

Microencapsulation of Butyl Palmitate in Polystyrene-co-Methyl Methacrylate Shell for Thermal Energy Storage Application

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ABSTRACT: *Micro Encapsulated Phase Change Materials (MEPCM) are green materials which could be used for thermal energy saving applications in buildings as a non-pollutant method for environmental. PCMs could passively reduce peak cooling loads in hot seasons because of their high energy storage capacities at a constant temperature. Purpose of this paper is manufacturing Microencapsulated PCM (MPCM) products for use in gypsum wall applications, with the aim of expanding in use from butyl palmitate in polystyrene-co-methyl methacrylate shells. This type of micro-encapsules synthesis had not been previously described in the literature, nor patented. PCM (butyl palmitate) can be encapsulated by these processes and in the form of core-shell structure with the use of different stirring rates and hybridized suspension agents. SEM micrographs of microencapsulated MPCMs show that spherical microcapsules were obtained with a narrow PSD (0-150 μm) with a stirring rate of 800 rpm and hybridized suspension agent (TCP). About, 65 % (wt.) of MPCMs was butyl palmitate with 70.6 J/g of latent heat energy which indicates the applicability of this synthesis MPCMs for thermal energy storage in gypsum walls. Our synthesis results on the basis of suspension like polymerization process show good encapsulation efficiency with proper thermal energy storage capacity in gypsum walls.*

KEYWORDS: *Phase change materials; Microencapsulation; Suspension-like; Styrene; Methyl methacrylate.*

INTRODUCTION

In our world, energy is one of the economic parameters of social activity. Then, improved and clean methods of storing renewable energy need to be found [1-2].

To store thermal energy the Phase Change Materials (PCMs) are widely used because of their high latent heat of fusion [3]. Phase change materials are substances

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that can absorb, store and release energy on a change of phase. Furthermore, for the house application target, the temperature range of PCMs (melting/solidification) should be convenient. Also, the phase changing process should be reversible and the materials need to be stable. During the phase change, the materials remain at a closely constant temperature [4-7].

The uses of PCMs for thermal energy storage require some forms of containment to prevent leakage of the liquid PCMs. This can be achieved via the method of encapsulation [8-9]. Encapsulation is a process which forms a coating around small solid particles, liquid droplets or gas bubbles. There are many factors that may influence the size distribution of microcapsules [10].

The type of shell material is important to ensure the thermal stabilities and shelf life of MPCM applications. Previous research showed that the poly methyl methacrylate (PMMA) and polystyrene are general shell materials for MEPCMs synthesis although MEPCMs can be produced by various methods [10-11]. Suspension-like polymerization of PCMs in polymeric shells is a well-known heterogeneous polymerization technique used for the production of solid polymer particles [11-18], typically in the range 50-500 μm .

Integration of MicroEncapsulated Phase Change Materials (MEPCM) into various construction materials (like gypsum) has been introduced as a key technology for minimizing energy consumption in the buildings including residential buildings because of they could be used to reduce the diurnal indoor air temperature variations and the occurrence of peak indoor temperatures in hot seasons [3-5], it also reduces the mechanical strength of gypsum [6-9]. Gypsum is a commonly used building material type and has been proven to be very suitable and relatively safe [5].

In order to achieve the advantages of PCMs application in the buildings, some problems must be solved, for example, modification of material properties [6-8], development of the methods of incorporation of these materials in the structure of the building [9-11] or enhancement of heat transfer rate between the air and PCM [12, 13]. Zhou *et al.* [9] have conducted extensive research into appropriate PCMs and uses for thermal energy storage in building applications. Their research identified many suitable materials, both commercial and non-commercial, that have properties suitable for residential use.

This paper has now established that the suspension-like polymerization method can be used for microencapsulation of butyl palmitate in polystyrene-co-methyl methacrylate shell. This is accomplished by replacing approximately 65% of the monomers with an oily core material; the monomers must be miscible with the core material, and the copolymer product insoluble in the core material. Polymerization of the styrene/ methyl methacrylate is carried out, and the butyl palmitate is then encapsulated by the co-polymeric shell to give a core-shell structure.

