Multiphase Change Materials for Energy Storage Application in Buildings

J. Darkwa[1]
The University of Nottingham, Nottingham, NG7 2RD UK

W. Su[2]
Qilu University of Technology, Jinan, China

Experimental study has been carried out towards the development of a multiphase change material (MCM) by combining two fabricated microencapsulated phase change materials (MEPCM-oct and MEPCM-eic) samples. The study also covered the characterization of the developed samples for their thermal properties. For the purpose of validation the thermal properties of the developed MCM sample were compared with that of the core components. The developed MCM sample achieved a combined energy storage capacity of 186 kJ/kg with two melting temperatures of 23.4ºC and 34.5ºC. Even though the two melting temperatures of the MCM were slightly reduced by 0.18℃ and 0.48℃ in comparison with the MEPCM-oct and MEPCM-eic respectively, their mean energy storage capacities were in perfect agreement. The study has therefore shown that it is possible to overcome some of the scientific barriers towards the development of multiphase change materials but further investigations are needed to enhance overall thermal response.

[1] Professor of Energy Storage Technologies, Department of Architecture and Built Environment, University Park, University of Nottingham, UK, and Member of AIAA.
[2] Lecturer, School of Mechanical & Automotive Engineering, Qilu University of Technology.

I. Introduction

ENERGY consumption in the building sector still represents the highest proportion of energy usage in most developed and developing countries. According to recent publication, the building sector is responsible for approximately 40% of final global energy consumption and CO_2 emissions [1].

In the UK for instance, buildings account for about 43% of the country's total energy consumption with heating and hot water representing the bulk proportion [2-3]. Innovation in the building sector therefore represents a significant opportunity to help minimise energy consumption as well as reducing global greenhouse gas emissions targets. One promising and innovative technology that could make positive contribution and improve the thermal performance of existing and future building stock is through the use of phase change materials (PCMs). These materials such as alkenes (paraffin waxes) can be used for the passive/active storage and release of heat energy in buildings as they have relatively high energy storage capacities at constant temperatures. There are a number of past investigations which show that energy consumption in buildings could be reduced by integrating PCMs into building fabrics and ventilation systems [4-10]. For instance studies carried out by Darkwa [11] and Zhou et. al [12] showed that as much as 30% reduction in heating and cooling loads in buildings could be achieved with integrated PCM drywall systems. Other researchers [13-14] also demonstrated that PCM could be integrated into hot water storage system and used for shifting peak load from space conditioning and water heating systems.

However, there are some basic and applied research issues which need to be addressed before competitive scientific, technical and economic edge can be achieved. For instance commercially available microencapsulated PCMs can only function at fixed melting temperatures and unable to be tuned to other melting temperatures of say from 40^{o}C to 20^{o}C and vice versa. This means that in an area where both heating and cooling are required throughout the year, two separate PCMs would have to be applied to provide that dual function. This approach makes the materials thermally ineffective due to non-flexibility in their melting temperatures during energy storage/discharge process. The PCMs could also account for about 30% - 45% of the finished product in terms of content and cost which have direct impact on the profitability of the product. Above all they possess relatively low thermal conductivities and do display poor thermal response factor when combined with other construction materials [15-17]. Even though other investigations [18-23] have uncovered different methods and techniques for enhancing and developing high conductivity composite microencapsulated phase change materials they still possess single phase transition

temperatures. Other binary mixtures of PCMs have also been investigated but were unable to achieve the inherent functional and desirable variable temperature characteristics [24-27]. These limitations are barriers to the wider application of current PCMs. This study was therefore focused on developing a multiphase change material (MCM) capable of operating at two different melting temperatures.

II. Development of a Multiphase Change Material (MCM)

As summarised in Table 1, paraffins (n-octadecane and n-eicosane) were selected as the core materials for the fabrication of the MEPCMs. Melamine-formaldehyde solution was also selected and used as shell monomers and nano-silicon dioxide hydrosol as emulsifier. The other associated materials were ammonium chloride, sodium hydroxide and citric acid which were used as nucleating agents for modifying the pH values.

