

THERMAL ENERGY STORAGE USING CALCIUM CHLORIDE HEXAHYDRATE

Yafei GUO^{1,2,¶}, Daolin GAO^{2,¶}, Xiaoping YU^{1,2}, Chi MA², Shanping CHEN¹ and Tianlong DENG^{2,*}

[¶]These authors contributed equally as Co-First Authors.

¹ College of Chemistry and Materials Science, Northwest University, Xi'an 710127, PR China

² Tianjin Key Laboratory of Marine Resources and Chemistry, College of Chemical Engineering and Materials Science, Tianjin University of Science and Technology, Tianjin, 300457, PR China

*Corresponding author; E-mail: tl Deng@tust.edu.cn, Tel. & Fax +86-22-60602963

Abstract The solid–liquid phase change material named as PCM-Ca with 49.1% in mass water, 49.7% calcium chloride and 1.2% strontium chloride was discovered and outlined in this paper. Differential scanning calorimetry (DSC), simultaneous thermal analyzer, thermal conductivity analyzer, temperature recorder and digital vibrating-tube densimeter were used to characterize the thermal properties of PCM-Ca. The results indicated that PCM-Ca has the phase change temperature at 28.7°C, the latent heats in the process of fusing and crystallizing are 193.4 kJ/kg and 193.0 kJ/kg, the thermal conductivity is 1.2801 W·m⁻¹·K⁻¹ at the melting point, and the density is 1.48×10³ kg/m³ at room temperature. Thirty times repeated thermal cycling tests show excellent thermal stability in terms of latent heat and nucleation temperature, and the maximum deviations of the latent heat and the phase change temperature of PCM-Ca are 0.2% and 2.7%, respectively. Key words: phase change materials, supercooling, calcium chloride hexahydrate

1. Introduction

Phase change materials (PCMs) utilize latent heat to store or release thermal energy and the temperature can stay nearly constant during the process of phase change, which can be effectively solved the imbalance of energy supply and demand in time and space. On the basis of this feature, PCMs can be widely applied in solar energy utilization, heat exchanger, building energy-saving, textiles, electric peak-shaving and so on [1-6].

According to the phase change behavior, PCMs can be generally made up of four categories: solid–solid PCMs, solid–liquid PCMs, solid–gas PCMs and liquid–gas PCMs [7, 8]. According to the listed sequence order, the value of latent heat of PCMs is become bigger and bigger, but the latter two PCMs are never adopted because of the very large volume variations with the occurrence of the gas phase. Compared with solid–solid PCMs, solid–liquid PCMs are most widely application because of its suitable phase change temperature, large latent heat and relatively small volume. In addition, there are also some special PCMs whose phase change properties are laid between solid–solid PCMs and solid–liquid PCMs, which were being named form-stable or shape-stabilized PCMs and composed of working substances and supporting materials [9, 10].

Water is commonly regarded as the most suitable material for thermal energy storage for it is low-cost and high heat capacity. An alternate means for thermal energy storage is to use the latent heat of a reaction. The purpose of this paper is to describe a method for obtaining the advantages of the CaCl_2 and H_2O reaction while eliminate the solid state diffusion problem. The weight percent of calcium chloride in PCM-Ca was optimized and discussed, and the thermal characteristics of PCM-Ca were measured by differential scanning calorimeter, simultaneous thermal analyzer, thermal conductivity analyzer, temperature recorder and digital vibrating-tube densimeter, respectively. In addition, a thirty-run-cycling test was also conducted to investigate the thermal stability of PCM-Ca.

