

Microencapsulation of Butyl Stearate as Phase Change Material by Melamine Formaldehyde Shell for Thermal Energy Storage

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Abstract

Butyl stearate as a phase change material was microencapsulated within melamine-formaldehyde resin using emulsion polymerization. Morphology and thermal specification of produced microcapsules were studied by Fourier transform infrared spectroscopy, FT-IR, scanning electron microscopy, SEM, and Differential scanning calorimetry analysis, DSC. FT-IR spectra validated the existence of the butyl stearate in the core of microcapsules. SEM graphs showed that melamine formaldehyde polymer without core was spherical and almost uniform with an approximate size of $2\mu\text{m}$ and microcapsules of butyl stearate in melamine formaldehyde shell were also spherical with the average diameter of $4\mu\text{m}$. DSC results showed that microencapsulation reduced the latent heat of melting and freezing of butyl stearate and increased melting point. The performance of the produced microcapsules was obtained 36.64%. Moreover, the efficiency of energy storage by the microcapsules was obtained about 40%. It was observed that the rate of thermal energy conservation was high during the phase change process of microcapsule core and it was reducing after completion of the melting process.

Keywords

Butyl stearate;
Formaldehyde;
Melamine;
Microencapsulation;
Phase change materials.

1. Introduction

Heat storage systems are utilized in the recovery and preservation of energy source and solar thermal systems [1]. Due to its high heat capacity and small temperature variation during energy absorbing and releasing process, latent heat storing has drawn interest as an effective approach for energy storage and recovery

In a latent heat storage system, energy is stored by melting a phase change material (PCM) and released during freezing of it [2].

Heretofore, various PCMs have been investigated for application in the latent heat storage systems [3-6]. PCMs have been widely used for heat storage in some systems, such as heat pumps and solar systems [7-8]. In the last decade, many studies have been performed on application of these materials for cooling and heating of the buildings, maintaining comfort temperature inside an au-

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tomobile, smart temperature-adaptable textiles, heat exchangers, etc. [9-11].

Along with their benefits, PCMs have some disadvantages such as necessity of using a special device or heat transfer surface, which imposes an extra cost and creates a thermal resistance between PCM and environment. Extensive studies have been done on using a new system, namely, fixed-shape PCMs, formed by combining phase change materials with a preserving based material, usually a polymer. This composite is useable directly with no extra devices in different applications. Although these compositions can maintain their own shapes during the phase change from solid state to liquid state, the PCMs are inclined to move towards the outer boundary and gradual leakage [12].

The other disadvantages of phase change materials are low heat conductivity and, consequently, low heat transfer intensity, volume change during phase change, and reaction to the surrounding environment.

Microencapsulation is one of the most effective ways to overcome the above disadvantages. It is a process wherein the discrete particles or drops are covered with a continuous film and formed as a capsule within the size range of 1 μ m to 1mm [13].

PCMs microcapsules consist of two main parts: the core, including a PCM, and a polymeric or an inorganic shell. Generally, there are different physical, chemical, and physiochemical methods of microencapsulation. [14-16]. Chemical methods are usually along utilized with a polymerization process. This process can be surface, emulsion, or suspension polymerization. In the emulsion polymerization, monomer is firstly emulsified using a surfactant in the polymerization medium. Then, an initiator enters the continuous phase and starts the polymerization [17].

Baek et al. prepared the nano-capsules of n-octadecane PCM using emulsion polymerization of styrene. The encapsulation efficiency was obtained about 66.7% by using an appropriate surfactant [18].

Alkan et al. studied microencapsulation of some phase change materials by using emulsion polymerization. They used poly methyl methacrylate as the polymer shell and observed that

PMMA/PCM microcapsules had high potential in storing thermal energy [19].

There are other studies on preparing PCM microcapsules using emulsion polymerization by other researchers [20-21].