Table 1: Composition of MEPCMs

Paraffin	Melamine (g)	Formaldehyde (g)	Nano SiO_2 hydrosol (g)
10g n-octadecane	2.0	3.2	1.2
10g n-eicosane	2.0	3.2	1.2

The fabrication process was based on in-situ polymerization method as well as other processes covering synthesis of prepolymer solution, preparation of oil-in-water (O/W) emulsion and formation of shells. The pre-polymer melamine formaldehyde (PMF) solution initially was prepared by mixing melamine (2.0g) and formaldehyde (3.2g) with 10ml deionised water. The pH value of the solution was then controlled within a range of 8.5 - 9 and at a temperature of 65°C whilst stirring at 500 rpm until it became homogeneous.

The next stage covered the preparation of oil/water (O/W) emulsion by mixing 10g of each paraffin material with 90g of water and 1.2g of nano-silicon dioxide hydrosol. The mixture was then stirred at a speed of 7000 rpm for 10 minutes at a temperature of 60°C to establish a uniform and stable mixture. A certain amount of nucleating agent was then added to the O/W emulsion to reduce the pH value and to enable the PCM capsules to be cross linked with the

PMF polymer. The emulsion was then stirred at a reduced speed of 300-500 rpm at a temperature of 60°C for 4 hours. This enabled the pH value to be adjusted to 9 and to terminate the cross linking reaction process.

In order to produce the MCM, equal proportion of the manufactured microencapsulated PCM samples (n-octadecane and n-eicosane) were mixed together with deionised water at a stirring speed of 200 rpm for 10 minutes to achieve a uniform particle size distribution. The mixture was finally washed and dried in an oven at a temperature of 60°C for 20 hours to obtain the MCM sample.

III. Results and Analysis

A. Energy storage and melting temperature

A differential scanning calorimetric (DSC) (EXSTAR SII DSC6220, SII Nanotechnology Inc.) equipment was used in determining the enthalpies of fusion and melting temperature of the MEPCM samples in accordance with ISO 11357 Standards under the dynamic testing method. They were tested at atmospheric pressure and at a heating rate of 2 °C /min from 5 °C to 50 °C. As shown in Fig. 1, the energy storage capacity of the MEPCM-oct and MEPCM-eic were obtained as 179 kJ/kg and 194 kJ/kg respectively with corresponding melting temperatures of 23.54℃ and 34.99℃. In Fig 2, the developed MCM sample achieved a combined energy storage capacity of 186 kJ/kg with two melting temperatures of 23.4ºC and 34.5ºC.

By comparing these sets of results, it can be seen that even though the melting points of the MCM sample were slightly reduced by 0.18℃ and 0.48℃ respectively, its energy storage capacity was in perfect agreement with the mean value of the MEPCM-oct and MEPCM-eic.