2. Experimental

2.1. Materials

The chemicals used were of analytical reagent: calcium chloride (CaCl_2 , 96% in mass) and magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 98% in mass) were purchased from the Tianjin Guangfu Fine Chemical Research Institute, strontium chloride hexahydrate ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, 99.5% in mass) and barium carbonate (BaCO_3 , 99%) were purchased from the Tianjin Fuchen Chemical Reagents Factory, borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, 99.5% in mass) was purchased from the Tianjin Yingda Rare Chemical Reagents Factory, and barium fluoride (BaF_2 , 98% in mass) was purchased from the Tianjin Beifang Medical Chemical Reagents Factory. Doubly deionized water (DDW) with conductivity less than $1 \times 10^{-4} \text{ S} \cdot \text{m}^{-1}$ and pH 6.60 at room temperature (25°C) was used in this study.

2.2. Analysis methods

The heat of fusion and melting point of PCM-Ca were determined using a differential scanning calorimeter (DSC 200F3, Netzsch Instrument Inc., Germany; Labsys, Setaram Co. Ltd., France) with the scanning rate of $1^\circ\text{C}/\text{min}$ under the nitrogen atmosphere from 0 to 50°C . The exothermic curves were determined using the temperature recorder (Shanghai Yadu Electronic Technology Co. Ltd, VX2103R/C2/U/TP1, China) in the biochemistry incubator (Shanghai Yiheng Scientific Instruments Co. Ltd, LRH-150, China) with the constant temperature of 5°C . Thermal conductivity was metered by thermal conductivity analyzer (DRE-2B, Xiangtan Instrument Co. Ltd., China) with the uncertainty within $\pm 3\%$ in mass. In addition, the density was measured by using a digital vibrating-tube densimeter (DMA 4500, Anton Paar Co. Ltd., Austria) with an uncertainty of less than $\pm 0.01 \text{ mg} \cdot \text{cm}^{-3}$.

2.3. Preparation

Ca-based solution was prepared with calcium chloride and DDW with the mass ratio of 50.7 : 49.3. Calcium chloride and DDW were weighted and adequately diversified in a closed container until dissolved completely. Then strontium chloride hexahydrate was added into the calcium-based solution under stirring and the solution was heated until it was melted completely at 80°C in a water bath (K20-cc-NR, Huber Co. Ltd, Germany). After that, the sample cooled down to room temperature and the target product was obtained.

2.4. Thermal cycle test

In this work, thermal cycle test was used to evaluate thermal stability of PCM-Ca, and the test was performed consecutively up to thirty times of thermal cycling by using a biochemistry incubator

as the heating and cooling facility. Schematic diagram of thermal cycle test apparatus was shown in Fig. 1. Twenty-gram samples were weighted and placed in a test tube (20 mm diameter and 300 mm high), and the thermocouple of temperature recorder was inserted into the center of the test tube, after then they were put in a constant temperature of 5°C biochemistry incubator for solidification. When the exothermic process ended, the temperature of the biochemistry incubator was set up to 35°C and the endothermic process was beginning. While the endothermic process ended, the temperature of the biochemistry incubator was set up to 5°C again to lead the next exothermic process.

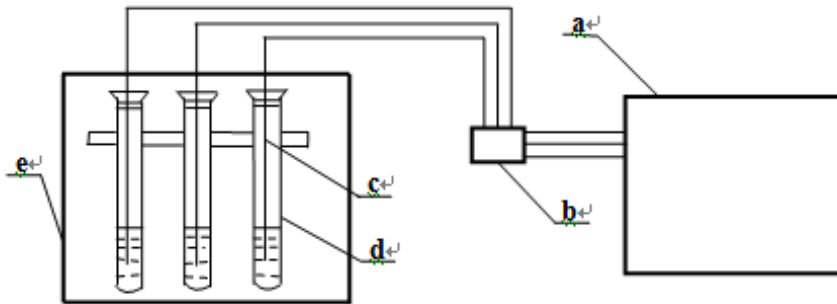


Fig. 1. Schematic diagram of thermal cycle test apparatus: a), computer processor; b), temperature recorder; c), thermocouple; d), test tube; e), biochemistry incubators