Fatty acids are included as one of the phase change materials. The advantages of these materials are unified melting process, chemical stability and lack of intoxication, and inappropriate range of meting temperature when used in solar systems. These specifications have made them suitable for applications such as heating or cooling of the buildings and solar systems [22]. Butyl stearate is a fatty acid with phase change temperature of about 20°C that has relatively high heat storage capacity. Therefore, it can be used as an effective thermos-regulating material at room temperature. For example, microencapsulated butyl stearate can be used as an additive in indoor or outdoor coatings or it may be built in insulating materials, such as foams.

Melamine formaldehyde resin is commonly used in industry. It has great mechanical strength and desired thermal resistance. The thermal decomposition temperature of melamine formaldehyde is above 300°C, which is suitable for use as wall material of the microcapsules.

In the present work, butyl stearate is microencapsulated using melamine formaldehyde polymer as shell. Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), and differential scanning calorimetry (DSC) are used for analyzing the microcapsule structure and specifications.

2. Materials and Methods

2.1. Materials

Butyl stearate, polyvinyl alcohol, sodium carbonate, sodium lauryl sulfate (SLS), melamine, 37 % formaldehyde, and acetic acid were purchased from Merck Company.

2.2. Microencapsulation procedure

The microencapsulation process was performed in 3 steps as follows:

Melamine formaldehyde prepolymer preparation: 4.9gr of Melamine and 9.5gr of 37% formalde-

hyde were added to 100mL of distilled water. Then, pH was adjusted to 8.5–9.0 by 10% sodium carbonate solution. Then, the mixture was magnetically stirred at 60°C for 1h to prepare melamine-formaldehyde prepolymer.

Preparation of emulsion: 10gr of butyl stearate was added to 100mL of 1% SLS aqueous solution and stirred vigorously by a mechanical stirrer with the rate of 1000rpm. After about 30min, a relatively stable oil in water emulsion was achieved.

Polymerization: The prepared emulsion was added to the prepolymer to start polymerization, and the pH was regulated to 4.0 –5.0 by acetic acid. Subsequently, in order to prevent the agglomeration of emulsion droplets, 0.6gr of poly vinyl alcohol was added into the emulsion/prepolymer system and the mixture was stirred at 50°C for 1h. Finally, the obtained slurry was filtered, washed in distilled water, and dried at room temperature to obtain microcapsule powders.

2.3. Morphology and thermal analysis

Fourier transform infrared spectroscopy, FT-IR, (by Spectrum65, Perkin Elmar, USA) was used for qualitative identification of functional groups and the chemical bonds in the samples.

The samples during this test were grinded in a mortar with KBr salt. The mixture was reformed into a tablet due to the sieve on it. The tablets were placed in a container inside the spectrophotometer (FT-IR), and the spectrum of each sample was obtained to be in the wavenumber range of 450-4000cm⁻¹.

A scanning electron microscope, SEM, (XL30, Philips, Netherlands) was used for morphological identification of the surface and the method of accumulation, and shape and size of particles. In this test, the surface of the nonconductor samples was covered by gold to obtain an appropriate conductivity on the surface. Electron radiation strikeed the surface of the material, scanning all the points on the sample. Thus, a topographical image was obtained from the surface of the material.

Differential scanning calorimetry "DSC" (Diamond DSC, Perkin Elmar, USA) was used to analyze the phase change properties of the microcapsules. This test was performed under nitrogen, with the

heating/cooling rate of 10°C/min, in the temperature range of 0-60°C.

Furthermore, an instrument was designed and built to analyze the trend of storing thermal energy by the produced microcapsules. This device consisted of a glass column with 10mm diameter and height of 30cm, which was filled with the microcapsules. The device had two glass containers on the top and the bottom of the column. Water with temperature of 50°C entered the column with constant flow, and reached the lower container after heat exchange with the microcapsules. The rate of heat absorption by the microcapsules was obtained by measuring the difference of the water temperatures in the two containers. Moreover, the system was completely insulated during the test. Fig. 1 shows a schematic view of the instrument.



Figure 1. A schematic view of the thermal energy storage device

3. Results and Discussion

3.1. FT-IR spectrum

The results from FT-IR test on pure butyl stearate samples and microcapsules are shown in Fig. 2.

