Research on Expanded Graphite Matrix Phase Change Composites

Yizhe Bai *

Shanghai University School of Materials Science and Engineering, Shanghai, China

* Corresponding Author Email: byz1234@shu.edu.cn

Abstract. As a new functional material, expanded graphite has many excellent properties such as light weight, low density. non-toxic and harmless, high and low temperature resistance, environmental protection and energy saving. With the continuous progress of science and technology and scientific research, expanded graphite composite materials such as expanded graphite are continuously used in various research fields. For example, absorb environmental pollution, sealing materials, flame retardant materials, shielding interference materials, etc. In this paper, the microstructure, excellent properties of EG, the preparation of EG matrix composites, and the research and development of graphitization for special applications of expanded graphite and expanded graphite matrix are reviewed. Through these studies and reviews, it is hoped that some inspiration can be given to the research on the direction of expanded graphite matrix composites, which will help to explore new fields in the future.

Keywords: Expanded graphite; Composite materials; Phase change materials; Energy storage material

1. Introduction

Facing the energy crisis today, it is of great significance to improve the utilization rate of present energy. Energy storage can address the mismatch between the need in space and time and energy provide, where the most widely used and most important is phase change latent heat storage. The heat absorption and release in the process of phase change energy storage can be carried out at a constant temperature, and the heat storage density is large, so it is widely used in construction, road traffic, food, biomedical items, solar energy use, and agricultural greenhouse [1-3]. Transportation and cooling, medical care, heat dissipation of electronic equipment, specific temperature regulation closure, aerospace technology, IR military camouflage, power peak shifting, industrial waste heat storage and utilization, heat energy recovery and many other fields have obvious application prospects. However, because of the phase transition energy storage materials' poor heat transfer efficiency and thermal conductivity, their energy storage and energy release efficiencies are affected. Expanded graphite has similar features to natural graphite, such as corrosion resistance, strong electrical and thermal conductivity, radiation resistance, oxidation resistance, high temperature resistance, and self-lubrication. At the same time, expanded graphite has larger specific surface area and higher surface activity, and a unique network pore structure.

Therefore, in this paper, the author starts with the microstructure analysis of expanded graphite, and fundamentally analyzes the reasons for the superior performance of expanded graphite as a PCM. At the same time, it is compared with traditional phase change materials storing energy such as paraffin, and its performance is analyzed from multiple angles. After that, this paper summarizes the existing preparation methods of expanded graphite and analyzes its application value. Finally, the author reviews and prospect the current and future applications of expanded graphite, and thinks about its future development direction.

2. Microstructure of EG

The appearance of the EG electron microscope scanning image is worm-like, that’s why it’s also called graphite worm, as shown in Fig. 1. The expanded graphite obtained by different preparation methods is worm-like in different shapes. Although the appearances are different, they are all made up of many graphite flakes that are adherent and layered. Between the flakes, there are many honeycomb-like fine pores, and the scales are nearly the same thickness. Generally, it is between 30 and 80 nm, while the pore size varies greatly, mostly between 10^{-3} and 10^{-2} μm [4]. There are reports that expanded graphite particles have a quaternary pore structure: 1) Graphite worms are composed of multiple "microcells" connected, the microcells are irregular ellipsoids, and the V-shaped cracks between the microcells are the first-level pores; 2) The microcells are composed of several graphite sub-sheets, and the pores between the sub-sheets are willow-like and interconnected, that is, the second-order pore structure; 3) The sub-sheet itself also has a rich polygonal pore structure, that is, expanded graphite The tertiary pore structure of 4; 4) the fourth pore structure is located on the pore wall of the tertiary pore, although it cannot be observed on the scanning electron microscope, but it does exist by the N_2 adsorption method [5].

In terms of the number of pores, fourth-order pores are the least, followed by first-order pores, second-order pores are more than first-order pores, and third-order pores are more than second-order pores. The pore volume of the green pores has an absolute advantage. After testing, the porosity of expanded graphite accounts for more than 85%, of which the porosity of open pores is greater than 13%, and the porosity of closed pores is less than 1% [6].