3. Results and discussion

3.1. Composition of PCM-Ca

Salt-water system phase diagram of the binary system ($\text{CaCl}_2 + \text{H}_2\text{O}$) at different temperatures is presented in Fig. 2 [11]. It can be seen that curve AB is the solubility curve of ice, and curve BCDEF are the solubility curves of calcium chloride hydrated salts including $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ which was precipitated at different stages with an increasing in the concentration of calcium chloride. When the composition of calcium chloride is more than 50.68% in mass, there is a phenomenon of conversion solution with the increasing of temperature, that is to say, once the composition of calcium chloride is over 50.68% in mass, generated salts are all of unstable hydrated salts. Herein, we choose the composition of calcium chloride at 50.68% as the main research object (named calcium-based solution), in such case the solid state diffusion problem can be eliminated as a reaction. In other words, the calcium-based solution as the main research object was prepared with the mole ratio of calcium chloride and DDW by 1 : 6, and the precipitated hydrated salt was only $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.

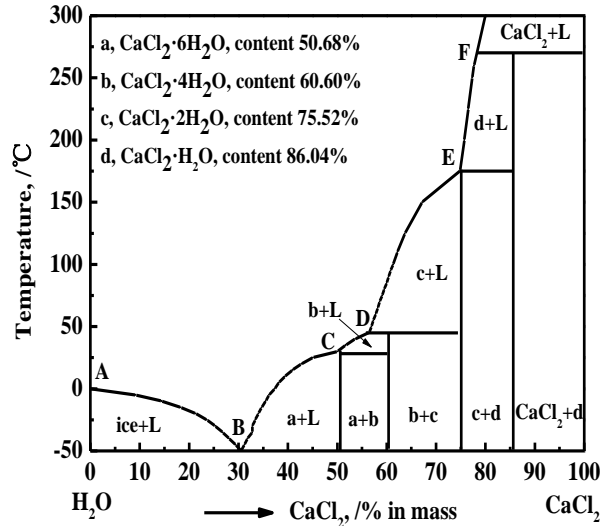


Fig. 2. Phase diagram of the binary system ($\text{CaCl}_2 + \text{H}_2\text{O}$) at different temperatures

3.2. Reduction of the supercooling degree of PCM-Ca

Supercooling is a serious problem associated with almost all inorganic PCMs [12]. In order to solve the problem of supercooling, researchers use many ingenious methods to reach a reasonable rate of nucleation. At present the most frequently-used method is adding a suitable nucleating agent which provides the nucleon for crystal formation [13, 14]. The calcium-based solution as a PCM was found to undergo serious supercooling degree up to 15.5°C below the phase change temperature. According to nucleating agent screening principle of the scope of lattice parameter within 15% in mass [15], borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), barium fluoride (BaF_2), barium carbonate (BaCO_3) and strontium chloride hexahydrate ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) were chosen to act as the candidate nucleating agent of the calcium-base solution, and the results show that $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ was the most effective nucleating agent for the calcium-base solution.

Influence of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ concentration on the supercooling degree of the calcium-base solution was also investigated, and the results was illustrated in Fig. 3. Supercooling degrees of the calcium-base solution after adding 0.0%, 0.5%, 1.0%, 2.0%, 3.0% in mass $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ were 15.5°C , 2.9°C , 1.8°C , 0.4°C and 1.7°C , respectively. With the increasing concentration of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, supercooling degree of the calcium-base solution was decreased sharply, but once the mass percent of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ was more than 2% in mass, supercooling degree was increased instead. Therefore, 2% in mass $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ was selected as the nucleating agent. Hence, the composite PCM named as PCM-Ca was a mixture solution with the mass ratio of DDW : CaCl_2 : $\text{SrCl}_2 = 49.1 : 49.7 : 1.2$. In addition, cooling curve of PCM-Ca under the condition of room temperature was also measured and presented in Fig. 4. It can be seen from Fig. 4 that the degree of supercooling in the cooling process of PCM-Ca is 1.2°C , the phase change temperature is 28.8°C and the exothermic lasting time is more than 90 minutes. In other word, the latent heat of PCM-Ca was large for thermal energy storage.