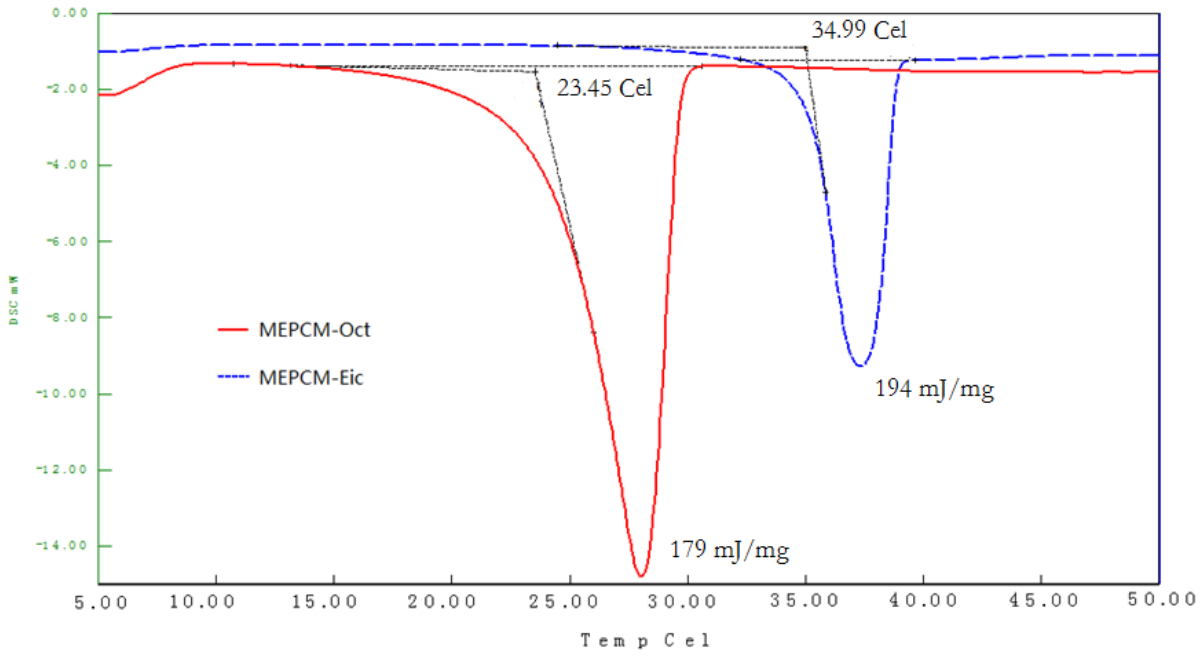

Figure 1: DSC profiles of MEPCM samples

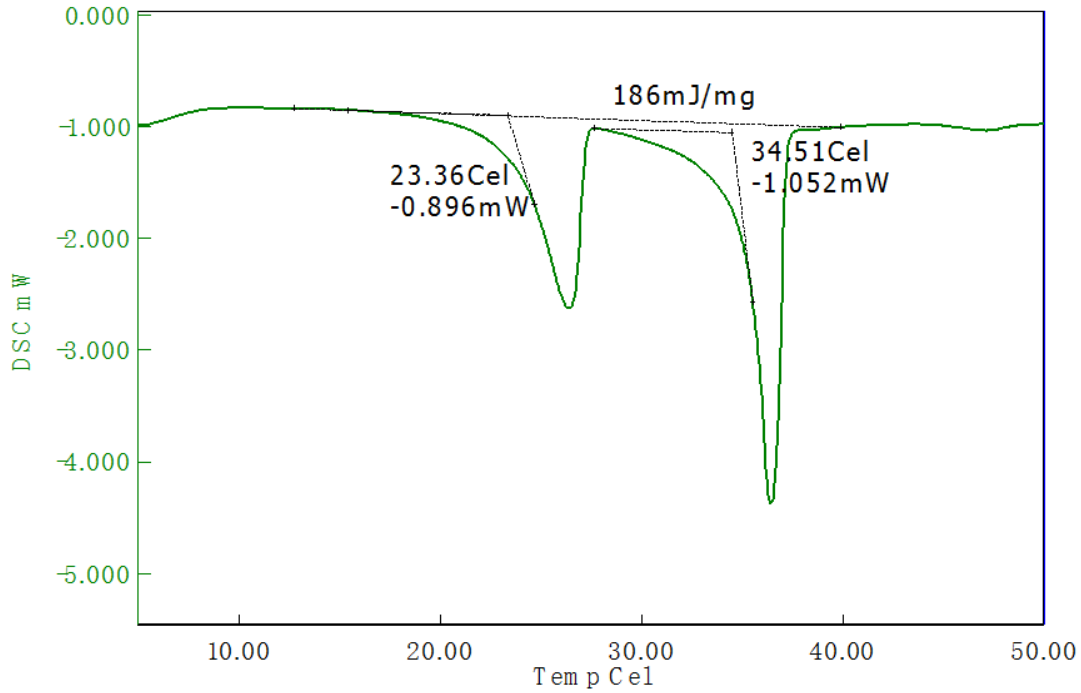

Figure 2: DSC profile of MCM sample

B. Thermogravimetric analysis (TGA)

Thermogravimetric analysis were conducted on the samples in order to examine the physical and thermal resilience of the samples in relation to their molecular structure.These tests were was carried out under nitrogen gas protection covering a heating range of 50 °C to 500 °C and at a heating rate of 10 °C /min. Fig. 3 represents the characteristic TG curves for the MEPCMs which show that the MEPCM-oct and MEPCM-eic achieved thermal stability up to 207.6°C and 211.9°C respectively. In Fig. 4, the MCM sample also displayed relatively good thermal stability behaviour up to about 197 ℃ which satisfies the environmental requirements for most applications in buildings.