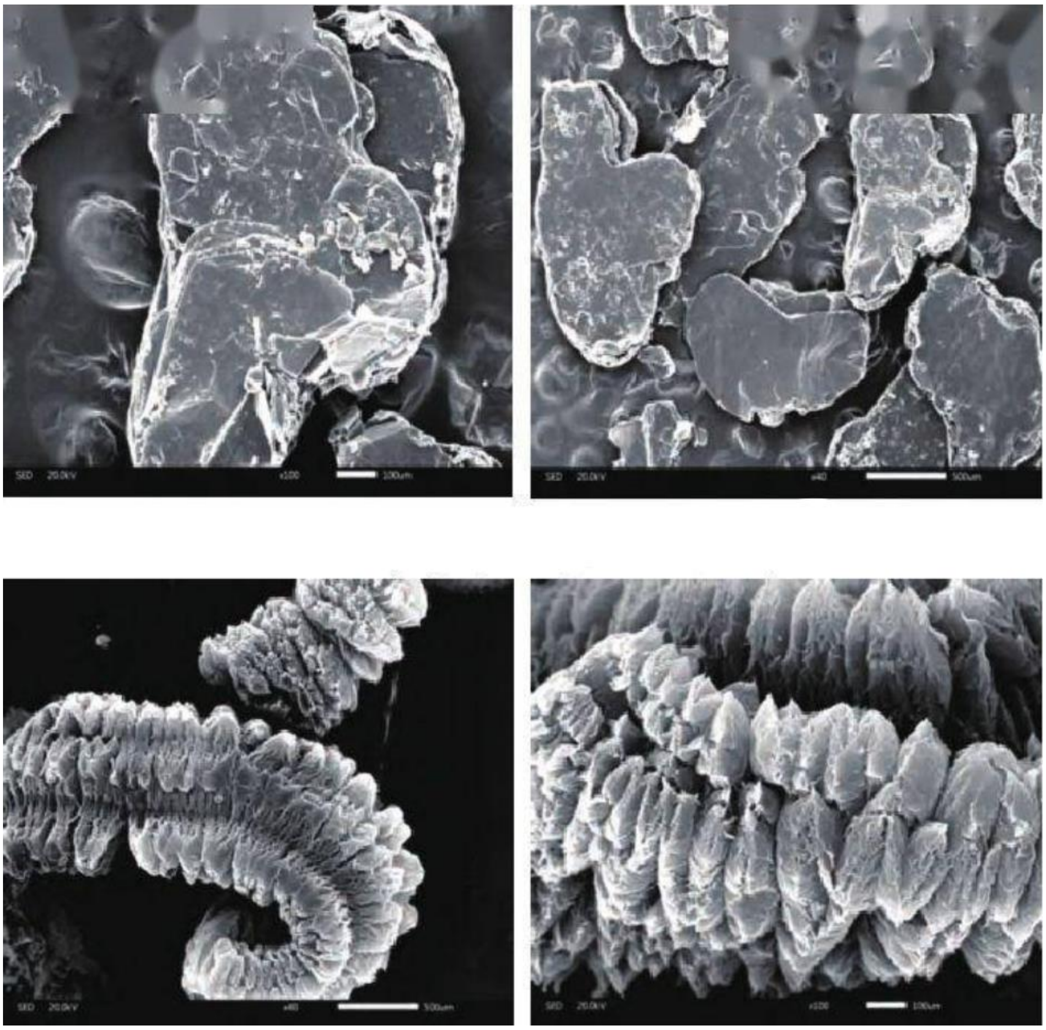

Fig. 1 SEM before and after the expanded graphite’s expanding [6].

As shown in the Figure 1, when subjected to high temperatures, expanded graphite can immediately expand 150300 times its volume, changing from flake to worm-like, so that the structure is loose, porous and curved, the surface area is enlarged, the energy in the surface is improved, and the flake graphite’s adsorption force is enhanced. combined, which increases its softness, resilience and plasticity.

3. Performance comparison with traditional PCMs

Among the universally used PCMs, the advantages of paraffin include a high latent heat of phase transition, a high crystallization rate, no supercooling or precipitation, consistent performance, non-toxicity, non-irritation, non-corrosion, and a low price. Meanwhile, paraffin waxes have low thermal conductivity and are fluid liquids above the phase transition temperature [7].

Therefore, this paper compares the paraffin phase change material with the PA wax and EG composite PCMs to observe the effect of the addition of EG on the properties of the PCM.

3.1. Phase transition latent heat and temperature of phase transition

Fig. 2 depicts the composite phase transition material's DSC curve with varying paraffin content. It can be seen that, apart from the paraffin-based PCM's solid-liquid phase transition, and below its melting point, a solid-solid phase transform also occurs. While the liquid phase change temperature is roughly 61°C, the solid-solid phase transition temperature is at 41°C.

