

# Preparation And Characterization of Cellulose Acetate Microencapsulated N-Octadecane for Thermal Regulation Applications

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**ABSTRACT:** *In this research, a systematic study was carried out to prepare microcapsules with cellulose acetate as a shell polymer and n-octadecane as a core material with a phase separation technique. This study aimed to investigate and clarify conditions for optimal morphology and behavior of these microcapsules for Phase Change Materials (PCMs). The optimal core-shell weight ratio, polymer molecular weight, and emulsification method were investigated. Using cellulose acetate with higher molecular weight (52,000 g/mol) and a core-to-shell weight ratio of 2:1, microcapsules with a high encapsulation efficiency of 86.7%, melting and crystallization enthalpies of 132.33 (J/g) and 91.24 (J/g) were obtained. It was also observed that the optimal method for preparation of the primary emulsion phase was via magnetic stirring in comparison with ultra-sonication (40.9%). The average particle size distribution of microcapsules was 20.48  $\mu\text{m}$ , with an average shell thickness of 0.777  $\mu\text{m}$ . The method used in this study was simple, fast, and low cost-effective. With an easy-to-scale-up feature, and not requiring high temperatures or phase change starters, these novel microencapsulated PCMs are ideal for industrial use.*

**KEYWORDS:** *Microcapsules; Microencapsulation; n-Octadecane; Phase Change Materials (PCMs); Thermal regulation.*

## INTRODUCTION

Phase Change Materials (PCMs) are substances that have capacity to absorb and release large amounts of latent thermal energy during the process of melting, freezing, and phase change [1-3]. PCMs are developed for various

building applications such as thermal energy storage, thermal protection, cooling, air-conditioning, and solar heating systems, as well as in textile industries for smart fabrics or garments [2, 4-9]. Generally, there are three

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types of phase change materials: organic, inorganic and eutectic. The most commonly used PCMs include hydrated inorganic salts, linear chain hydrocarbons known as paraffin waxes, polyethylene glycols (PEGs), fatty acids, polyalcohols, eutectics of organic and non-organic compounds [10, 11].

Among these phase change materials, paraffin waxes such as heptadecane, hexadecane, octadecane, nonadecane and eicosane are commonly applied to fabrics [3, 12]. They are versatile PCMs as they are melted and solidified at wide temperature ranges. Paraffin waxes have large latent heat capacity, negligible super-cooling, low vapor pressure, and self-nucleating behavior [13]. These PCMs have different phase-change temperatures ( $T_m$ ) and crystallization temperatures ( $T_c$ ) depending on the number of carbon in the molecular structure [3, 11, 12]. Unfortunately, these paraffin waxes could not be incorporated directly into fabrics due to their low melting point. Thus, they need to be microencapsulated which involves enclosing them in thin and resilient polymeric shells [3, 10, 14]. Microencapsulation allows an increase in the heat transfer area, reduces PCM reactivity towards the external environment, and helps to withstand frequent volume changes as phase change occurs [11, 13-15].

Microencapsulation methods could be broadly categorized into three types i.e. physical, physicochemical, and chemical methods [11, 16]. Among different microencapsulation methods, the most commonly carried out in the research studies are interfacial polymerization, suspension polymerization, emulsion polymerization, in-situ polymerization, spray drying, coacervation and phase separation method [11, 14-16]. The emulsification of polymer-volatile organic solvent in water followed by solvent removal is called phase separation or solvent evaporation [14-17]. Phase separation or solvent evaporation method is a relatively simple method and its experimental parameters are easy to control [14-16]. Phase separation technique is involved two main mass flows: solvent diffusion and solvent evaporation [17]. After that, the droplets of the dispersed phase become saturated in polymer due to solvent removal and they begin to solidify [17, 18]. The main advantages of the phase separation method are particle size (0.05-5  $\mu\text{m}$ ), encapsulation ratio range of 14-67% as well as its relatively low cost [16].