Pure butyl stearate and microcapsules FT-IR spectra are shown in Figs. 2(a) and 2(b), respectively. Absorption peak in both figures (close to 2927cm^{-1}) is related to C-H bond. The absorption peak near 2856cm^{-1} is known as aldehyde C-H bond, having weak absorption near $2750\text{-}2850\text{cm}^{-1}$ always being placed in the right side of C-H absorptions. Also, there are no absorption bonds in $1800\text{-}2650\text{cm}^{-1}$ in both spectra. The absorption peak in both graphs in 1741cm^{-1} shows C=O bond, and this bond is known as carbonyl group, which includes strong absorption in $1660\text{-}1820\text{cm}^{-1}$ range. In both figures, the absorption peak in 1175cm^{-1} shows C-O bond. C-O strong absorptions usually occur in $1000\text{-}1300$ range.

FT-IR spectra in both graphs are almost identical, having slight differences in partial peaks, which are negligible. This validates the existence of the butyl stearate in the core of microcapsules.

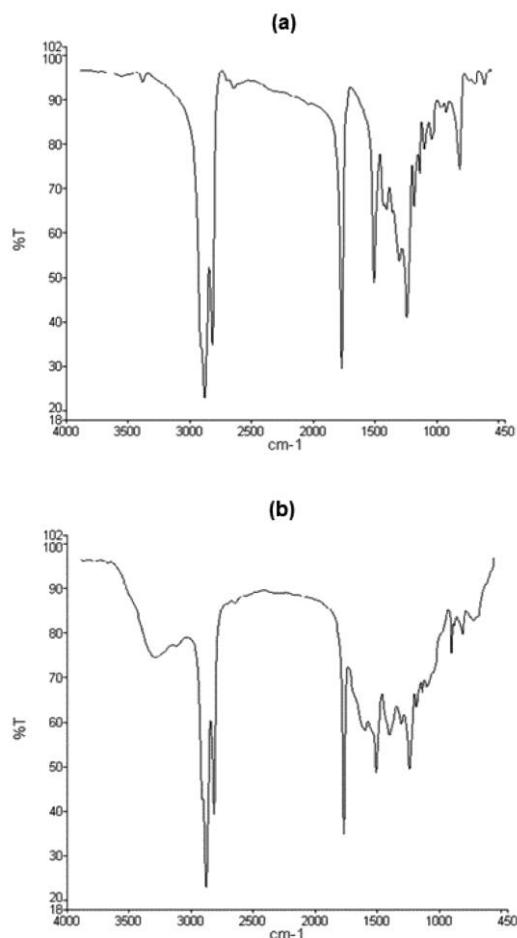


Figure 2. Graphs of infrared spectra; (a) pure butyl stearate, (b) butyl stearate microcapsules

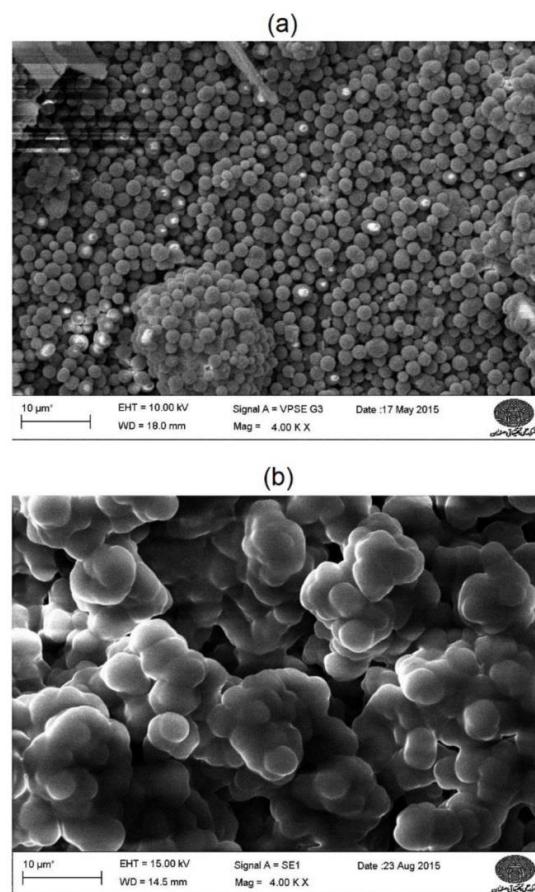


Figure 3. SEM images of (a) polycondensed melamine formaldehyde without core material, (b) melamine formaldehyde microcapsules containing butyl stearate as core

