Thermal performances and characterization of microencapsulated phase change materials for thermal energy storage

Yanhong Ma 1, Qifei Xie 1, Yue Li 1,2, Xianhao Min 1,3, Xinzhong Wang 1*

1 School of Electronic Communication Technology, Shenzhen Institute of Information Technology, Longgang District, Shenzhen, Guangdong, 518172, China.
2 School of Ecology and Environment, Inner Mongolia University, Hohhot, Inner Mongolia Autonomous Region, 010021, China
3 School of Mechanical Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China.

*Corresponding author e-mail: xzwang2188@163.com

Abstract. A series of microencapsulated phase change materials (micro-PCMs) contained butyl stearate and octadecane as core materials were synthesized by suspension-like polymerization method. Methyl methacrylate (MMA), divinylbenzene (DVB), pentaerythritol triacrylate (PETA) and pentaerythritol tetraacrylate (PETTA) were introduced in polymerization system to form shells. DSC results indicated that microencapsulation ratio could reach as high as 75 wt.%. After 500 times thermal cycling test, the microencapsulation ratio of these as-prepared micro-PCMs decreased only by 2.3 wt.%. SEM images showed that these micro-PCMs have relatively spherical morphology and compact surfaces with diameter ranging from 5 to 40 μm.

1. Introduction

With the development of era, people have higher request on the quality of the environment, so we formulated more severe rules on fuel use. In order to meet the green concept of energy saving, the utilization of solar energy has obtained large-scale development. Phase change materials (PCMs) have a good application value as thermal energy storage materials. Microencapsulated phase change materials (micro-PCMs) make PCMs more widely available. Therefore, micro-PCMs have been used in various fields, for example, solar energy [1, 2], buildings [3, 4] and other domain of energy saving [5-8]. For instance, Wu et al, designed a kind of PCMs based heat pipe heat sink to decrease the LED heating rate and temperature in LED cyclic working modes. The results indicated that compared with those of the water base and air base at 30 W, PCMs based sink could reduce the heating rates by 0.46 °C/min and 0.22 °C/min, and the reductions in temperature are more than 16 °C and 32 °C, respectively [9].

In this paper, poly-functional group cross-linking agents, such as pentaerythritol triacrylate (PETA) and pentaerythritol tetraacrylate (PETTA), were introduced in polymerization system to react with methyl methacrylate (MMA) or divinylbenzene (DVB) to form different shells. Chemical structure, morphologies and thermal properties and reliabilities were all studied, and the results indicated that these prepared micro-PCMs could be used as desirable thermal energy storage materials.
2. Experimental

2.1. Materials
Octadecane (99 %), butyl stearate (BS) are selected as core materials. 2, 2′-azobisisobutyronitrile (AIBN, 98 %) is chosen as initiator. Monomers such as, methyl methacrylate (MMA), divinylbenzene (DVB), pentaerythritol triacrylate (PETA, 96%), pentaerythritol tetraacrylate (PETTA, >80.0%, MEHQ as stabilizer), Sodium salt of styrene-maleic anhydride copolymer (TA) is selected as stabilizer. The chemical structures of the related reagents were schematically displayed in figure 1.

Figure 1. Chemical structures of used reagents.
(a) BS; (b) MMA; (c) DVB; (d) PETA; (e) PETTA; (f) TA.

2.2. Characterizations of the micro-PCMs
Fourier transformed infrared (FT-IR) spectra were tested by a spectrophotometer (Nicolet 6700, USA). The spectrum was collected by scanning number of 32 at a resolution of 4 cm⁻¹ in the wave number range of 400 to 4000 cm⁻¹. The morphologies of micro-PCMs were studied by field emission scanning electron microscope (FE-SEM, ZEISS SUPRA® 55, Carl Zeiss, Germany). Differential scanning calorimeter (DSC1, METTLER TOLEDO, Switzerland) was used to measure the phase change performances of these prepared micro-PCMs. Besides, thermal reliability of sample 1 was tested through alternative heating and cooling test in the temperature range of 15 to 50 °C. Sample 1 was subjected to repeated cycles of melting and freezing using heating-cooling cyclic oven for 500 times. The microencapsulation ratio was defined as following equation 1 [10]:

\[ R \% = \left( \frac{\Delta H_{m, \text{PCMs}}}{\Delta H_{m, \text{OCBS}}} \right) \times 100 \text{ wt.}% \]