Cellulose Acetate (CA) is widely known as the most substantial organic ester of cellulose according to its convenient characteristics such as good stiffness and relatively low cost [19-22]. While it was initially believed that CA was virtually non-biodegradable, it has been

shown that initial partial deacetylation of cellulose backbone is readily biodegraded by cellulose enzymes. In biologically highly active soil, CA fibers are completely destroyed after 4-9 months [23]. Thus, it endeavored to prepare a series of micro-PCMs using paraffin waxes as core material and cellulose acetate as shell material.

Three types of paraffin waxes ( $C_nH_{2n+2}$ ) namely, n-hexadecane, n-octadecane, and n-eicosane are usually preferred for PCM encapsulation since they are non-toxic, non-corrosive, chemically inert, and easily obtained with no unpleasant odor [11, 12, 24]. These waxes are immiscible in water and thus, they offer an advantage to serve as an organic emulsion phase in the solvent evaporation technique [11]. n-Octadecane is an ideal PCM due to its excellent ability of thermal storage and release within an appropriate phase change temperature range (23-280°C) [12, 25]. n-Octadecane as a PCM is comfortable for human body and its latent heat (241.2 J/g) is higher than that of the other PCMs with similar phase change temperature range [12].

The aim of this study is to develop the preparation of cellulose acetate shell for microencapsulation with better stability as well as to clarify the conditions for optimization of morphologies and PCM behaviors of these novel microcapsules with n-octadecane as core material. Since the results of this method depend on many factors, the effect of different variables including the type of polymeric shell and molecular weight, core-to-shell weight ratio, emulsion method, as well as weight percent of surface active agent in the aqueous phase were investigated during the encapsulation of this phase change material.

## EXPERIMENTAL SECTION

### Materials

n-Octadecane (0.78 g/cm<sup>3</sup>, 254.49 g/mol, Merck, CAS No.: 593-45-3) was used as core material. Cellulose acetate with two molecular weights (30,000 g/mol, Sigma Aldrich and 52,000 g/mol, Fluka, CAS No.: 9004-35-7) was used as polymeric shell material. Dichloromethane (1.33 g/cm<sup>3</sup>, boiling point: 39.6°C, CAS No.: 75-09-2) and acetone (0.791 g/cm<sup>3</sup>, boiling point: 56°C, CAS No.: 67-64-1) were used as solvent and co-solvent to reduce the particle size of organic phase during emulsification. The emulsifier used was poly (vinyl alcohol) (PVA, 72,000 g/mol, Fluka, CAS No.: 9002-89-5). Distilled water and ethanol (0.789 g/cm<sup>3</sup>, Merck, CAS No.: 64-17-5) were used as continuous phases of emulsion and materials to wash microcapsules.

**Table 1: Test conditions for preparation of microcapsules**

| Number | Emulsification method | Polymer (g/mol) | Core/shell weight ratio |
|--------|-----------------------|-----------------|-------------------------|
| 1      | Ultra-sonication      | 30,000          | 2:1                     |
| 2      | Ultra-sonication      | 52,000          | 2:1                     |
| 3      | Stirring              | 52,000          | 2:1                     |
| 4      | Stirring              | 52,000          | 3:1                     |
| 5      | Stirring              | 52,000          | 1:1                     |

### Preparation of microcapsules

In order to encapsulate n-octadecane, phase separation technique was used as the main method. This technique requires an organic phase, which contains phase change material and shell polymer, to be dispersed in an aqueous phase. To prepare the organic phase, acetone and dichloromethane at a volume ratio of 40:60 were mixed and a certain amount of cellulose acetate as the shell polymer was added to this mixture at ambient temperature for 4 h. A certain amount of n-octadecane as the core phase change material was added to the mixture and mixed at ambient temperature for 2 h. The total weight of core phase change material plus shell polymer in all tests was equal to 4% wt. of entire solvent mixture. To prepare aqueous phase, polyvinyl alcohol (as a surfactant and agent to reduce the size of emulsion droplets and stability) at concentration of 3% wt. was added to distilled water and mixed at temperature of 90°C for 3 h. Volume ratio of solvent mixture to water was set at 30:70.