EXPERIMENTAL SECTION

Materials

Styrene (STM, 99 wt %, Merck) and methyl methacrylate (MMA, 99 wt %, Merck) were used as shell forming monomers. α,α -azoisobutyronitrile (AIBN, 98 wt%, Merck) was used as an initiator. Butyl palmitate (99 wt %, Merck) was used as PCM. Polyvinylpyrrolidone (PVP, polyvidone 25, Merck), polyvinyl alcohol (PVA, 145000, Merck) were used as stabilizers and suspension agents, and tri-Calcium phosphate (TCP, extra pure, Merck) was used as a suspension agent. Sodium lauryl sulfonate (SDS, 99 wt %, Merck) was used as a surfactant. All these reagents were used as received.

Microcapsules synthesis

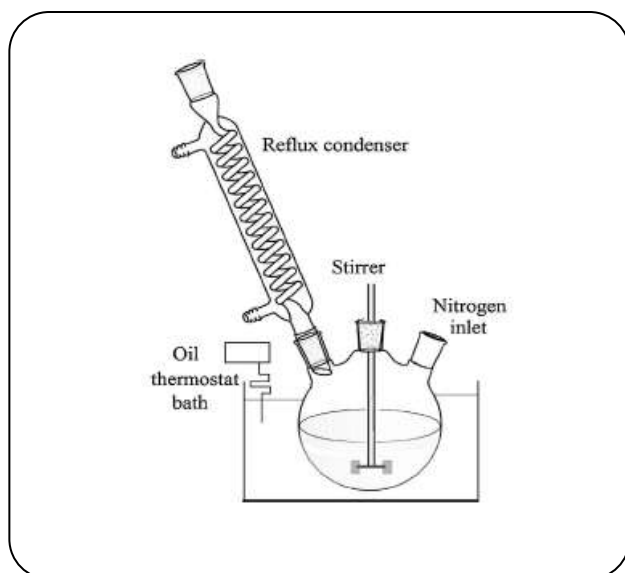
PCM microcapsules containing butyl palmitate were prepared by suspension-like polymerization technique. Microencapsulation was carried out in a 500-ml three-neck flask equipped with digital control of stirring rate, an oil thermostat bath, a reflux condenser, and a nitrogen gas inlet tube, set-up of this work shown in Fig. 1. Rushton turbine stirrer with six vertical blades was used in the reactor.

Microencapsulated butyl palmitate in polystyrene-co-methyl methacrylate shell synthesized in two ways, one of them with use of tri-calcium phosphate and the other without it.

The synthesis process involves two phases: a continuous phase (water phase) containing water, polyvinyl alcohol, polyvinylpyrrolidone, Sodium lauryl sulfonate (and tri-Calcium phosphate) and a discontinuous phase (oil phase), containing styrene, methyl methacrylate, PCM and α,α -azoisobutyronitrile (AIBN). The recipe shown in Table 1 is based on suspension-like polymerization technique.

Table 1: Recipes for production of microencapsulated phase change materials (PCMs) in polystyrene-co-methyl methacrylate shell in two ways, (1) with use of TCP and (2) without TCP.

Set of experiments	DMW (g)	SDS (g)	PVA (g)	PVP (g)	TCP (g)	STM (g)	MMA (g)	PCM (g)	rpm	Mea diameter (μm)	T_m ($^{\circ}\text{C}$)	ΔH_m (J/g)
1	238.2	0.0	0.5	0.8	0.00	41	29	132	800	160	21.1	70.0
2	238.2	0.10	0.7	1.1	14.2	41	29	132	800	70	21.05	70.1

**Fig. 1: Detail of the experimental set-up.**

The continuous phase was transferred gradually to a glass reactor with mild agitation and maintain at $T = 50\text{ }^{\circ}\text{C}$. The initiator was already mixed with the monomers and PCM material. Next, the discontinuous phase was added into the continuous phase maintained under vigorous agitation. The temperature was set at $80\text{ }^{\circ}\text{C}$ in the thermostat bath and remain in this condition for a 1 h. For completing of synthesis and reducing of residual monomers the synthesis temperature increase to the $T = 90\text{ }^{\circ}\text{C}$ and maintain fixed for other 3 h. The polymerization process was carried out for 4 h under a nitrogen atmosphere and send to gradually cooling down at the end of the reaction.

Once obtained, the polymerized microcapsules were repeatedly washed with methanol, diluted HCl solution and then with DM-water and filtrated to remove impurities. The purified microcapsules were dried at room temperature. Dried microencapsulated PCMs were used with the 30:70 ratio of MPCM to gypsum to prepare a gypsum wall.

