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Preparation and characterization of an inorganic magnesium chloride/nitrate/graphite composite for low temperature energy storage

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ABSTRACT

In this study, an inorganic mixture of 40 wt% $MgCl_2 \cdot 6H_2O$ and 60 wt% $Mg(NO_3)_2 \cdot 6H_2O$ was impregnated into two types of the expanded graphite (EG): EG flakes and EG matrix. Different methods of preparation usually used in the organic composite preparation, such as direct blending, vacuum impregnation, ultrasonic impregnation and immersion were applied in this work. Considering the samples with EG matrix, it can be concluded that the optimal result of the encapsulation and ΔH ratio can be reached with the experimental time of 1, 3 and 4 h using the vacuum, ultrasound and immersion methods, respectively. Moreover, the percentage of encapsulation increases with the experimental time and with the EG percentage for the EG matrix and for the EG flakes, respectively. Concerning the supercooling phenomena, the results show that the presence of EG reduces the difference between fusion and crystallization temperature for up to 65%, acting as a nucleating agent. The resulting composite samples (CPCM) were proved to have good latent heat and a significant reduction of the supercooling effect, which eliminates the need to use nucleating agents, that are essential for pure PCM of 40 wt% $MgCl_2 \cdot 6H_2O$ and 60 wt% $Mg(NO_3)_2 \cdot 6H_2O$. Moreover, using EG suppresses significantly the melting time which indicates the heat transfer enhance of the mixture. This circumstance could allow to empower the utilization of the mentioned mixture in different fields of thermal energy storage at low temperature.

1. Introduction

Under today's increase of energy demand, using phase change materials is one of the most promising methods for thermal energy storage. The energy is stored as a combination of sensible and latent heat. During the process of phase change, thermal energy is absorbed or released at a constant temperature which allows to control temperature during the thermal energy storage (TES) process.

Inorganic salt hydrates are particularly convenient as materials for low temperature TES. However, one of the main problems of their use is supercooling due to weak nucleating properties. At the melting temperature, nucleation rate in most of the cases is very low. That is why, to reach a reasonable nucleation rate, the solution has to be supercooled and thus the energy is being discharged at much lower temperature. Thereby, a liquid crystallizes much below its melting point. G. Lane [1] indicated that this effect is not acceptable because this reduces the utility of the material, and if too severe, can completely prevent heat recovery. Many factors determine whether an additive will promote nucleation: crystal structure, solubility, and hydrate stability are some of them. Such additives are called nucleating agents. The criteria to choose the nucleating agent was described and reported by different authors [1,2]. Based on these investigations, the best nucleating agents will have similar crystallographic parameters to the material under study, stable structure and stable state under the working conditions. Furthermore, for heterogeneous nucleation the nucleating agent must have lower solubility in water, higher melting point and must bind water in its structure.

Another important problem of inorganic PCM is that of low heat charging and discharging rates due to their low thermal conductivity. So far, the methods carried out to enhance heat transfer in energy storage systems include adding finned configurations, dispersing high conductivity particles (metal, ceramic, graphite, graphene), impregnating a porous matrix (metallic or carbon), and encapsulating the material [3–5]. Among them, expanded graphite (EG) with porous structure was proved to be an excellent heat fortifier to improve heat transfer of materials. EG can be easily obtained from the graphite flakes, reaching a high external heat transfer coefficient, low bulk density, resistance to corrosion and chemical stability [6–8]. Currently,

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Table 1
Literature data for $MgCl_2·6H_2O/Mg(NO_3)_2·6H_2O$ mixtures studied as PCM.

wt% of $MgCl_2·6H_2O$	**T_f, °C**	**ΔH_f, kJ kg^{-1}**	**Reference**
7	78	152.4	[21]
10	64.4–93.2[a]	160.2 (after 80 cycles)	[22]
10	78	76[b]	[21]
20	62–72[a]	70[b]	
30	50–60[a]	87[b]	
40	50–60[a]	97[b]	
eutectic, 38.4 wt%	58.3	136.8	[23]
eutectic, 41.3 wt% (47 mol%)	59.1	145	[24]
eutectic, 41.7 wt%	59.0	132.2	[25]
eutectic, 49.3 wt%	58.2	no data	[26]

[a] Useful temperature range for PCM.
[b] Available specific enthalpy.

Table 2
Summary of CPCM samples preparation methods.

Graphite type				
Expanded graphite matrix Preparation method			Expanded graphite flakes	
Vacuum impregnation	Immersion	Ultrasound	Ultrasound	Direct blending
Experimental time, h			**EG flakes, wt%**	
0.25	1	0.25	5	5
0.5	3	0.5		
1	4	1	10	10
2	7	2		
4	12	3	15	15
7	24	7		

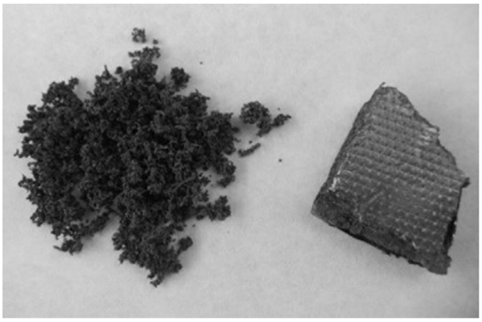

Fig. 1. Expanded graphite flakes (left) and matrix (right).