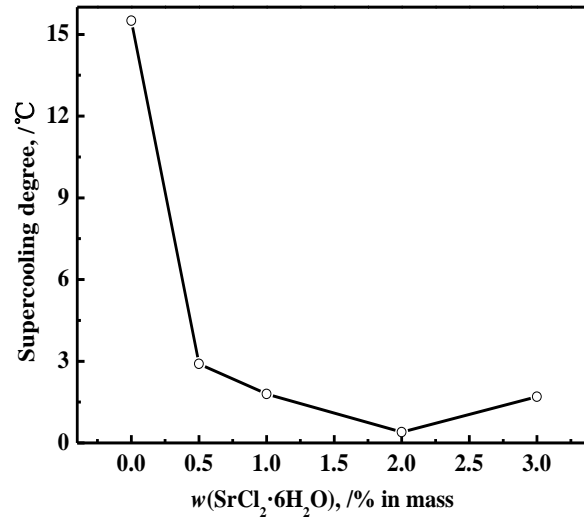


Fig. 3. Effect of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ concentration on the supercooling degree of PCM-Ca

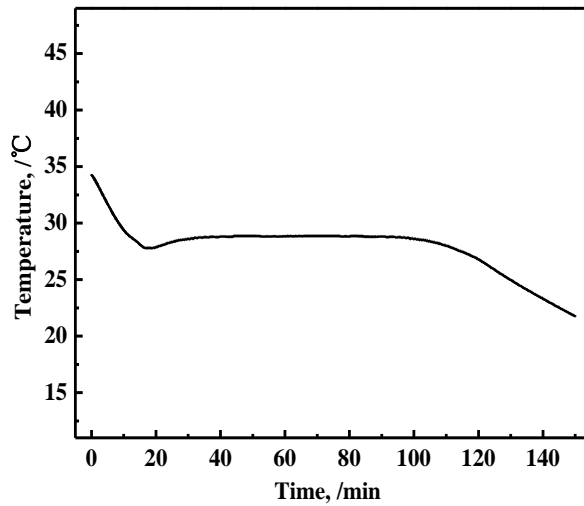


Fig. 4. Cooling curve of PCM-Ca

3.3. DSC analysis

Fig. 5 presents DSC curve of PCM-Ca in the process of heating and cooling. It can be seen that the melting and crystallizing temperature of PCM-Ca are 28.8°C and 27.9°C , the latent heat of phase change in fusing and crystallizing process are 193.4 kJ/kg and 193.0 kJ/kg , respectively. Almost all of the total absorbed thermal energy in the process of melting was released in the process of crystallizing. From the DSC thermal analysis results, it can be suggested that the phase change temperature and the latent heat of fusion of PCM-Ca make it potential material for thermal energy storage.