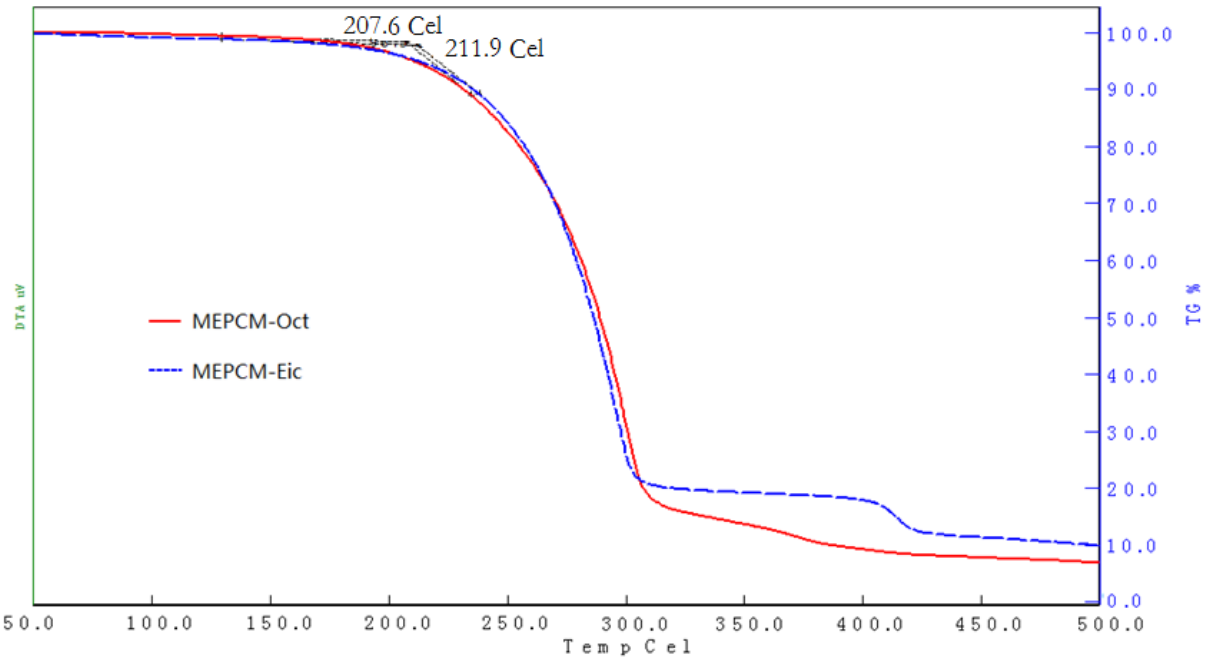

Figure 3: TG curves for MEPCMs

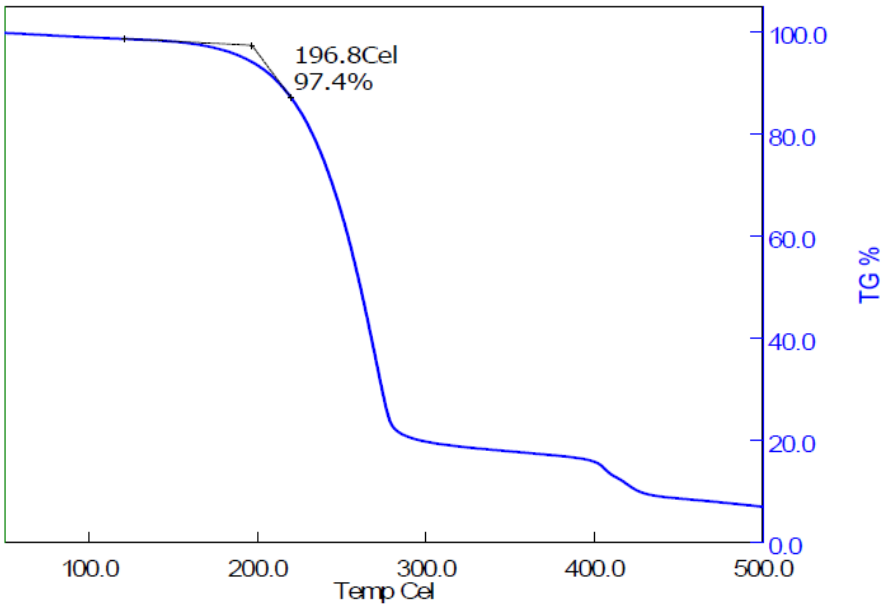

Figure 4: TG curve for MCM sample

C. Scanning Electron Microscopy (SEM) analysis

The SEM analysis was conducted in order to examine the external morphology (texture) and crystalline structure of the particles making up the samples. Figs. 5a and 5b are the results for the MEPCM samples. It can be seen that, most of the particles did achieve fairly good structural integrity of the shell materials after encapsulation without obvious sign of degradation. Similarly in Fig. 6, the structure and morphology of the MCM particles were good and physically well bonded. This shows that the MCM sample should be able to operate at the two specified temperatures for multiphase change processes.