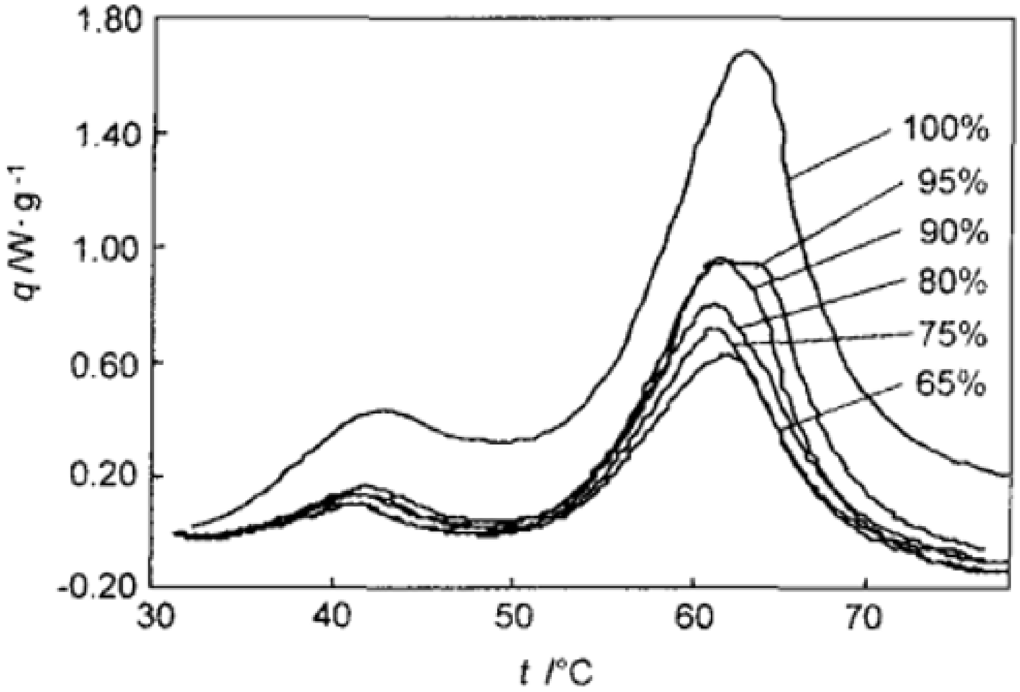

Fig. 2 PA/EG composites with varying content of paraffin's DSC curves [8].

According to Table 1, the phase change temperature of EG and PA is a little lower the pure PA. One probable explanation is that PA is an amorphous solid that softens and becomes liquid only gradually towards its melting point. Because of the presence of graphite crystallites in the composite material, and the composite material's thermal conductivity is improved, so compared to pure PA, the rate of softening is increased, and the temperature required to reach the liquid condition is lower [9].

Table 1. Phase transform temperatures of PA/EG composites [8].

Paraffin w/%	65	75	80	90	95	100
Solid-solid phase change temperature t/℃	41.3	41.3	41.2	41.9	41.5	42.6
Solid-liquid phase change temperature t/℃	61.8	61.2	61.3	62.0	61.7	63.1

Fig. 3 is the relationship of the paraffin/expanded graphite composite material between latent heat of variable and PA content. It could be observed that the latent heat of phase transition of the composites improves with the improving of PA content. The latent heat of phase transition is between 80J/g and 150J/g, of course, it can be adjusted within a larger range as required.

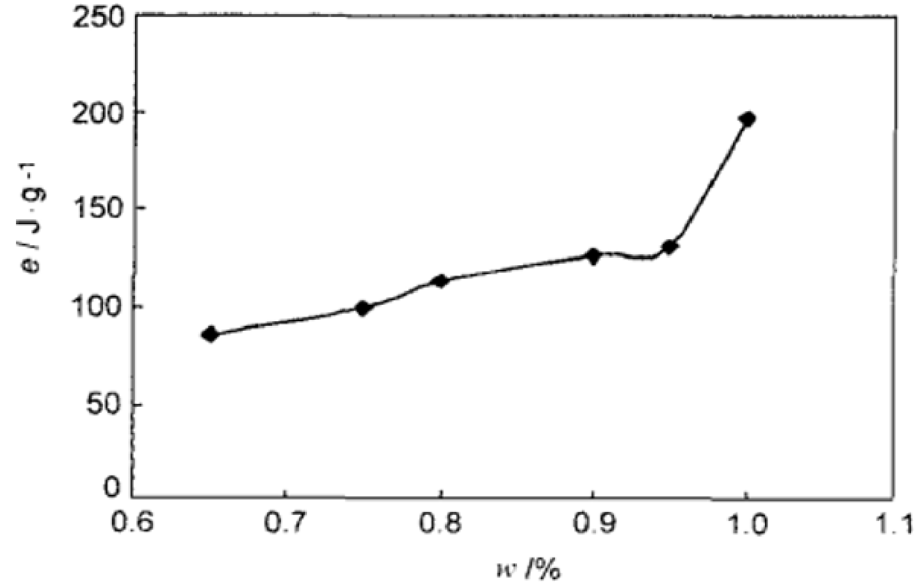

Fig. 3 Paraffin/expanded graphite composites' latent heats with varying amount of paraffin [8].