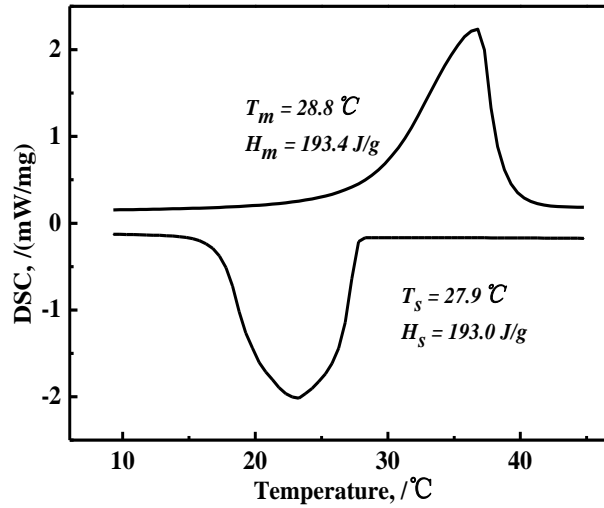


Fig. 5. DSC curve of PCM-Ca

3.4. Thermal conductivity and density analysis

One of the key measure gauge for the rates of heat storage and release in the process of fusing and crystallizing is thermal conductivity. A low thermal conductivity not only reduced the rate of endothermic and exothermic but also restricted it applications. To increase thermal conductivity, some additives such as Fe_3O_4 nanoparticles can be added [16]. In this studied, thermal conductivity of PCM-Ca was measured by a thermal conductivity analyzer, and thermal conductivities of PCM-Ca from 15°C to 40°C were shown in Fig. 6. Thermal conductivity of PCM-Ca in the solid state was slowly increasing from 0.7453 W/m·K at 15°C to 0.9327 W/m·K at 28°C and in the liquid state is approximate to 0.6311 W·m⁻¹·K⁻¹, but the thermal conductivity is significantly increases to 1.3637 W·m⁻¹·K⁻¹ in the phase change process. That is to say, PCM-Ca with a high thermal conductivity is suitable to be used as a PCM.

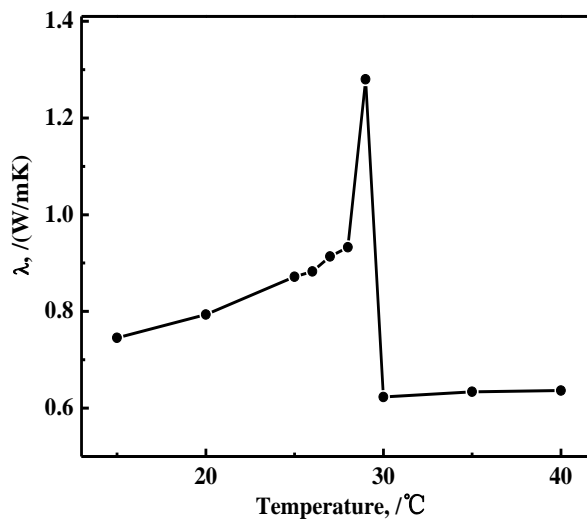


Fig. 6. Thermal conductivity of PCM-Ca at different temperatures

During the process of experiment, empirical observation of the volume change of PCM-Ca from solid to liquid is very small. Hence, the density of PCM-Ca was measured only at room temperature with the value of $1.48 \times 10^3 \text{ kg/m}^3$. In other word, the heat of fusion of PCM-Ca is $2.86 \times 10^5 \text{ kJ/m}^3$, which was large latent heat as a PCM for thermal energy storage.