Where, \( \Delta H_{m, \text{OCBS}} \) is the melting enthalpy of the bulk PCMs, \( \Delta H_{m, \text{micro-PCMs}} \) is the melting enthalpy of the micro-PCMs.
Table 1. Basic compositions and thermal properties of the samples.

| NO. | Octadecane (g) | BS (g) | MMA (g) | DVB (g) | PETA (g) | PETTA (g) | $T_{pm}$a (°C) | $\Delta H_m$b (J/g) | $R_c$c (Wt.%) |
|-----|----------------|--------|---------|---------|----------|----------|----------------|------------------|-----------------|
| 1   | 3.00           | 3.00   | 3.00    | --      | 3.00     | --       | 27.7          | 82.8             | 75.0            |
| 2   | 3.00           | 3.00   | --      | 3.00    | 3.00     | --       | 27.7          | 68.1             | 62.0            |
| 3   | 3.00           | 3.00   | 3.00    | --      | --       | 3.00     | 29.2          | 70.7             | 64.0            |
| 4   | 3.00           | 3.00   | --      | 3.00    | --       | 3.00     | 27.9          | 60.0             | 54.2            |
| 5   | 6.00           | --     | 3.00    | --      | --       | 3.00     | 33.2          | 152.4            | 70.6            |
| 6   | --             | 6.00   | 3.00    | --      | --       | 3.00     | 30.7          | 70.4             | 67.7            |

a. Melting peak temperatures of the micro-PCMs.
b. Melting enthalpies of the micro-PCMs.
c. Microencapsulation ratios of the micro-PCMs.

3. Results and discussion

3.1. Chemical structures of the micro-PCMs

Figure 2 represented the FT-IR spectra of the micro-PCMs. The belongings of the absorption peaks were summarized as follows [11]: The peaks ascribed to C=C stretching and bending mode of benzene ring were located at at about 1620 cm$^{-1}$ and 1115 cm$^{-1}$, respectively. The peak assigned to C–H stretching vibration of $–$CH– was at about 1460 cm$^{-1}$. The peaks belonged to stretching vibration of carbonyl group and C–O bond in esters were at about 1730 and 1167 cm$^{-1}$, respectively. The peak assigned to C–H symmetrical deformation vibration of $–$CH$_3$ was at about 1370 cm$^{-1}$. The peaks belonged to C–H stretching vibration of $–$CH$_2$ were at about 2920 and 2850 cm$^{-1}$, respectively.

![Figure 2. FT-IR spectra of the micro-PCMs.](image)

3.2. Thermal performances of the micro-PCMs

Table 1 and figure 3 displayed thermal performances of these samples. The phase change temperature of these micro-PCMs was in the range of 27 °C to 33 °C. The melting peak temperatures and enthalpies of octadecane and butyl stearate were respectively 30.7°C, 28.2 °C and 216.0 J/g, 104.0 J/g.
When introduced MMA in polymerization system, compared with DVB, sample 1 and sample 3 had higher thermal enthalpy than that of sample 2 and sample 4, respectively. Besides, sample 5 had much higher heat capacity than that of sample 6, because octadecane had much higher heat capacity than butyl stearate, these as-prepared microcapsules have better thermal properties. Third, when put the best sample under heating and cooling cycling test, sample 1 could also show desirable thermal performances. After 500 times thermal cycling, melting enthalpy of sample 1 decreased to 80.3 J/g, the microencapsulation ratio only decreased by 2.3 wt.%. Therefore, these samples could be used as thermal storage materials because they had desirable thermal reliabilities.

3.3. Morphologies of the micro-PCMs
Figure 4 represented SEM images of the micro-PCMs, the diameters of these samples ranged from 5 to 40 μm and most of the microcapsules had relatively spherical profiles and compact surfaces. According to the different composition of core and shell materials, these 6 kinds of samples could be divided into three series. The first set was sample 1 and 2, the micro-PCMs contained OCBS (octadecane and butyl stearate mixture with the weight ratio of 1/1) as cores and P(PETA-co-MMA) or P(PETA-co-DVB) as shells. The second set was sample 3 and 4, the micro-PCMs contained OCBS as cores and P(PETTA-co-MMA) or P(PETTA-co-DVB) as shells. The last set was sample 5 and 6, they have the same shells P(PETTA-co-MMA), but the core materials were different as shown in table 1.