So, as the figures shows: the latent heat of phase transformation of the material drops with the increasing of the content of expanded graphite;

3.2. Thermal performance

Figure 4 shows the paraffin's and PA/EG composite PCMs' heat storage curves. It can be observed that when temperature rises from 30 °C to 80 °C and reaches equilibrium with the system temperature, the paraffin needs 260S, while the paraffin/graphite composite phase change material only needs 40S~70S, and the time is reduced by 4 to 6 times.

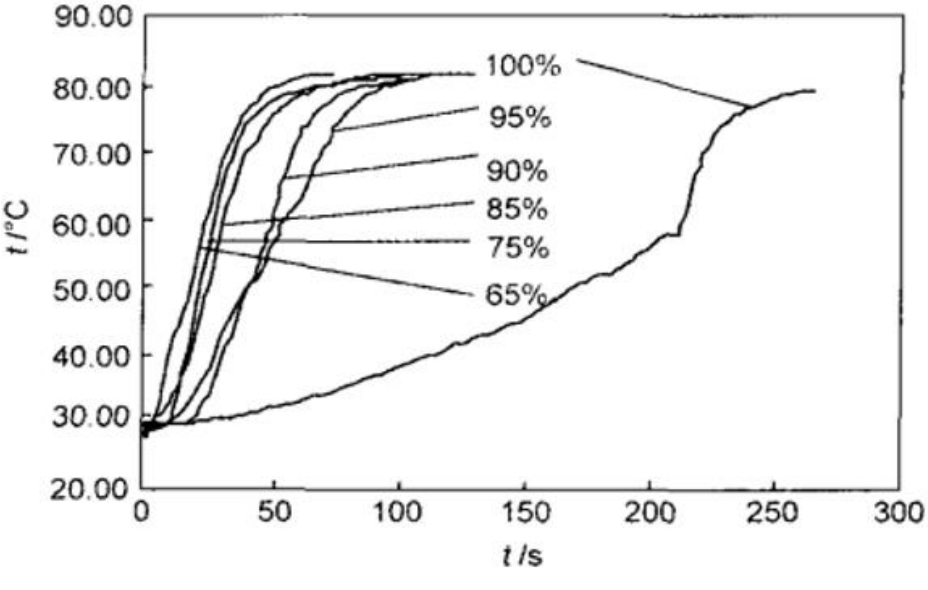

Fig. 4 Curves of heat storage of a PA/EG composite [8].

Figure 5 shows the exothermic curves of paraffin and PA/EG composite PCMs. It can be observed from the figure that when the heat storage process is completed, and the temperature decreased from 100°C to about 22°C, paraffin wax needs 600s, while the paraffin/expanded graphite composite PCMs only needs 80-150s, and the time demanded is decreased by 4 to 8 times. It can be observed that the storage time of the PA/EG composite PCM is much shorter than that of paraffin, whether it is heat storage or exotherm. The reason for this is that the EG in the composite material has high thermal conductivity, which considerably enhances the heat transfer efficiency during the heat storage procedure and shortens the heat release and storage time.

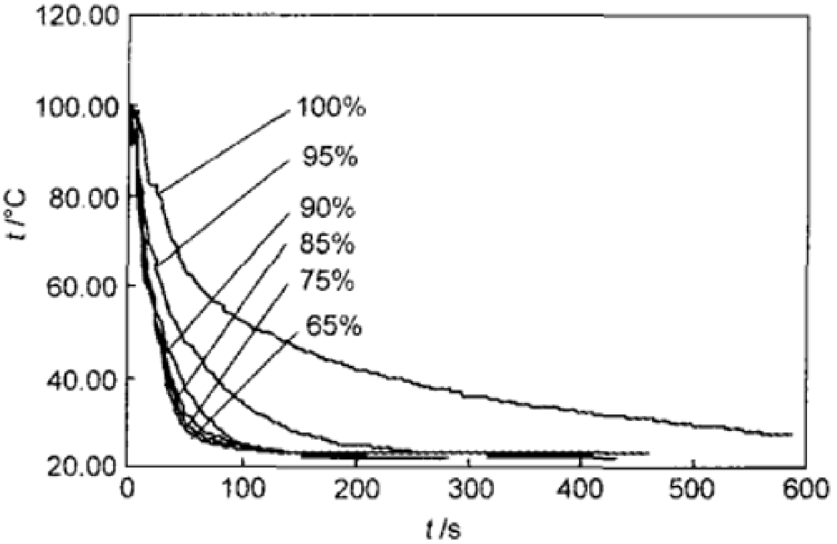

Fig. 5 Paraffin/expanded graphite composites' heat release curves [8].