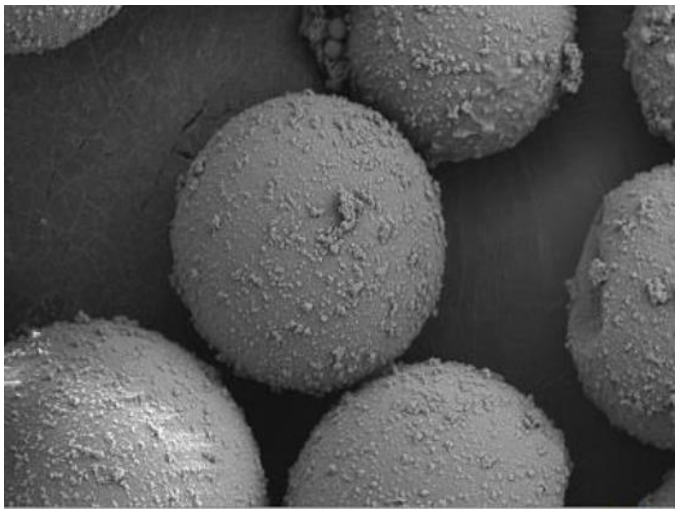

Figure 5a: SEM image of MEPCM-oct

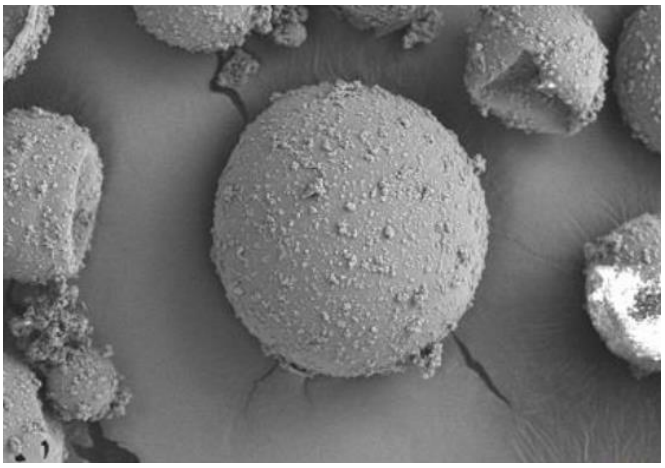

Figure 5b: SEM image of MEPCM-eic

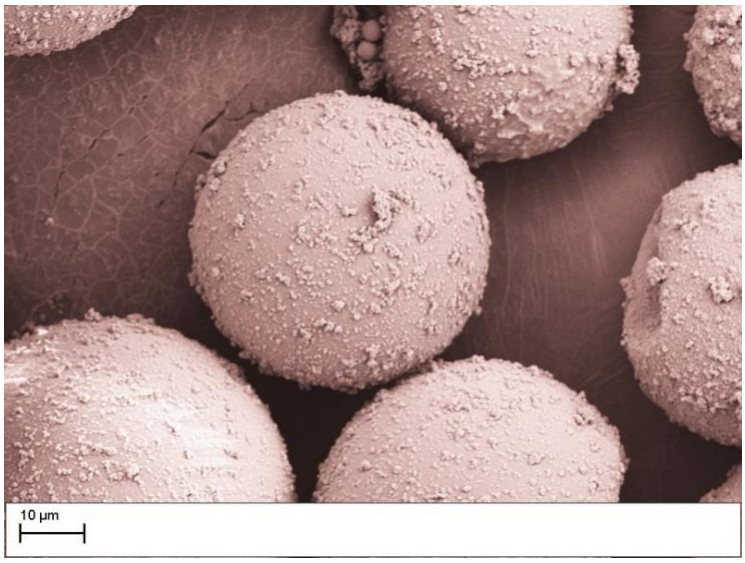

Figure 6: SEM image of MCM sample

IV. Conclusion

The study has shown that some of the scientific and technical barriers associated with the development of multiphase change materials can be overcome. For instance thermal analysis of the test results clearly shows that it is possible to achieve multiple phase transitional temperatures with relatively good energy storage capacity and thermal stability. The findings may be therefore summarised as follows:

- The maximum combined energy storage capacity for the MCM sample was obtained as 186 kJ/kg as compared with 179 kJ/kg and 194 kJ/kg for the individual MEPCM-oct and MEPCM-eic respectively. The energy storage capacity of the MCM was therefore in perfect agreement with the mean value of the MEPCMs
- The two melting points for the MCM were 23.4^{o}C and 34.5^{o}C as against 23.54℃ for MEPCM-oct and 34.99℃ for MEPCM-eic.
- The MCM sample displayed relatively good thermal stability behaviour up to about 197 ℃ as against 207.6°C and 211.9°C for MEPCM-oct and MEPCM-eic respectively.

It is believed that the technology could significantly reduce the material content, cost, size and ultimately payback period of integrated MCM components since they should be able to perform multiple functions. There is however the need to develop it further to enhance its thermal conductivity.