3.5. Thermal stability of PCM-Ca

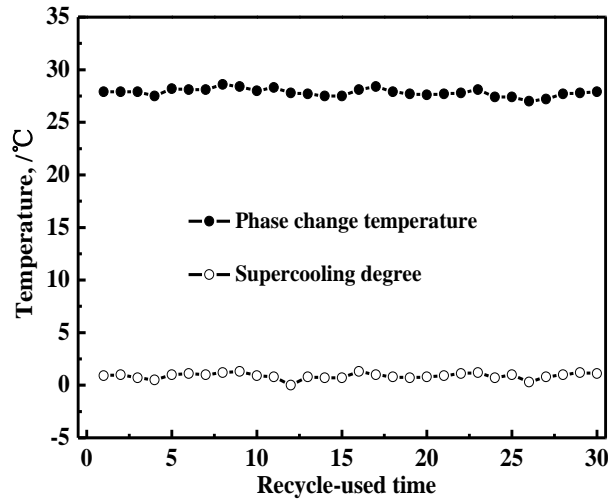


Fig. 7. Repeatability properties tests for PCM-Ca

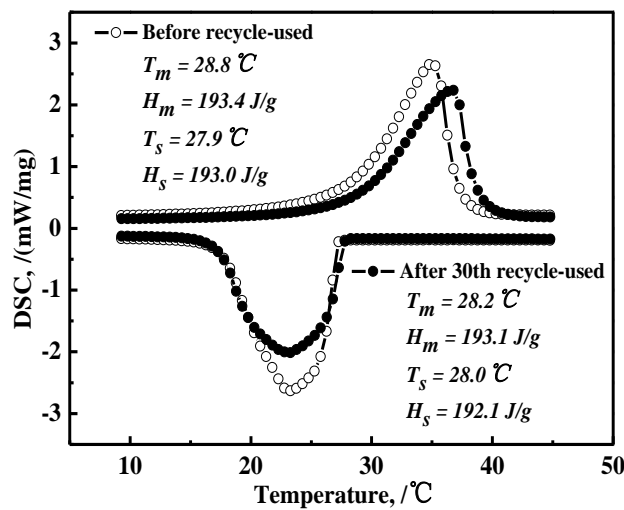


Fig. 8. Comparison of DSC curve of PCM-Ca before and after 30 times recycle-used

In this work, thermal stability of PCM-Ca was monitored through thermal cycle test. Depending on the experimental data, repeatability properties tests of PCM-Ca and comparison of DSC curves of PCM-Ca before and after 30 times recycle-used are presented in Figs. 7 and 8. From Figs. 7 and 8, it shows that PCM-Ca has a good thermal stability, i.e. the highest and lowest temperatures are 28.6°C and 27.0°C , and the supercooling degrees are within the range of $0\sim 1.5^\circ\text{C}$. Before recycle-used, absorbed heat, energy released, melting and crystallizing temperature of PCM-Ca are 193.4 kJ/kg , 193.0 kJ/kg , 28.8°C and 27.9°C , respectively. While after 30 times recycle-used, absorbed heat, energy released melting and crystallizing temperature of PCM-Ca are 193.1 kJ/kg , 192.1 kJ/kg , 28.2°C and

28.0°C, respectively. Within thirty times repeated melting and crystallizing recycles, the maximum deviations of melting temperature and latent heat of PCM-Ca are 2.7% and 0.2%, respectively.

3.6. Advantages of PCM-Ca

Industrial product of calcium chloride is one of abundant raw materials on the industrial chemical market and its price is less than 0.3 US\$/Kg. Hence, the price of PCM-Ca with the mass ratio of DDW: CaCl₂: SrCl₂ = 49.1 : 49.7 : 1.2 will be cheaper. From a cost point of view, PCM-Ca as a PCM for thermal energy storage has the most appealing advantages.

So far as we know, calcium chloride is one of non-toxic chemical materials, and the toxicity of strontium chloride hexahydrate is rather small. That is to say, the toxicity of calcium chloride and strontium chloride hexahydrate are very low and they are almost harmless. In addition, PCM-Ca is nearly closed to neutral and has no flammability. From these facts, there is no legal problem with using the composite substances including calcium chloride and strontium chloride hexahydrate as a PCM for thermal energy storage. Although the investigation of corrosion has not been conducted yet, empirical observation on the inner surface of the stainless steel thermocouple of temperature recorder used for determining cooling curve indicated that typical stainless-steels are not damaged by these substances. In practice, it would be better for PCM-Ca to be encapsulated in a durable container. Hence, the authors think that the testing methods and procedures described above are useful and PCM-Ca can be as an ideal PCM for thermal energy storage.

4. Conclusion

A novel solid–liquid PCM named as PCM-Ca was prepared with the mass ratio of DDW : CaCl₂ : SrCl₂ = 49.1 : 49.7 : 1.2. The results show that phase change temperature of PCM-Ca was 28.7°C, latent heats in the process of fusing and crystallizing are 193.4 kJ/kg and 193.0 kJ/kg, thermal conductivity is 1.2801 W·m⁻¹·K⁻¹ at phase change temperature, and the value of density is 1.48×10³ kg/m³ under room temperature environment. Thirty times repeated thermal cycling tests show that PCM-Ca has a good thermal stability in terms of latent heat and nucleation temperature, and the maximum deviations of latent heat and melting temperature are 0.2% and 2.7%, respectively. In addition, low cost is also one of the advantages for PCM-Ca because there is no legal restriction with using PCM-Ca for thermal energy storage.