The impact of paraffin content on the thermal diffusivity of composite phase transition materials is depicted in Figure 6. The figure shows that when the paraffin content of the composites decreases, the thermal diffusivity of the composites significantly rises.

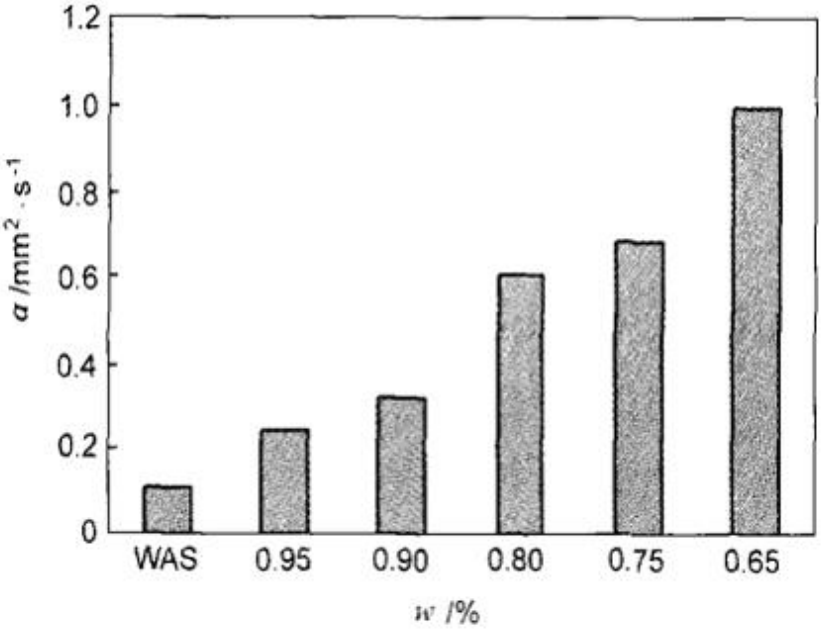

Fig. 6 The effect of PA content on the thermal diffusivity of PA/EG composites [8].

So, we can come into conclusions that: the thermal conductivity of the composite material increases with the increase of the expanded graphite content.

4. Preparation of EG

EG is a porous and loose worm-like substance formed via intercalation, water wash, evaporation, and high temperature expansion of natural graphite flakes. The commonly used oxidation intercalation methods include chemical oxidation method, electrochemical method and improved sulfur-free method; expansion There are also three methods, namely high temperature expansion method, microwave method and low temperature expansion method [10].

After using chemical oxidation method, potassium permanganate as co-oxidant, and microwave method to prepare EG, the adsorption performance of expanded graphite to methylene blue was investigated and adsorption properties [11].

After compounding with mesophase pitch and polyamic acid as binders and densifiers with pre-pressed expanded graphite, the compactness and thermal conductivity of the composites were studied. The findings demonstrate that mesophase pitch on expanded graphite has significantly better density and thermal conductivity than polyamic acid, and that other ingredients are responsible for the composite material's compactness and thermal conductivity [12].

After the graphite nanosheets were prepared by the secondary intercalation method and the corresponding products were characterized by XRD, SEM and TEM, graphite nanosheets were added to lubricating oil to study their tribological properties. The results show that secondary intercalation can reduce the thickness of graphite nanosheets, and the thin graphite nanosheets have the best friction reduction effect [13].

5. Application of Expanded Graphite

Due to the excellent characteristics of EG, the current application of EG is mainly focused on the utilization of its heat storage properties.

5.1. Expanded Graphite/Paraffin Form-Stable Phase Change Solar Collector

The high thermal conductivity EG/PA shaped phase change materials were prepared by melt blending and compression molding. Meanwhile, expanded graphite has an ultra-high light absorptivity in the visible light band, which can effectively absorb and convert solar energy into thermal energy. Shaped PCMs were used in the design of solar collectors, and Fluent was used to simulate the light absorption process of paraffin and EG/PA shaped phase change materials under illumination. The heat transfer behavior of paraffin and EG/PA shaped phase change materials in this solar collector model is then further analyzed.