References

[1] Nejat, P., et al., "A global review of energy consumption, CO2 emissions and policy in the residential sector (with an overview of the top ten CO2 emitting countries)," *Renewable and Sustainable Energy Reviews*, 2015. 43(0): p. 843-862.

[2] https://www.gov.uk/government/publications/2010-to-2015-government-policy-energy-efficiency-in-buildings/2010-to-2015-government-policy-energy-efficiency-in-buildings, 15 April 2016

[3] Soares, N., Costa, J.J., Gaspar, A.R., Santos, P., "Review of passive PCM latent heat thermal energy storage systems towards buildings' energy efficiency," *Energy and Buildings*, 2013, *59, 82-103*

[4] Bogdan M., Diaconua, M., Cruceru, M., "Novel concept of composite phase change material wall system for year-round thermal energy savings," *Energy and Buildings* 34 (2010) 560-572

[5] Pasupathy A., Velraj R., "Effect of double layer phase change material in building roof for year round thermal management," *Energy and Buildings*, 40, 2008, 193–203

[6] Shilei, F. Guohui, Z. Neng, D. Li, "Experimental study and evaluation of latent heat storage in phase change materials wallboards," *Energy and Buildings*, 39, 2007, 1088–1091.

[7] Darkwa J., O'Callaghan PW., "Simulation of phase change drywalls in a passive solar building," *Applied Thermal Engineering*, 2006, 26(8-9), 853-858.