To obtain oil-in-water emulsion, two methods (ultra-sonication and magnetic stirrer) were utilized. For preparation of the primary emulsion of oil in water, the organic phase was first added slowly to the aqueous phase while the emulsion was stirred by a magnetic stirrer at 400 rpm. After 2 min of mixing, the emulsion was exposed to ultrasonic waves for 30 s at maximum power (400 W). The container was placed in an ice-water bath during the ultra-sonication to prevent the temperature from rising. In the second method, only a magnetic stirrer was utilized for the formation of emulsion. For this purpose, the mixing of the organic phase in the aqueous phase was carried out at 400 rpm for 2 min. Testing conditions for each sample can be seen in Table 1.

The obtained emulsion, which consisted of scattered droplets of organic phase (containing n-octadecane, cellulose acetate, dichloromethane, and acetone) in the aqueous continuous phase, was stirred by a magnetic stirrer (200 rpm) overnight at room temperature (25°C) to

attain phase separation. By evaporating the solvents (acetone and dichloromethane) in the organic phase, sequestration of n-octadecane occurred as core material by polymeric shell. Time and temperature of solvent evaporation were based on the review of preceding studies [26, 27]. After cooling the suspension to room temperature, microcapsules were separated by centrifugation for 5 min (11,500 rpm) and additional aqueous phase was drained. The microcapsules obtained were then washed with ethanol for two times.

### Characterization

#### Scanning Electron Microscopy (SEM)

The morphology of obtained microcapsules was investigated by Scanning Electron Microscopy (SEM) (LEO 1450 VP, England). Prior to imaging of microcapsules, samples were dispersed in ethanol via ultrasonic bath for 5 s. A droplet of suspension was added onto a base and set aside for 30 min to dry. Plates containing microcapsules were coated with gold-palladium by spray coating (SC7620, England).

#### Differential Scanning Calorimetry (DSC)

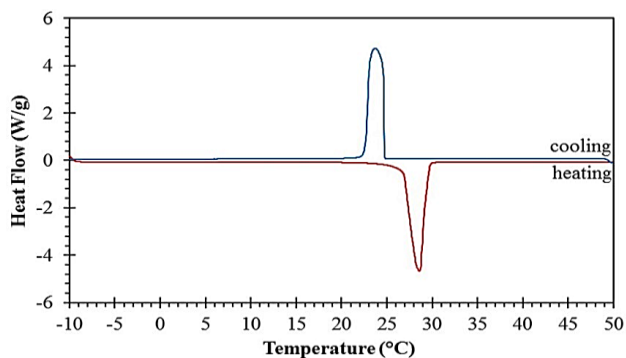
To evaluate the thermal characteristics of the microcapsules of phase change materials, Differential Scanning Calorimetry (DSC) (DSC1-Star system, Switzerland) was used. Thermal analysis was performed in a nitrogen atmosphere while heating the samples from -10°C to 50°C and then, cooling to a temperature of -10°C. The rate of temperature alteration was 2°C/min. In addition to the phase change microcapsules, pure n-octadecane was also analyzed. In all samples, the beginning of the peak was considered as the temperature of phase change. It was observed that some of microcapsules were broken and some were empty. In that case, the micro-encapsulated PCMs obtained in the real condition had a lesser amount of n-octadecane. As a result, the enthalpy of phase change materials in real conditions was reduced. To evaluate the efficiency of the microencapsulation process in different samples, Encapsulation Efficiency (EE) was used as in Eq. (1):

$$EE(\%) = \frac{\Delta H_{DSC}}{\Delta H_{cal}} \times 100 \quad (1)$$

Where  $\Delta H_{DSC}$  (J/g) is the real fusion enthalpy calculated by DSC analysis and  $\Delta H_{cal}$  (J/g) is the ideal fusion enthalpy for encapsulated phase change materials which was obtained based on Eq. (2):