As shown in the Figure 7, the porous thermal conductive framework of EG/PA enables the composite to absorb heat quickly, and the nanoscale thermal conductivity enhancement of expanded graphite promotes the melting of paraffin. Therefore, under the same time conditions, the liquid phase region and the two-phase haze region of 80% EG/PA shaped phase change materials are much larger than those of paraffin. However, the solid-liquid interface of the EG/PA-shaped phase change materials always maintained a vertically moving state after t = 10 min because the micro-scale pore structure of expanded graphite would greatly weaken the natural convection of phase change materials [14].

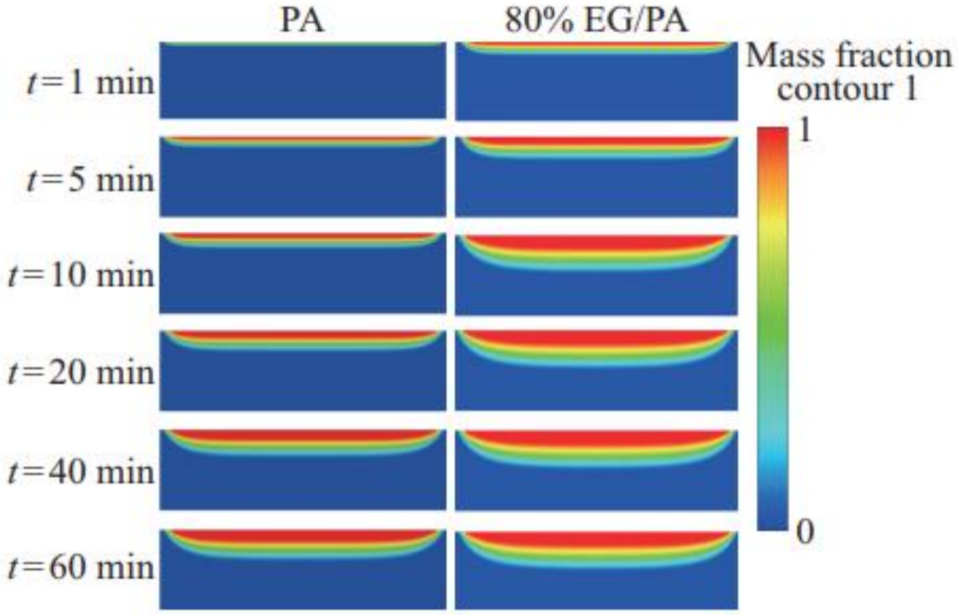

Fig. 7 Contours of the change in solid-liquid volume during the light absorption of paraffin and 80% EG/PA form stable phase change materials [15].

It can be found from the Figure 8 that the temperature increases of EG/PA shape-set phase change composites is larger and the temperature distribution is larger than that of paraffin at the same time. During the light absorption process, the high light absorption and thermal conductivity of EG/PA shaped PCMs can quickly transfer the heat irradiated from the surface to the bottom, making the overall temperature distribution of the system more uniform. Overall, EG/PA shaped phase change materials have better light absorption and heat transfer properties than pure paraffin, and are suitable for solar collector applications.