RESULTS AND DISCUSSION

The effect of hybridized suspension agents system (TCP) on the particle size was investigated. Particle size and Particle Size Distribution (PSD) were determined on a Malvern Mastersizer Hydro 2000 SM light-scattering. Table 2 reports the thermal properties and the average diameter of the obtained microcapsules. It is obvious when we used TCP as hybridized suspension agent system, the average diameter of MPCMs was about 70 microns and when we did not use hybridized suspension agents, obtained average diameter were about 160 microns. This fact indicates that our system exhibits suitable behavior on particle size distribution control where we used hybridized suspension agents in polymerization possess and caused to the narrow particle size distribution in comparison to a similar process that we did not use hybridized suspension agents. Microencapsulation processes were successful in both of these syntheses (Fig. 2).

In addition, it was important to know what stirring rates were appropriate for use with this encapsulation method, so that different stirring rates with a different compound of hybridized suspension agents were assayed with the same experimental conditions that reported in Table 1. The stirring rates 1200, 1000, 800, and 600 were used in polymerization possess, respectively. PSDs in number related to the stirring rates obtained after the polymerization process is shown in Fig. 3. On the basis of our results, 800 rpm was the best rate for our microencapsulation process because of an exhibition of unimodal distribution with an average diameter of $70\text{ }\mu\text{m}$ and its narrow PSD ($5\text{-}120\text{ }\mu\text{m}$) with use of hybridized suspension agents.

The weight loss of the microcapsules with increasing of temperature was investigated by using a ThermoGravimetric Analyzer (TGA) model TGA7 of Perkin Elmer TGA7 at a rate of $10\text{ }^{\circ}\text{C}/\text{min}$ in an atmosphere of helium.

Table 2: Table of used hybridized suspension agent with various stirring rates in microencapsulation process and the related mean diameter of earned MPCMs for each of the experiments.

Set of experiments	Continuous phase				Discontinuous phase			Stirring Rate	Temp
	SDS (g)	PVA (g)	PVP (g)	TCP (g)	STM (g)	MMA (g)	PCM (g)	rpm	(°C)
1	0.1	1.4	2.0	14.2	41	29	132	800	80
2	0.0	2.0	2.8	0.0	41	29	132	800	80

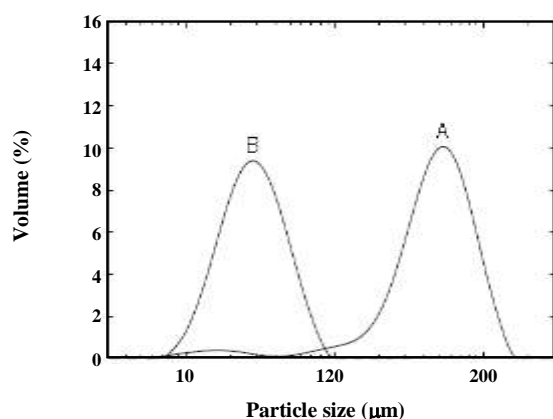


Fig. 2: particle size distribution of MPCMs produced: (A) without hybridized suspension agents and (B) with the use of hybridized suspension agents in suspension-like polymerization technique (rpm=800).

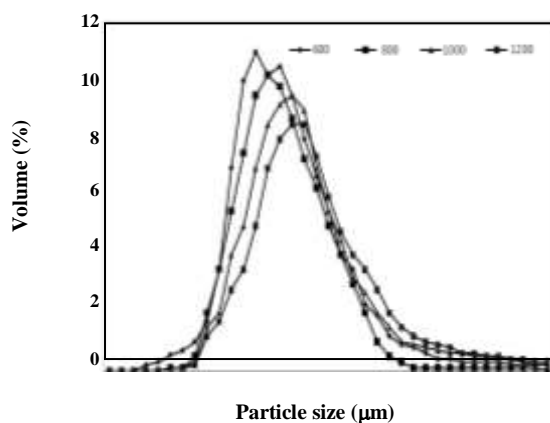


Fig. 3: Volume distribution curves of microcapsules with different stirring rates (600, 800, 1000 and 1200 rpm).