**Table 2: Effects of emulsification method on thermal analysis of microencapsulation (core/shell weight ratio: 2:1 and MW: 52,000 g/mol).**

| Emulsification method | Encapsulation efficiency (%) | Melting   |                        |                        | Crystallization |                        |
|-----------------------|------------------------------|-----------|------------------------|------------------------|-----------------|------------------------|
|                       |                              | T (°C)    | $\Delta H_{DSC}$ (J/g) | $\Delta H_{cal}$ (J/g) | T (°C)          | $\Delta H_{DSC}$ (J/g) |
| Ultra-sonication      | 40.9±1.0                     | 28.10±1.0 | 62.47±2.0              | 152.56±2.0             | 25.80±0.7       | 35.09±1.0              |
| Stirring              | 86.7±1.5                     | 26.41±0.7 | 132.33±4.0             | 152.56±2.0             | 24.61±0.7       | 91.24±1.5              |

**Fig. 1: DSC curves of pure n-octadecane.**

$$\Delta H_{cal} = \Delta H_0 \times C_{core} \quad (2)$$

$\Delta H_0$  is fusion enthalpy (228.84 J/g) of pure and non-encapsulated n-octadecane and  $C_{core}$  is weight ratio of n-octadecane in the organic phase.

#### Size distribution of microcapsules

Size distribution of microencapsulated phase change materials and shell thickness were analyzed by microstructure image analysis software. The analysis was conducted only on optimized sample. This analysis was based on Fraunhofer diffraction theory. Light diffraction analysis was performed by Shimadzu SALD 210 (Japan) and the average diameter of obtained microcapsules was calculated on the basis of this analysis. Microscopic images of microcapsules were taken by Olympus camera (DP71, Japan) mounted on Olympus microscope (BX51, Japan). Then, shell thickness was measured at 20 points of two microcapsules and the averages were reported.

## RESULTS AND DISCUSSION

In order to improve the performance of n-octadecane as a phase change material in textile industries for smart fabrics or garments, this paraffin wax was encapsulated *via* a phase separation technique. In this method, a polymeric shell surrounds the molecules of n-octadecane which gives excellent properties to this PCM. Also, two phases, organic and aqueous, are needed to prepare the microcapsules.

It should be stated that cellulose acetate with two molecular weights was selected as the shell polymer. During the procedure, there are some factors such as molecular weight of shell polymer, core/shell weight ratio, and emulsification method which could have influenced the preparation and performance. These factors were properly studied in this research for n-octadecane encapsulation.

#### Effects of molecular weight

To investigate the influence of molecular weight on microcapsule features and efficiency, cellulose acetate with two molecular weights of 30,000 and 52,000 g/mol was used. Emulsification was conducted by ultra-sonication and core/shell weight ratio was 2:1. First of all, DSC analysis of pure n-octadecane was carried out as a reference to evaluate encapsulation efficiency, as shown in Fig. 1. Calorimetric results showed that temperatures of melting and crystallization of n-octadecane were at 26.70 and 24.81°C, respectively, and the enthalpy of each process was 228.84 and 244.46 J/g. DSC curves of microcapsules with two different polymer molecular weights are also shown in Figs. 2A and B. The Emulsification method in the preparation procedure was ultra-sonication. The peak of the heating curve in the obtained microcapsules was the point of phase change of n-octadecane from solid to liquid in the core of microcapsules. However, there were two peaks corresponding to crystallization,  $\alpha$  and  $\beta$  crystalline phases, in the cooling curve of n-octadecane [28]. The calorimetric results of microencapsulated PCMs obtained from cellulose acetate with a molecular weight of 30,000 g/mol demonstrated that the onset of melting temperature and enthalpy were at 28.6°C and 41.98 J/g, respectively (Fig. 2A). The onset of the temperature of crystallization of  $\alpha$  and  $\beta$  crystalline phases were shown at 23.2 and 9.2°C and enthalpy of each transition were 6.34 and 31.03 J/g, respectively. Results of thermal analysis for microcapsules prepared with cellulose acetate (MW: 52,000 g/mol) and two emulsification methods are summarized in Table 2 and Fig. 2B. Encapsulation efficiencies were calculated by Eq. (1).

