 6.12 W/(m^2·K) and specific heat capacity of 0.7 J/(g·°C). Its thermal insulation and thermal preservation effects were 92.3% and 60% higher than that of ordinary GB, respectively. Also, its other properties were suitable for thermal insulation of building wall.

(3) Experimental model box simulated phase change building. Application of PC-GB increased the duration of indoor comfortable temperature by 275% compared to that of ordinary GB. In winter, it could decrease the opening times of heating equipment, save electric energy and achieve energy conservation and emission reduction.

Acknowledgments

This study was supported by A Project of Shandong Province Higher Educational Research and Development Program (J18KB070), Doctor Fund Project of Heze University (XY19BS02), and Innovation and Entrepreneurship

Training Program for College Students in Shandong Province (S202010455047, S202110455064).

REFERENCES

[1]. *F. L. Liu, J. Q. Zhu, B. G. Ma, et al*, "Research progress on preparation and application of gypsum phase change wallboard in building wall", in Journal of the Chinese ceramic society, vol. 44, no. 8, 2016, pp. 1178-1190.

[2]. *B. N. Zhang, Y. Q. Cui, G. Q. Yin, et al*, "Preparation and properties of expanded graphite phase change composite for thermal storage", in Guangzhou chemical industry, vol. 39, no. 15, 2011, pp. 70-72.

[3]. *T. Shi, W. Sun*. "Revive on application technology progress of phase change building materials", in Journal of the Chinese ceramic society, vol. 36, no. 7, 2008, pp. 1031-1036.

[4]. *Y. Qiu, Q. S. Wu, S. P. Li, et al*, "Study on wall phase change energy storage materials", in Wall material innovation & energy saving in buildings, no. 11, 2011, pp. 39-42.

[5]. *L. F. Cabeza, A. Castell, C. Barreneche, et al*. "Materials used as pcm in thermal energy storage in buildings: a review", in Renew Sustain Energy Rev, no. 15, 2011, pp. 1675-1695.

[6]. *Q. Y. Yan, W. Wang, D. Yu*, "An study on PCM applied in the building envelope", in Materials Review, vol. 19, no. 8, 2005, pp. 102-105.

[7]. *H. Gao, J. Y. Wang, Y. X. Zhang, et al*. "Heat transfer behavior analysis of expanded graphite/paraffifin form-stable phase change solar collector", in Journal of Shanghai Polytechnic University, vol. 39, no. 1, 2022, pp. 36-42.

[8]. *Y. Zhou, S. X. Wang, Z. H. Liu, et al*. "Simulation study on composite phase change thermal insulation walls in solar greenhouse based on ANSYS", in Acta energiae solaris sinica, vol. 41, no. 4, 2020, pp. 113-122.

[9]. *J. Zhao, P. J. Gao*, "Study on preparation of composite phase change energy storage aggregate", in Urban construction theory research(Electron Ed), vol. 23, no. 5, 2015, pp. 8.

[10]. *T. J. Wu*. "Study on the preparation and properties of paraffin phase change energy storage of the concrete", in New building materials, vol. 43, no. 12, 2016, pp. 91-93.

[11]. *F. X. Li, Y. Z. Chen, S. Z. Long, et al*. "Development and application of clean energy-saving for gypsum resource", in The world of building materials, vol. 30, no. 1, 2009, pp. 48-50.

[12]. *T. Y. Zhang, M. Shen, D. Zhang*. "Study on phase change composite of plasterboard with exfoliated graphite and butyl stearate", in Materials Review, vol. 23 no. 7, 2009, pp. 61-63.

[13]. *S. X. Zhu, X. F. Hu*. "Research on relationship between particle size distribution of energy storage paraff'm and the conductivity factor of phase change energy storage composite gypsum board", in New building materials, vol. 36, no. 1, 2009, pp. 16-19.

[14]. *R. Becker*. "Improving thermal and energy performance of buildings in summer with internal PCM", in J Build Phys, no. 37, 2014, pp. 296-324.

[15]. *W. W. Zhang, X. W. Fang, Q. Y. Zhou, et al*. "Hydrodynamic performance prediction and strength analysis of propeller in abnormal working condition", in Science technology and engineering, vol. 15, no. 1, 2015, pp. 112-115.

[16]. *F. Li, H. X. Chen, X. Y. Sun, et al*. "Application and annual running performance test of a light fabricated building with phase-change gypsum boards", in New building materials, vol. 47, no. 10, 2015, pp. 113-118.

[17]. *Y. H. Wang*, "Research on water resistance of FGD gypsum-based composite materials", PhD Thesis, Zhengzhou University, 2013.

[18]. *S. G. Zhou, D. Y. Yang, Z. Guo, et al*. "Experimental study on preparation of fire-proof and water-resistant gypsum board for wood structure building", in Shanxi Architecture, vol. 46, no. 15, 2020, pp. 102-103.

[19]. *W. G. Qin*, "Study on the preparation and properties waterproof phase change heat storage gypsum board", PhD Thesis, Wuhan University of technology, 2018.
[20]. *M. X. Ai, L. Q. Cao, X. Y. Guo, et al*. "Energy efficiency evaluation of phase change energy storage building materials", in Construction conserves energy, vol. 36, no. 4, 2008, pp. 40-44.