The TGA plot of the microcapsules as shown in Fig. 4, showed a loss of about 1.7 wt % below 224.47 °C because of methanol and water elimination (drying of surface wetting agents), and between 224.47 and 376.23 °C, other weight loss 59.7 wt% was observed, attributed to the butyl palmitate. Finally, at temperatures higher than 376.23 °C, an additional weight loss of 32 wt% took

place; this weight loss was due to the polystyrene-co-methyl methacrylate shell. All remained inorganic materials belong to our TCP content as a suspension agent. This result confirmed our basis amount of PCM and monomers content in our formula with a yield of 91.8 % for microencapsulation efficiency.

Apparatus Measurements of melting point and melting heats for different materials in this study were performed by a Differential Scanning Calorimetry (DSC) model DSC Q100 of TA Instruments. These measurements were done in the temperature range from -30 to 300 °C with a heating rate of 10 °C/min.

DSC curves of pure butyl palmitate and micro-encapsulated butyl palmitate in polystyrene-co-methyl methacrylate shell with stirring rates of 800 rpm are shown in Figs. 5 and 6, respectively. The melting temperature of the pure butyl palmitate is 21.1 °C and in micro-encapsule form is 21.6 °C. According to our tests the phase change enthalpy of the pure butyl palmitate is 116.6 J/g and the latent heat of the fusion for our obtained microcapsules with use of hybridized suspension agent is 70.6 J/g, which indicate that butyl palmitate of the recipe have been successfully encapsulated inside the microcapsules and obtained MPCMs have a considerable heat storage capacity. The proportion of core butyl palmitate to shell copolymer is actually about 65 %.

The surface features of the microcapsules (MPCMs) after polymerization process were observed by using a scanning electron microscope SEM, HITACHI S-510, and LEO 1530VP.

SEM micrographs of microencapsulated butyl palmitate in polystyrene-co-methyl methacrylate shell are shown in Fig. 7. It can be observed that the microcapsules for different stirring rates have semi-spherical shapes, but as it can be seen in Fig.7-B for obtained micro-encapsules with stirring rate of 800 rpm and hybridized suspension agent (TCP), we observed the totally spherical shape and narrow PSD in the range of (0-150 µm) which indicate

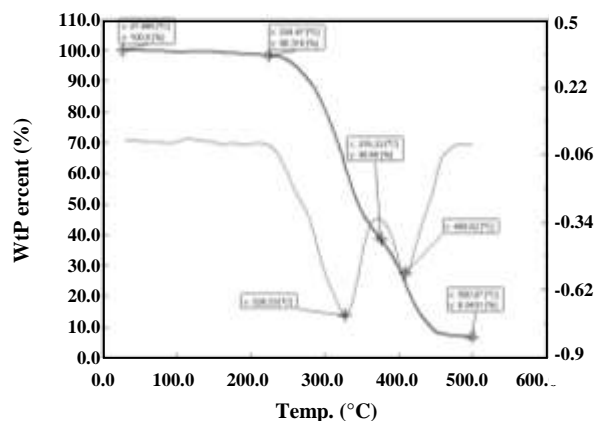


Fig. 4: The TGA plot of PCM microcapsules containing 60% butyl palmitate which prepared by suspension-like polymerization technique.

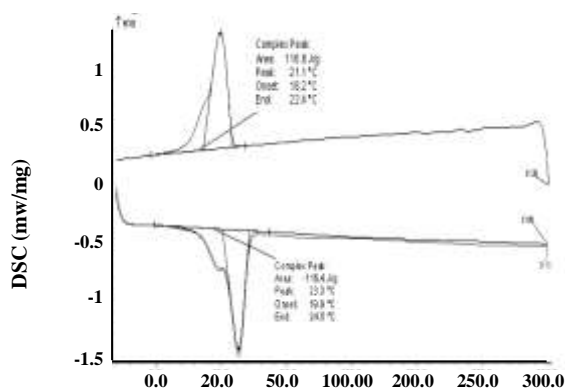


Fig. 5: The DSC curves of pure butyl palmitate. The enthalpy of fusion is 116.6 J/g.

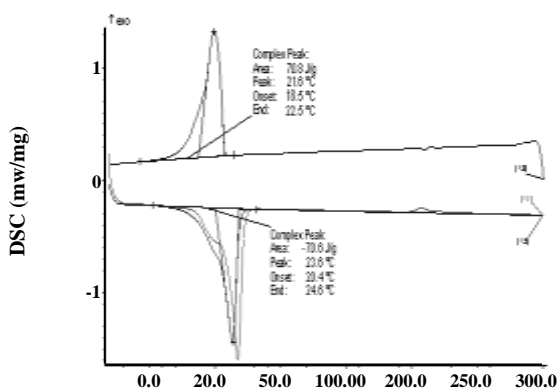


Fig. 6: The DSC curves of microencapsulated butyl palmitate in polystyrene-co-methyl methacrylate shell. The enthalpy of fusion is 70.6 J/g.