3.2. Results from scanning electron microscopy imaging

Fig. 3 shows SEM images related to polycondensed melamine formaldehyde without core material and melamine formaldehyde microcapsules containing butyl stearate as core. Fig. 3(a) shows SEM images of melamine formaldehyde polymer. It is seen that polymer granules are spherical and almost uniform with an approximate size of $2\mu\text{m}$. Fig. 3(b) of SEM shows microcapsules of butyl stearate in melamine formaldehyde shell. These particles are also spherical with the average diameter of $4\mu\text{m}$. in fact, placement of butyl stearate as the core in the polymer shell increases its volume. Thus, the size of microcapsules is about twice that of the pure polymer. It is seen that the microcapsules particles are reunited, while the polymer particles do not generate agglomeration. The method used in preparation of microcapsules is emulsion polymerization. In

this method, the melamine-formaldehyde prepolymer is first prepared. Then, the emulsion of butyl stearate in water is formed by the assistance of a surfactant. When prepolymer is added to the emulsion, it likely reduces surface tension of water and butyl stearate and, consequently, agglomerates the droplets during polymerization. Therefore, it seems to be the reason of reuniting of final microcapsules. However, it has no considerable effect on performance of microcapsule.

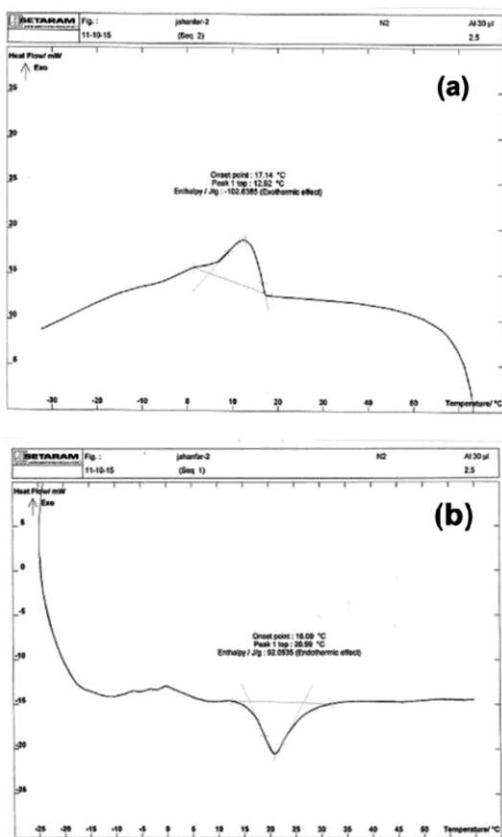


Figure 4. DSC graphs related to raw butyl stearate (a) heating, (b) cooling

3.3. Results from DSC thermal analysis

Figs. 4 and 5 show the DSC graphs of pure butyl stearate and the prepared microcapsule, respectively.

Thermal properties attained in DSC thermal analysis are shown in Table 1. It is seen that the latent heat for melting and freezing of butyl stearate is considerably reduced by microencapsulation. The performance of the produced microcapsules can be obtained by the following relation:

$$E_{en} = \frac{\Delta H_{m_{microcapsule}}}{\Delta H_{m_{butyl\ stearate}}} \times 100 \quad (1)$$

The performance of the produced microcapsules is obtained to be 36.64%. Moreover, the efficiency of energy storage by the microcapsules is obtaining as follows:

$$E_{es} = \frac{\Delta H_{m_{microcapsule}} + \Delta H_{c_{microcapsule}}}{\Delta H_{m_{butyl\ stearate}} + \Delta H_{c_{butyl\ stearate}}} \times 100 \quad (2)$$

The value of this relation is 39.44%.