[8] Darkwa J.; "Mathematical evaluation of a buried phase change concrete cooling system for buildings," *Applied Energy Journal*, Vol. 86, 2009, pp 706-711

[9] Tung-Chai, L., and Chi-Sun, P., "Use of phase change materials for thermal energy storage in concrete: An overview," *Construction and Building Materials*, 46, 2013, 55–62

[10] Reza, B., John, J., Chen, J., Young, B.R., and Farid., M.M., "Application of PCM energy storage in combination with night ventilation for space cooling", *Applied Energy*, 158, 2015, 412–421

[11] Darkwa J., Zhou T., "Enhanced laminated composite phase change material for energy storage", *Energy Conversion and Management*, 52, 2011, 810–815

[12] Zhou, T., Darkwa, J. and Kokogiannakis, G., "Thermal evaluation of laminated composite phase change material gypsum board under dynamic conditions", *Renewable Energy*, 2015, 78, 448-456

[13] Anuar Sharif, M.K, Al-Abidi, A.A., Ma, S., K., Sopian, Ruslan, M.H., Sulaiman, M.Y., and Rosli, M.A.M., "Review of the application of phase change material for heating and domestic hot water systems", *Renewable and Sustainable Energy Reviews*, 42, 2015, 557–568

[14] Najafiana A., Haghighata F., Moreau A., "Integration of PCM in domestic hot water tanks: Optimization for shifting peak demand", *Energy and Buildings*, 2015, 106, 59–64

[15] Koschenz M. and Lehmann B., "Development of a thermally activated ceiling panel with PCM for application in lightweight and retrofitted buildings", *Energy and Buildings*, 2004, 36[6], 567-578.

[16] Ana Vaz Sáa,, Miguel Azenhab, Hipólito de Sousaa, António Samagaio, Thermal enhancement of plastering mortars with Phase Change Materials: Experimental and numerical approach, Energy and Buildings 49 (2012) 16–27

[17] Darkwa, K., and Kim, J.S., "Heat transfer in neuron-composite laminated phase change drywall", *Journal of Power and Energy*, Proc. Instn. Mech Engrs., 2004, 218, Part A, 83-88

[18] Darkwa K., and Kim J.S., "Dynamics of energy storage in phase change drywall systems", *International Journal of Energy Research*, 2004, 228, 22-32.

[19] Darkwa, K., Kim, J-S., "Thermal Analysis of Composite Phase Change Drywall Systems", *Journal of Solar Energy Engineering*, 2005, 127, 352-356

[20] Darkwa, J., Su O., and Zhou, T., "Development of Non-Deform Micro-Encapsulated Phase Change Energy Storage Tablets" *Applied Energy*, 2012, 98, 441-447

[21] Darkwa, J., Su, W., and Zhou, T., "Evaluation of Thermal Energy Dynamics in a Compacted High-Conductivity Phase-Change Material" *Journal of Thermophysics and Heat Transfer*, 2015, 24-34

[22] Wu, Y., Wang, T., "Hydrated salts/expanded graphite composite with high thermal conductivity as a shape-stabilized phase change material for thermal energy storage", *Energy Conversion and Management*, 101, 2015, 164–171.

[23] Ziye, L., Chen, J., Xu, T., Fang, X., Gao, X., and Zhang, Z., "Thermal conductivity of an organic phase change material/expanded graphite composite across the phase change temperature range and a novel thermal conductivity model", *Energy Conversion and Management*, 102 (2015) 202–208

[24] He, B., Mari, G.E., and Setterwall, F., "Tetradecane and hexadecane binary mixtures as phase change materials (PCMs) for cool storage in district cooling systems", *Energy.*, 1999;24:1015-28.

[25] He, B., Martin, V, Setterwall, F., "Phase transition temperature ranges and storage density of paraffin wax phase change materials", *Energy*, 2004;29:1785-804

[26] Ma, Y., Chu, X., Li, W., Tang, G,. "Preparation and characterization of poly(methyl methacrylate-co-divinylbenzene) microcapsules containing phase change temperature adjustable binary core materials", *Solar Energy*, 2012;86:2056-66.

[27] Ma, Y., Sun, S., Li, J., Tang, G., "Preparation and thermal reliabilities of microencapsulated phase change materials with binary cores and acrylate-based polymer shells", *Thermochimica Acta*, 2014.