800 rpm was the optimum rate for our microencapsulation process to preparing a mean diameter of 70 μm with utilizing of hybridized suspension agent.

Thermal behavior of gypsum-MPCM walls was studied by Thermovision camera model FLIR thermovision 2000/3000 MS.

Dried microencapsulated PCMs were used with the 30:70 ratio of MPCM/gypsum (P01) to prepare a wall with dimensions of (10*10) cm^2 and 1 cm thickness. This MPCM/gypsum wall compared with three other walls which had the same dimensions and consisted of gypsum (P02), gypsum/polystyrene-co-polymethyl methacrylate (30/70) (P03) and gypsum/polystyrene-co-polymethyl methacrylate (10/90) (P04), respectively for comparison. These manufactured walls put in the oven (40°C for 48 h) to complete our curing process.

These prepared walls held in 15 °C temperature for 4 h to complete our MPCMs charge cycle and then exposed to ambient temperature (29.6 °C) in the same condition. As it can be seen in Fig. 8, thermo-vision camera was used to show the thermal behavior of prepared for 4 types of gypsum walls (P01, P02, P03, and P04). At the beginning of the test, as shown in Fig. 8-A, at the beginning times all of these gypsum walls had the same temperature about 15 °C, but after passing 600 S (Fig. 8-B), 3 gypsum walls including (P02, P03, and P04), lost their resistance in front of ambient temperature and reach the thermal equilibrium with the surrounding environment. However, our MPCM/gypsum wall compared to the other three walls showed good thermal regulation ability and a too long time till isothermal point with ambient (29.6 °C) about 8400 S.

Therefore, the thermal energy storage of the butyl palmitate inside the microcapsule shells was demonstrated confirming the applicability of these capsules for 2 h and 20 min thermal energy storage in gypsum walls.

Summary

A method based on a suspension-like free radical polymerization process with use of hybridized suspension agent has been used for the microencapsulation of butyl palmitate in polystyrene-co-methyl methacrylate shells. This type of micro-encapsules synthesis had not been previously described in the literature, nor patented. PCM (butyl palmitate) can be encapsulated by these processes and in the form of core-shell structure with use of different stirring rates and hybridized suspension agents.