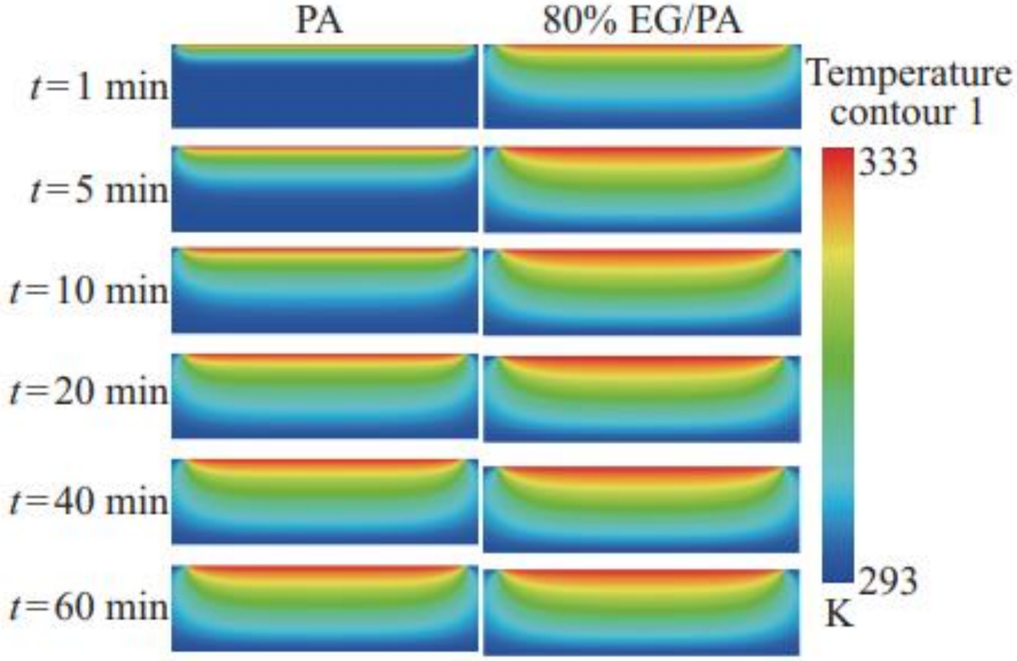

Fig. 8 Temperature field diagram of the light absorption process of paraffin and 80% EG/PA form stable phase change materials [15].

The data simulation results show that the heat transfer of paraffin mainly depends on heat conduction in the initial stage of melting, and the heat convection gradually dominates as time goes on. Under light intensity, the internal heat transfer rate of EG/PA shaped phase change materials is faster than that of paraffin, indicating that the introduction of EG improves the light absorption and thermal conductivity performance of paraffin, which is consistent with the experimental results. Experiments and numerical simulations demonstrate that EG/PA shaped PCMs have excellent heat transferring performance, and the numerical model can more accurately predict the heat and mass transfer behavior of EG/PA shaped PCMs in the process of solar energy storage. Solar thermal collectors based on shaped phase change materials have great potential for solar thermal utilization [15].

5.2. Thermal Storage Defrosting Air Conditioning System

In the air-conditioning system with heating and defrosting, a heat accumulator with good performance is the key, and the reasonable choice of heat accumulating material is undoubtedly the top priority.

The 30% ethylene glycol aqueous solution in the EG/PA phase change composite material and the sensible heat material was selected to compare the heat storage performance of the two.

Considering that the temperature distribution in the heat accumulator is not consistent, and the physical parameters of the heat storage material will also change with the temperature, it is impossible to quantitatively compare and test the heat storage performance of different materials; therefore, an indirect test calculation method is used, that is, the calculation of water The heat released by the bathtub replaces the heat stored in the heat accumulator.

It can be observed from the data that the heat storage capacity and heat storage capacity per unit volume of ethylene glycol and expanded graphite/paraffin are equivalent at the same time; however, the heat release and heat release capacity of expanded graphite/paraffin are far superior to that of ethylene glycol aqueous solution, that is, The heat utilization rate (heat release and storage efficiency) of the expanded graphite/paraffin composite PCMs is quite high, reaching 66.89%, which is precisely due to the good thermal conductivity of expanded graphite. high. These two points are exactly what the thermal storage defrost system requires. From this experiment, it can be seen that expanded graphite/paraffin is more suitable for regenerative defrosting system than ethylene glycol aqueous solution [1].

6. Discussion

However, expanded graphite still has some shortcomings in field applications, including: 1) Expanded graphite has low hardness, low tensile strength and brittleness, and is prone to deformation and breakage; 2) The current preparation process consumes a lot of energy, and a large amount of strong acid wastewater will be generated during the preparation process. It is necessary to further explore green and efficient preparation of expanded graphite. Regeneration method; 3) The adsorption mechanism of some substances is not clear, which affects the large-scale application; 4) The research depth on the preparation, performance and application of expanded graphite and other materials and composite materials is not enough, and most of the researches are laboratory researches, lack of pilot test and practical engineering application examples.

In view of some shortcomings of the above-mentioned expanded graphite, the author believes that in-depth research can be carried out from the following aspects: 1) With the help of modern microscopic characterization methods such as high-performance scanning electron microscopy, the adsorption process and adsorption mechanism of expanded graphite for specific substances are studied and analyzed. The inherent relationship between adsorption and desorption processes, so as to realize the process control of adsorbing specific substances; 2) Further improve the mechanical hardness of expanded graphite, prolong the service life, and reduce the preparation cost of expanded graphite; 3) Further explore the pollutants in the regeneration process. The process and mechanism of migration and transformation, and the search for green and environmentally friendly regeneration methods, etc.

With the in-depth research of expanded graphite and the solution of the above problems, expanded graphite will be widely used in the fields of phase change composite materials, sound absorbing materials, medical materials and so on.