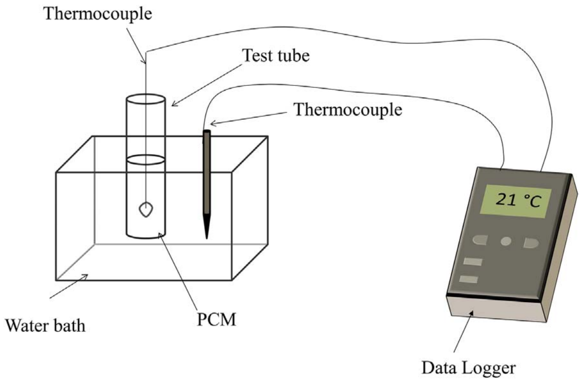

Fig. 2. Scheme of experimental installation to characterize the thermal performance [27].

there are many research works dealing with the preparation of composite materials using EG and PCM. However, almost all of them employ organic PCM [9–18] and there are only two studies that prepare composite with inorganic PCM for medium [19] and high [20] temperature applications.

According to the provided literature, there is still a lack of understanding on developing of the EG/inorganic PCM composite. To help reduce this knowledge gap, this work reports the results of the preparation of composite materials, using an inorganic mixture of 40 wt% $MgCl_2·6H_2O$ and 60 wt% $Mg(NO_3)_2·6H_2O$.

Binary magnesium nitrate/magnesium chloride mixtures with different compositions are well-studied and characterized in literature as phase change materials [21–26]. The literature review indicates that it is possible to obtain a number of mixtures $MgCl_2·6H_2O/Mg(NO_3)_2·6H_2O$ with various fusion temperatures and heat of fusion, some of which are reported as eutectic, and have potential to be used as PCM. Available literature data related to the mixture of $MgCl_2·6H_2O$ and $Mg(NO_3)_2·6H_2O$ is summarized in Table 1.

Two different types of EG (matrix and flakes) to prepare composite EG/PCM (CPCM) samples were utilized in order to improve thermophysical properties of the selected mixture of 40 wt% $MgCl_2·6H_2O$ and 60 wt% $Mg(NO_3)_2·6H_2O$. In this case, expanded graphite meets nearly all requirements for a nucleating agent, therefore, its application for thermophysical properties improvement appears to be reasonable.

In order to provide the best way of preparing the composite EG/inorganic PCM, different methods, usually applied for organic composite, including direct blending, vacuum impregnation, ultrasonic impregnation, and immersion, were studied in this research. The composite samples (CPCM) were proved to have excellent latent heat and significant reduction of the supercooling effect, which eliminates the need of nucleating agents. Moreover, the usage of EG suppresses significantly the melting time which indicates the heat transfer enhance of the mixture of 40 wt% of $MgCl_2·6H_2O$ and 60 wt% of $Mg(NO_3)_2·6H_2O$. All this allows empowering the utilization of the mentioned mixture in different fields of TES at low temperature.

2. Experimental

2.1. Materials

Both magnesium chloride $MgCl_2·6H_2O$ and magnesium nitrate hexahydrate $Mg(NO_3)_2·6H_2O$ were purchased from Merck (99.0%). Expanded graphite (EG) flakes and matrix (Fig. 1) were purchased from SGL Carbon, Germany.

2.2. Sample preparation

Both salts were dried at 40 °C for 12 h with the subsequent placement in a desiccator. Then salts were grinded in a pounder and blended in the desired proportion (40/60 wt%). After that, prepared mixtures were melted, well mixed and then crystallized again to ensure the composition homogeneity throughout the volume.

The CPCM samples were prepared using different techniques, including vacuum impregnation, ultrasound impregnation, immersion and direct blending. Two types of the expanded graphite were used: EG flakes in different weight fractions (5–10–15 wt%) and EG matrix samples of 1 × 1 × 1 cm^3 each. Details of the samples preparation can be found in Table 2.

For vacuum impregnation, the solid salt mixture and the EG matrix samples were placed into the vacuum rotary evaporator (Rotavapor BUCHI R-210). The ultrasound impregnation was performed with an Ultrasonic Elmasonic S 30 (H). For this experiment, the mixture of inorganic salts and EG matrix samples were placed in a beaker inside the ultrasonic bath. For the immersion, EG matrix samples were put into a beaker with the molten salt mixture and were contained in a THERMOSCIENTIFIC FD1500M oven. A number of samples was