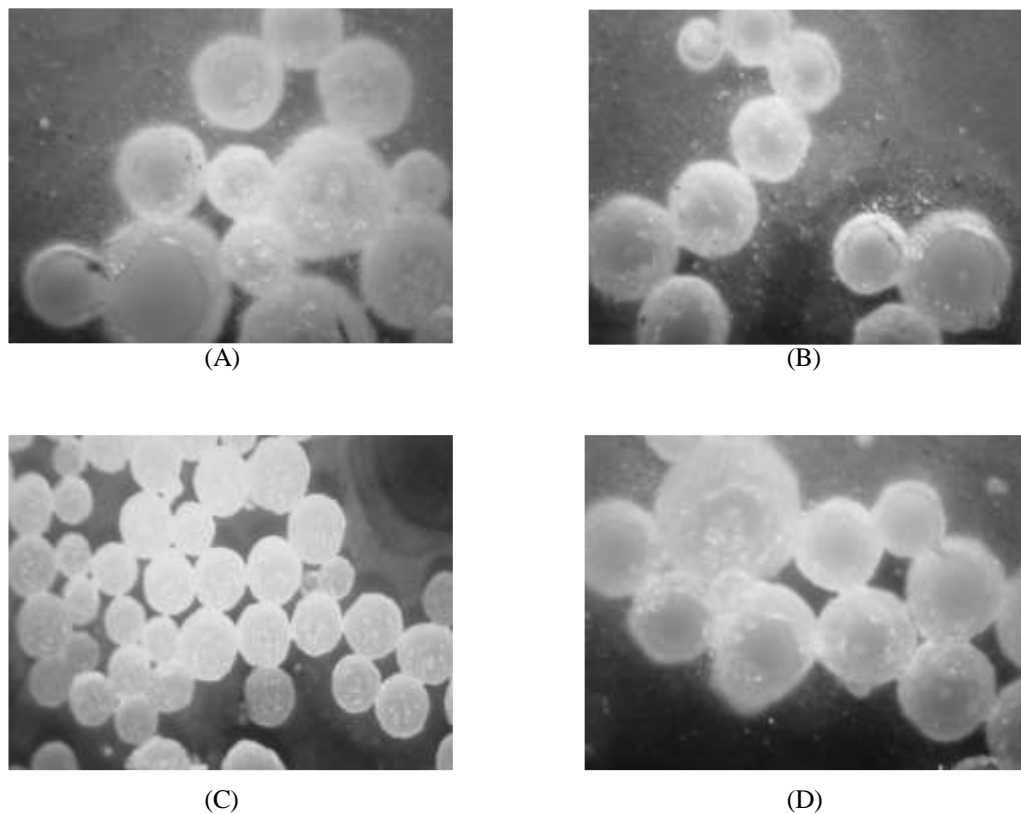


Fig. 4: The TGA plot of PCM microcapsules containing 60% butyl palmitate which prepared by suspension-like polymerization technique.

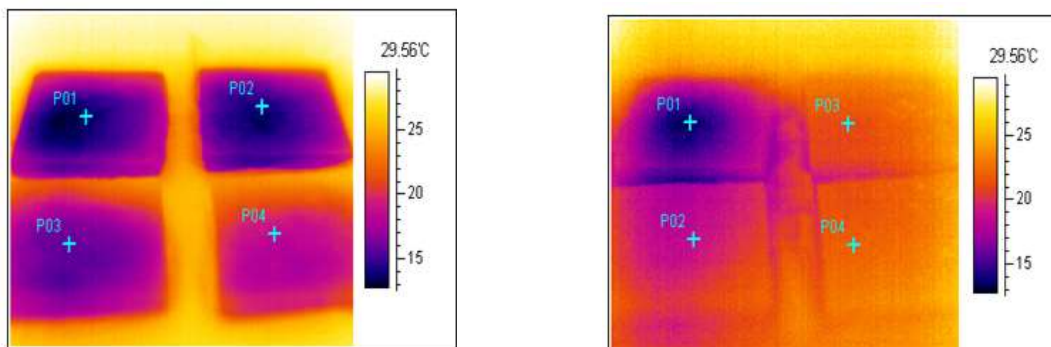


Fig. 8: Thermal behavior of gypsum walls prepared by the thermo-vision camera, in these pictures, P01, P02, P03, and P04 relate to (gypsum: MPCM), (gypsum), (gypsum: polystyrene-co-polymethyl methacrylate 30:70) and (gypsum: polystyrene-co-polymethyl methacrylate 10:90) respectively. Also, (A: time=0 S, B: time: 600 S).

On the basis of TGA and DSC analysis results, it is possible to obtain particles where almost 65% by weight of microcapsules is PCM which play a key influence on the thermal energy saving (releasing) potential in the buildings.

Particle size and Particle Size Distribution (PSD) determination showed hybridized suspension agents in polymerization process causes to narrow particle size distribution in the microencapsulation process in comparison

to a similar process without it, the particle size of MPCMs products in this study is the same of buildings materials sizes (gypsum) which cause to homogeneity of the mixture. Latent heat of the fusion for butyl palmitate inside of microcapsules was 70.6 J/g, which indicate that our butyl palmitate have been successfully encapsulated inside the polystyrene-co-methyl methacrylate shells. The experimental results show that the thermal stability of synthesis MPCM samples was 224.47 °C.

SEM micrographs of microencapsulated MPCMs show that spherical microcapsules were obtained with a narrow PSD (0-150 µm) with a stirring rate of 800 rpm and hybridized suspension agent (TCP). Thermovision tests which used for thermal energy storage investigation of MPCM/gypsum walls demonstrated the applicability of these micro-encapsules for thermal energy storage in gypsum walls. Also, this test results showed the good thermal regulation ability of gypsum walls for a too long time (about 8400 S) in ambient condition.