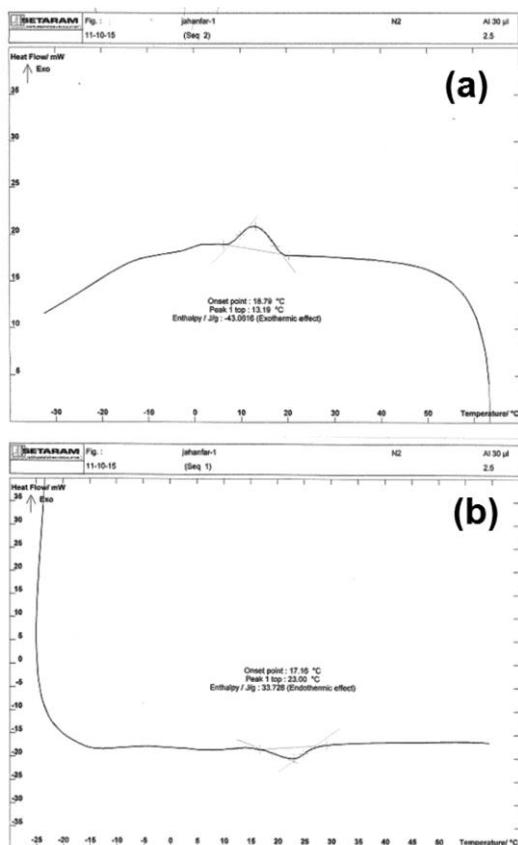


Figure 5. DSC graphs related to butyl stearate microcapsule (a) heating, (b) cooling

3.4. Thermal energy storage test results

Fig. 6(a) shows the rate of heat transfer from water without microcapsules as reference for comparison with thermal storage of microcapsules. Fig. 6(b) shows the trend of storing of thermal energy by hot water flow from a column of prepared microcapsules.

It is observed in Fig. 6(b) that the rate of thermal energy conservation is high during the phase change process of microcapsule core, and it is reduced after melting process is completed. In fact, the duration of using microcapsules can be obtained by this graph for using in thermal energy storage. Comparing with reference curve, it is seen that the rate of thermal energy storing in the microcapsules is higher than heat transfer from water to ambient.

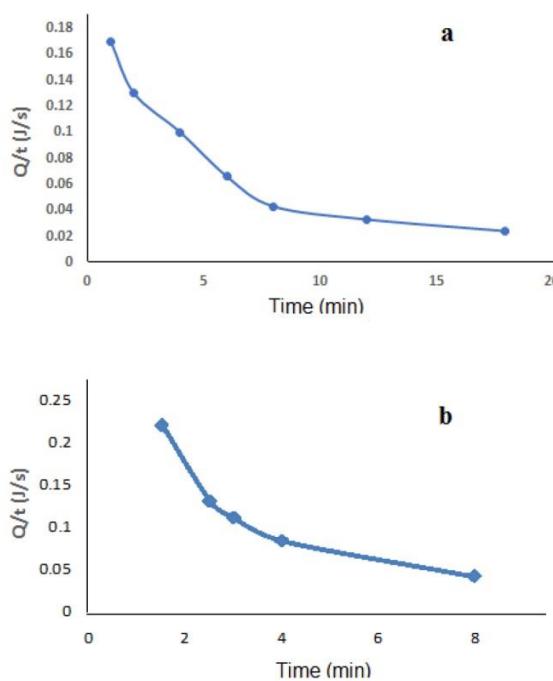


Figure 6. (a) rate of heat transfer from water without microcapsules as reference curve, (b) rate of energy storage with time, by microcapsules

4. Conclusion

Microencapsulation of butyl stearate phase change material by melamine formaldehyde polymer shell was considered in this study. The prepared microcapsules were almost spherical with a diameter of about 4 μm . the efficiency of the prepared microcapsules was obtained to be 36.64% and the efficiency of energy storage by the microcapsules was 39.44%. Also, the rate of supercooling increased by about 1.7°C by micro-encapsulation.