Compared with sample 1 and 2, they all had dimples on the surface, but there were some fragments formed in sample 2. The reason could be attributed to the chemical structure of the monomers. For instance, DVB was introduced in sample 2, PETA and DVB polymerized to form more strong but less flexible shells. Therefore, during the cooling process after polymerization, the shells were inclined to rupture than that of P(PETA-co-MMA) shells. This phenomenon could be also verified by sample 3 and 4. Additionally, when the core material was octadecane, the microcapsules had more fragments than that of containing butyl stearate as core. Therefore, all the micro-PCMs had desirable morphologies and they had desirable potential as thermal energy storage materials.
Fig. 4. SEM photographs of micro-PCMs. 
(a) Sample 1; (b) Sample 2; (c) Sample 3; (d) Sample 4; (e) Sample 5; (f) Sample 6.

4. Conclusions
A series of micro-PCMs with different shells were obtained by suspension-like polymerization method, the cross-linking agents, PETA and PETTA was respectively introduced in polymerization process to form different shells. Chemical structures, morphologies and thermal properties of these prepared microcapsules were all investigated. The results indicated that, first, the microencapsulation ratio of the micro-PCMs was in a high range from 54 wt.% to 75 wt.%. Besides, most of the microcapsules had relatively spherical profiles and compact surfaces and the diameters ranged from 5 to 40 $\mu$m. And
finally, all the above results suggested that these prepared micro-PCMs had desirable application prospect in the field of thermal energy storage.

Acknowledgments
The authors are appreciated for the financial support from the Science and Technology Project of Shenzhen City in 2016 (Grant No. JCYJ20160330101037385, JCYJ20160509100737182), Guangdong Province Higher Vocational Colleges & Schools Pearl River Scholar Funded Scheme (GDHVPS, 2016), and the Science and Technology Project of Shenzhen City in 2017 (Grant No. JSGG20170414102704519). Moreover, the authors are also grateful for the Project of Innovation and Strong School (2017GKCXTD007).

References
[1] M. Zayed, J. Zhao, A. Elsheikh, F. Hammad, L. Ma, Y. Du, A.E. Kabeel, S.M. Shalaby. (2019) A review. Sol. Energ. Mat. Sol. C., 199: 24-49.
[2] H. Liu, X. Wang, D. Wu, S. Ji. (2019) Sol. Energ. Mat. Sol. C., 193: 184-197.
[3] Z. Liu, Z. Yu, T. Yang, D. Qin, S. Li, G. Zhang, F. Haghighat, M. Joybari. (2018) Build. Environ., 144: 281-294.
[4] P. Saikia, A. Azad, D. Rakshit. (2018) Int. J. Therm. Sci., 126: 105-117.
[5] S. Khanna, S. Newar, V. Sharma, K. Reddy, T. Mallick, J. Radulovic, R. Khusainov, D. Hutchinson, V. Becerra. (2019) J. Clean. Prod., 221: 878-884.
[6] W. Lu, G. Liu, X. Xing, H. Wang. (2019) Energ. Procedia, 158: 5020-5025.
[7] R. Rabie, M. Emam, S. Ookawara, M. Ahmed. (2019) Sol. Energ., 183: 632-652.
[8] Md. Zahir, S. Mohamed, R. Saidur, F. Al-Sulaiman. (2019) Appl. Energ. 240: 793-817.
[9] Y. Wu, Y. Tang, Z. Li, X. Ding, W. Yuan, X. Zhao, B. Yu. (2016) Appl. Therm. Eng., 108: 192-203.
[10] Sánchez-Silva L, J Tsavalas, D Sundberg. (2010) Ind. Eng. Chem. Res., 49 (23): 12204-12211.
[11] Karaipekli A, Sari A, Biçer A. (2016) Appl. Therm. Eng. 2016; 107 (25): 55–62.