7. Conclusion

The strong adsorption capacity of expanded graphite has been unanimously recognized by scholars from all over the world, and it has shown good application prospects in the environmental protection fields such as the preparation of energy-saving PCMs. In this paper, firstly, the author analyzes the expanded graphite’s microstructure, and the reasons why expanded graphite has great performance as phase change material. Then, the expanded graphite is compared with traditional energy storing phase change materials, which is paraffin, and the performance is analyzed from multiple aspects. After that, this paper reviews the existing preparation methods of expanded graphite and analyzes its application value. Finally, the author researches the current and future applications of expanded graphite, and thinks about its future. In the paper, the research shows that the expanded graphite has excellent performance in energy storage and transformation. Meanwhile, it can combine with paraffin to form PCMs, which can be widely used in many fields. The paper helps to integrate various researches about expanded graphite, offering a systematic overview for expanded graphite. The paper can help to inspire the development of the preparation and interaction of expanded graphite, giving the following researches a way forward. However, there are still many deficiencies in this paper. For example, the lack of literature references makes it hard to compare the expanded graphite with other energy storage materials, so it is hard to determine whether the expanded graphite have obvious advantages over other materials in terms of preparation or performance. So, I think in the future, we can pay more attention on the expanded graphite's preparation, and the interaction between expanded graphite and other materials also needs further studies.

References

[1] Mazman, M., Cabeza, L. F., Mehling, H., Nogues, M., Evliya, H., & Paksoy, H. O. (2009). Utilization of phase change materials in solar domestic hot water systems. Renewable energy, 34(6), 1639-1643.

[2] Kim, S., & Drzal, L. T. (2009). High latent heat storage and high thermal conductive phase change materials using exfoliated graphite nanoplatelets. SOLAR ENERGY MATERIALS AND SOLAR CELLS.

[3] Varol, K. Y. (2008). Energy and exergy analysis of a latent heat storage system with phase change material for a solar collector. Renewable Energy.

[4] Bai, L. M., & Liu, B. Y. (2009). Relations between the saturated absorption and micro-structure of expanded graphite. Journal of Harbin University of Science and Technology.

[5] ZHOU W, DONG J, ZHAO H, et al. Study on the structure of expanded graphite [J]. Carbon Techniques, 2000 (4): 26-30.

[6] Celzard, A., Mareche, J. F., & Furdin, G. (2005). Modelling of exfoliated graphite. Progress in Materials Science, 50(1), p.93-179.

[7] Py, X., Régis Olives, & Mauran, S. (2001). Paraffin/porous-graphite-matrix composite as a high and constant power thermal storage material. International Journal of Heat and Mass Transfer, 44(14), 2727-2737.

[8] Zhao, J. G., Guo, Q. G., Gao, X. Q., Wei, X. H., & Shi, J. L. (2009). The development of paraffin/expanded graphite composite phase change energy storage. New Carbon Materials, 24(2), 5.

[9] Lafdi, K., Mesalhy, O., & Elgafy, A. (2008). Graphite foams infiltrated with phase change materials as alternative materials for space and terrestrial thermal energy storage applications. Carbon, 46(1), 159-168.

[10] Boulton, A., Fornasiero, D., & Ralston, J. (2001). A comparison of methods to selectively suppress iron sulphide flotation.

[11] Yuan, Z. (2005). Effect of inorganic oxidizer on flotability of pyrite and chalcopyrite. Metal Mine.

[12] Qiu, T. S., Luo, X. P., & Fang, X. H. (2001). Study on depression behavior and oxidation mechanism of pyrite. Multipurpose Utilization of Mineral Resources.

[13] Guo, B., Peng, Y., & Espinosa-Gomez, R. (2015). Effects of free cyanide and cuprous cyanide on the flotation of gold and silver bearing pyrite. Minerals Engineering, 71, 194-204.

[14] Feng, D., Nan, J., Feng, Y., Zhang, X., & Yan, Y. (2021). Numerical investigation on improving the heat storage and transfer performance of ceramic /d-mannitol composite phase change materials by bionic graded pores and nanoparticle additives. International Journal of Heat and Mass Transfer, 179, 121748-.

[15] Gao, H., Wang, Z. Y., Zhang, Y. X., Li, Y. H., Bing, N. C., & Yu, W. (2022). Heat Transfer Behavior Analysis of Expanded Graphite/Paraffin Form-Stable Phase Change Solar Collector. Journal of Shanghai Polytechnic University, 39(1), 7.

[16] Li, J. F., Li, X., & Chen, H. Y. (2015). Analysis of heat storage materials selection in thermal storage defrosting air conditioning system. Electrical Appliances.