The special result of our work is the small size of obtained microcapsules. Microcapsules of small size have high contact surface for heat transfer. Therefore, rate of thermal energy storage in them

is high. In the present work, microcapsules were prepared with average diameter of 4 μm , which was very low in comparison with previous works. For example, Liang et al. Used polyurea as wall material. The particle diameter of microcapsules in their study was about 20-35 μm [23]. In another work by Lu et al., butyl stearate was microencapsulated via polyurea polymer. They produced microcapsules with the size of 4.5-10.2 μm [24]. Bendic and Amza produced polymethylmethacrylate (PMMA) microcapsules containing the butyl stearate as core with average diameter of 95 μm [25]. Alic et al. investigated the effect of pH on the composition and thermal stability of melamine microcapsules containing butyl stearate. They prepared microcapsules with the diameter of 20-50 μm [26].

Table 1. Thermal properties of butyl stearate PCM and microcapsules containing butyl stearate as core

Material	H _f freezing (J/g)	T _f freezing (°C)	H _m melting (J/g)	T _m melting (°C)	Supercooling (°C)
Butyl stearate	102.6385	12.92	92.0535	20.99	8.07
Microcapsule containing butyl stearate	-43.0616	13.19	33.7728	23	9.81

Symbols

E _{en}	Microcapsule performance
E _{es}	Energy storage efficiency
H _f freezing	Latent heat of freezing
H _m melting	Latent heat of freezing
T _f freezing	Freezing point
T _m melting	Melting point
ΔH _{c, microcapsules}	Latent heat of microcapsule crystallization
ΔH _{c, butyl stearate}	Latent heat of butyl stearate crystallization
ΔH _{m, microcapsules}	Latent heat of microcapsule melting
ΔH _{m, butyl stearate}	Latent heat of butyl stearate melting

References

1. Dincer, I. and Rosen, M. (2002). *Thermal energy storage: systems and applications*. 2th Ed. John Wiley and Sons.
2. Agyenim, F., Hewitt, N., Eames, P. and Smyth, M. (2010). "A review of materials, heat transfer and phase change problem formulation for latent heat thermal energy storage systems (LHTESS)." *Renewable and Sustainable Energy Reviews*, Vol. 14 (2), pp. 615-628.
3. Nkwetta, D.N. and Haghigat, F. (2014). "Thermal energy storage with phase change material a state of-the art review." *Sustainable Cities and Society*, Vol. 10, pp. 87-100.
4. Kenisarin, M.M. (2014). "Thermophysical properties of some organic phase change materials for latent heat storage. A review." *Solar Energy*, Vol. 107, pp. 553-575.
5. Liu, M., Saman, W. and Bruno, F. (2012). "Review on storage materials and thermal performance enhancement techniques for high temperature phase change thermal storage systems." *Renewable and Sustainable Energy Reviews*, Vol. 16 (4), pp. 2118-2132.
6. Rathod, M.K. and Banerjee, J. (2013). "Thermal stability of phase change materials used in latent heat energy storage systems: a review." *Renewable and Sustainable Energy Reviews*, Vol. 18, pp. 246-258.
7. Kenisarin, M. and Mahkamov, K. (2007). "Solar energy storage using phase change materials." *Renewable and Sustainable Energy Reviews*, Vol.11 (9), pp. 1913-1965.
8. Shalaby, S.M., Bek, M.A. and El-Sebaii, A.A. (2014). "Solar dryers with PCM as energy storage medium: A review." *Renewable and Sustainable Energy Reviews*, Vol. 33, pp. 110-116.
9. Jamekhorshid, A. and Sadrameli, S.M. (2012). "Application of Phase Change Materials (PCMs) in Maintaining Comfort Temperature inside an Automobile." *World Academy of Science, Engineering and Technology, International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering*, Vol. 6 (1), pp. 33-35.
10. Mondal, S. (2008). "Phase change materials for smart textiles-An overview." *Applied Thermal Engineering*, Vol. 28 (11), pp. 1536-1550.
11. Hosseini, M.J., Rahimi, M. and Bahrampoury, R. (2014). "Experimental and computational evolution of a shell and tube heat exchanger as a PCM thermal storage system." *International Communications in Heat and Mass Transfer*, Vol. 50, pp. 128-136.
12. Jamekhorshid, A., Sadrameli, S. M. and Farid, M. (2014). "A review of microencapsulation methods of phase change materials (PCMs) as a thermal energy storage (TES) medium." *Renewable and Sustainable Energy Reviews*, Vol. 31, pp. 531-542.
13. Alkan, C., Sarı, A., Karaipekli, A. and Uzun, O. (2009). "Preparation, characterization, and thermal properties of microencapsulated phase change material for thermal energy storage." *Solar Energy Materials and Solar Cells*, Vol. 93. pp. 143-147.
14. Zhao, C.Y. and Zhang, G.H. (2011). "Review on microencapsulated phase change materials (MEPCMs): fabrication, characterization and applications." *Renewable and Sustainable Energy Reviews*, Vol. 15, pp. 3813-3832.
15. Boh, B. and Šumiga, B. (2008). "Microencapsulation technology and its applications in building construction materials Tehnologija mikrokap- suliranja in njena uporaba v gradbenih materi- alih." *RMZ-Materials and Geoenvironment*, Vol. 55, pp. 329-344.
16. Tyagi, V.V., Kaushik, S.C., Tyagi, S.K. and Akiyama, T. (2011). "Development of phase change materials based microencapsulated technology for buildings: a review." *Renewable and Sustainable Energy Reviews*, Vol. 15, pp. 1373-1391.
17. Arshady, R. (1992). "Suspension, emulsion, and dispersion polymerization: A methodological survey." *Colloid & Polymer Science*, Vol. 270, pp. 717-732.
18. Baek, K.H., Lee, J.Y. and Kim, J.H. (2007). "Core/shell structured PCM nanocapsules obtained by resin fortified emulsion process." *Journal of Dispersion Science and Technology*, Vol. 28, pp. 1059-1065.
19. Alkan, C., Sarı, A. and Karaipekli, A. (2011). "Preparation, thermal properties and thermal reliability of microencapsulated n-eicosane as novel phase change material for thermal energy storage." *Energy Conversion and Management*, Vol. 52, pp. 687-692.