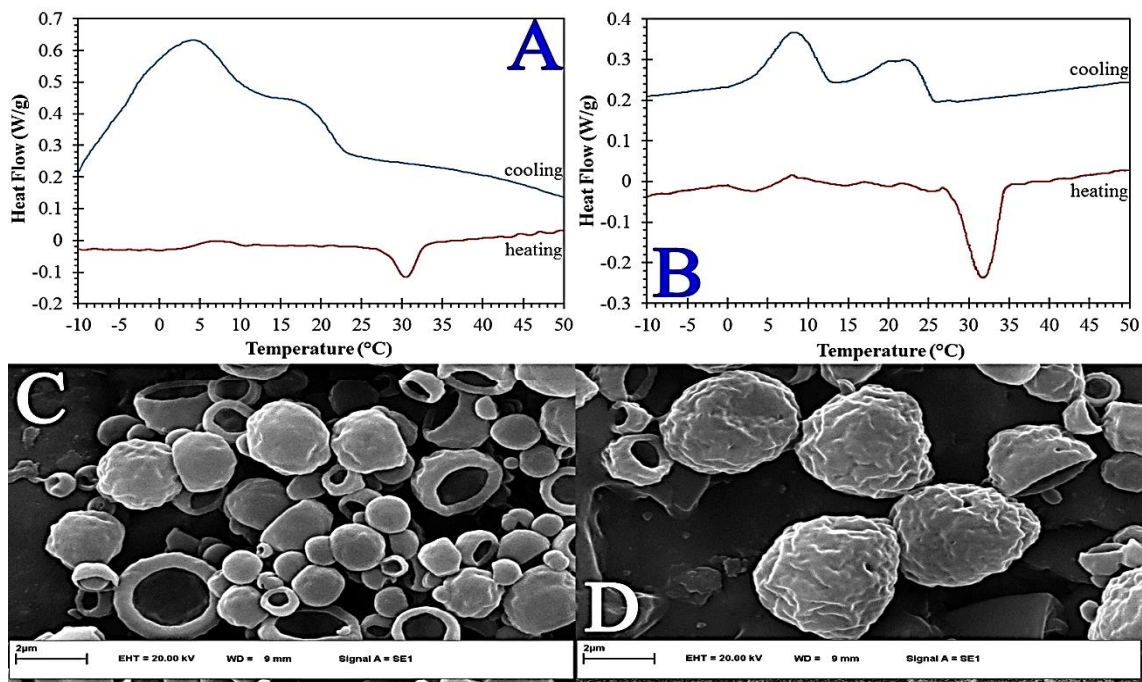


Fig. 2: DSC curves and SEM images of microcapsules composed of *n*-octadecane/cellulose acetate core/shell with a molecular weight of A, C: 30,000 g/mol and B, D: 52,000 g/mol (weight ratio of core/shell 2:1, ultra-sonication as emulsification method).

SEM images of microcapsules composed of cellulose acetate shell with two different molecular weights are shown in Figs. 2C and D. Applying cellulose acetate with a molecular weight of 30,000 g/mol resulted in inefficient encapsulation of *n*-octadecane and preparation of defective shells (Fig. 2C). After washing the microcapsules with ethanol, *n*-octadecane exuded out of defective capsules and particles remained consisting of a mixture of fully developed capsules and empty polymer shells. Thus, it was observed that phase change enthalpy and encapsulation efficiency were both reduced by decreasing the amount of *n*-octadecane encapsulated in microcapsules with low molecular weight cellulose acetate (30,000 g/mol). It should be noted that the size of microcapsules increased when the molecular weight of shell polymer from 30,000 to 52,000 g/mol increased (Figs. 2C and D). It could be described in this way that the viscosity of the organic phase increased with the increment of molecular weight. In that case, the fracture of droplets in the organic phase was more difficult during the emulsification process and thus, an emulsion with bigger droplets was constructed. Increasing the size of droplets eventually led to an increase in the size of capsules [29]. Other researchers had also reported this increment in the size of capsules by increasing the viscosity of the organic phase [18, 29]. According to the results,

cellulose acetate with a molecular weight of 52,000 g/mol was selected as a shell polymer for further experiments.