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REFERENCES

- [1] Dwivedi V.K., Tiwari P., Tiwari S., "Importance of Phase Change Material (PCM) in Solar Thermal Applications: A Review", *Proceedings of the International Conference on Emerging Trends in Electrical, Electronics and Sustainable Energy Systems (ICETEESSES)*, Sultanpur, India, 11–12 March (2016).
- [2] Mehling H., Cabeza F., "Heat and Cold Storage with PCM", Springer-Verlag Berlin Heidelberg (2008).
- [3] Gkanas E.I., Grant D.M., Kzhous M., Stuart A.D., Manickam K., Walker G.S., Efficient Hydrogen Storage in up-Scale Metal Hydride Tanks as Possible Metal Hydride Compression Agents Equipped with Aluminum Extended Surfaces, *Int. J. Hydrog. Energy*, **41**: 10795–10810 (2016).
- [4] Souayfane F., Fardoun F., Biwole P., Phase Change Materials (PCM) for Cooling Applications in Buildings: A Review, *Energy Build.*, **129**: 396–431 (2016).
- [5] Thambidurai M., Panchabikesan K., Mohan K.N., Ramalingam V., Review on Phase Change Material Based Free Cooling of Buildings—The Way Toward Sustainability, *J. Energy Storage*, **4**: 74–88 (2015).
- [6] Kosny J., PCM-Enhanced Building Components—An Application of Phase Change Materials in Building Envelopes and Internal Structures; Springer International Publishing: Steinhausen, Switzerland, (2015).
- [7] Graci, A.D., Cabeza L.F., Phase Change Materials and Thermal Energy Storage for Buildings, *Energy Build.*, **103**: 414–419 (2015).
- [8] Lin W., Ma Z., Cooper P., Sohel M.I., Yang L., Thermal Performance Investigation and Optimization of Buildings with Integrated Phase Change Materials and Solar Photovoltaic Thermal Collectors, *Energy Build.*, **116**: 562–573 (2015).
- [9] Zhou D., Zhao C.Y., Tian Y., Review on Thermal Energy Storage with Phase Change Materials (PCMs) in Building Applications, *Appl. Energy*, **92**: 593–605 (2012).
- [10] Dubey R., Shami T.C., Bhasker R., Microencapsulation Technology and Applications. *Defence Science Journal*, **59**(1): 82–95 (2009).
- [11] Sanchez L., Sanchez V., Lucas A., Carmona M., Rodriguez J.F., Microencapsulation of PCMs with a Polystyrene Shell, *Colloid Polym. Sci.*, **285**: 1377–1385 (2007).
- [12] Sanchez L., Sanchez V., Lucas A., Carmona M., Rodriguez J.F., Influence of Operation Conditions on the Microencapsulation of PCMs by Means of Suspension-Like Polymerization, *Colloid Polym. Sci.*, **286** (8-9): 1019–1027 (2008).
- [13] Sanchez L., Rodriguez J. F., Romero A., Borreguero A.M., Carmona M., Sanchez P., Microencapsulation of PCMs with a Styrene-Methyl Methacrylate Copolymer Shell by Suspension-Like Polymerization, *Chem. Eng. J.*, **157**: 216–222 (2010).
- [14] You M., Wang X., Zhang X., Zhang L., Wang J., Microencapsulated n-Octadecane with Styrene-Divinylbenzene co-Polymer Shells, *J. Polym. Res.*, **18**: 49–58 (2010).
- [15] Sanchez L., Tsavalas J., Sundberg D., Sanchez P., Rodriguez J.F., Synthesis and Characterization of Paraffin Wax Microcapsules with Acrylic Based Polymer Shells, *Ind. Eng. Chem. Res.*, **49**: 12204–12211 (2010).

- [16] Sanchez L., Carmona M., De lucas A., Sanchez P., Rodriguez J.F., [Scale-up of a Suspension-like Polymerization Process for the Microencapsulation of Phase Change Materials](#), *J. Microencapsulation*, **27**(7): 583-593 (2010).
- [17] Sanchez P., Sanchez-Fernandez M. V., Romero A., Rodriguez J.F., Sanchez-Silva L., [Development of Thermo-Regulating Textiles Using Paraffin Wax Microcapsules](#), *Thermochim Acta*, **498**: 16-21 (2010).
- [18] Sanchez L., Lacasa E., Carmona M., De lucas A., Rodriguez J.F., Sanchez P., [Applying an Experimental Design to Improve the Characteristics of Microencapsules Containing Phase Change Materials for Fabric Uses](#), *Ind. Eng. Chem. Res.*, **47**: 9783-9790 (2008).
- [19] 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*, **588**: 38-46 (2014).