20. Wang, Y., Zhang, Y., Xia, T., Zhao, W. and Yang, W. (2014). "Effects of fabricated technology on particle size distribution and thermal properties of stearic-eicosanoic acid/polymethylmethacrylate nanocapsules." *Solar Energy Materials and Solar Cells*, Vol. 120, pp. 481-490.
21. Alay, S., Göde, F. and Alkan, C. (2011). "Synthesis and thermal properties of poly (n-butyl acrylate)/n-hexadecane microcapsules using different cross-linkers and their application to textile fabrics." *Journal of Applied Polymer Science*, Vol. 120, pp. 2821-2829.
22. Chuah, T.G., Rozanna, D., Choong, T.S.Y., Sa'ari, M. and Salmiah, A. (2006). "Fatty acids used as phase change materials (PCMs) for thermal energy storage in building material applications." *JURUTERA*, pp. 8-15.
23. Liang, C., Lingling, X., Hongbo, S. and Zhibin, Z. (2009). "Microencapsulation of butyl stearate as a phase change material by interfacial polycondensation in a polyurea system." *Energy Conversion and Management*, Vol. 50, pp. 723-729.
24. Lu, S., Xing, J., Zhang, Z. and Jia, G. (2011). "Preparation and characterization of polyurea/polyurethane double-shell microcapsules containing butyl stearate through interfacial polymerization." *Journal of Applied Polymer Science*, Vol. 121, pp. 3377-3383.
25. Bendic, R. nad Amza, G. (2012). "Use of encapsulated butyl stearate as a phase change material for thermal energy storage in intelligent building walls." *Revista De Chimie*, Vol. 63, pp. 1148-1151.
26. Alic, B., Sebenik, U. and Krajnc, M. (2012). "Microencapsulation of butyl stearate with melamine-formaldehyde resin: effect of decreasing the pH value on the composition and thermal stability of microcapsules." *Express Polymer Letters*, Vol. 10, pp. 826-836.