Acknowledgment

Financial support from the National Natural Science Foundation of China (U1407113, U1607123 and U1607129), the Training Program for Yangtze Scholars and Innovative Research Team in University of China (2013-373), the Innovative Research Team of Tianjin Municipal Education Commission of China (TD12-5004) and the Chinese Postdoctoral Science Foundation (2016M592827 and 2016M592828) is acknowledged.

References

- [1] Ledesma, J. T., *et al.*, Numerical Simulation of the Solar Thermal Energy Storage System for Domestic Hot Water Supply Located in South Spain, *Thermal Science*, 17 (2013), 2, pp. 431-442
- [2] Jovanovic, D. B., *et al.*, Efficacy of a Novel Phase Change Material for Microclimate Body

- Cooling, *Thermal Science*, 18 (2014), 2, pp. 657-665
- [3] Medrano, M., Experimental Evaluation of Commercial Heat Exchangers for Use as PCM Thermal Storage Systems, *Appl. Energy*, 86 (2009), 10, pp. 2047-2055
- [4] Karaipekli, A., Capric–myristic Acid/Expanded Perlite Composite as Form-stable Phase Change Material for Latent Heat Thermal Energy Storage, *Renewable Energy*, 33 (2008), 12, pp. 2599-26055
- [5] Mondal, S., Phase Change Materials for Smart Textiles–An overview, *Applied Thermal Engineering*, 28 (2008), 11-12, pp. 1536-1550
- [6] Mohammed, M. F., *et al.*, A Review on Phase Change Energy Storage: Materials and Applications, *Energy Conversion and Management*, 45 (2004), 9-10, pp. 1597-1615
- [7] Gao, D. L., *et al.*, Energy Storage: Preparations and Physicochemical Properties of Solid-liquid Phase Change Materials for Thermal Energy Storage, in: *Materials and Processes for Energy: Communicating Current Research and Technological Developments* (ed. A. Méndez-Vilas), Formatex Research Center, Spain, 2013, pp. 32-44
- [8] Dincer, I., *et al.*, Thermal Energy Storage: Systems and Applications, John Wiley & Sons, Britain, 2002
- [9] Lia, W. D., *et al.*, Preparation and Characterization of Cross-linking PEG/MDI/PE Copolymer as Solid–solid Phase Change Heat Storage Material, *Solar Energy Materials and Solar Cells*, 91 (2007), 9, pp. 764-768
- [10] Fang, G. Y., *et al.*, Preparation, Thermal Properties and Applications of Shape-stabilized Thermal Energy Storage Materials, *Renewable and Sustainable Energy Reviews*, 40 (2014), pp. 237-259
- [11] Deng, T. L., *et al.*, Salt-water System Phase Diagrams and Applications, Chemical Industry Press, China, 2013
- [12] Zhang, R. Y., Phase Change Materials and Phase Change Energy Storage Technology, Science Press, China, 2009
- [13] Tang, X. F., *et al.*, Fabrication and characterization of microencapsulated phase change material with low supercooling for thermal energy storage, *Energy*, 68 (2014), pp. 160-166
- [14] Jamekhorshid, A., *et al.*, A review of microencapsulation methods of phase change materials (PCMs) as a thermal energy storage (TES) medium, *Renewable and Sustainable Energy Reviews*, 31 (2014), pp. 531-542
- [15] Kima, S., *et al.*, High Latent Heat Storage and High Thermal Conductive Phase Change Materials Using Exfoliated Graphite Nanoplatelets, *Solar Energy Materials and Solar Cells*, 93 (2009), 1, pp. 136-142
- [16] Sahan, N., *et al.*, Improving thermal conductivity phase change materials – A study of paraffin nanomagnetite composites, *Solar Energy Materials and Solar Cells*, 137 (2015), pp. 61-67

Submitted: 19.01.2017.

Revised: 29.04.2017.

Accepted: 3.05.2017.