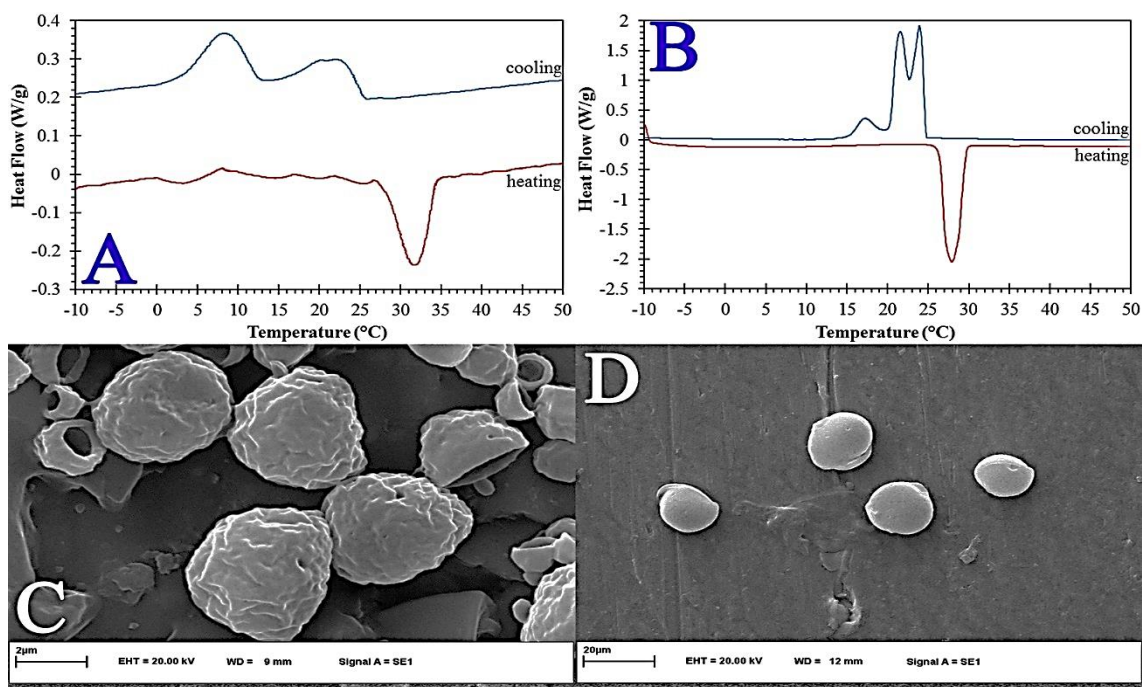
#### Effects of the emulsification method

To assess the influences of emulsification methods on the features of microcapsules, magnetic stirring, and ultrasonic waves were used to prepare oil in water emulsion. The molecular weight of shell polymer and weight ratio of core/shell was 52,000 g/mol and 2:1, respectively. Differential Scanning Calorimetry (DSC) curves of *n*-octadecane/cellulose acetate (core/shell) microcapsules prepared by magnetic stirring or ultrasonic waves are presented in Figs. 3A and B. Table 2 shows the results of thermal analysis for these *n*-octadecane capsules which were prepared by mixing the organic phase in water or applying ultrasonic waves to the pre-emulsion. Using magnetic stirring for the preparation of oil-in-water emulsions increased the enthalpies of melting and crystallization by 2.1 and 2.6 times higher than those microcapsules prepared by ultra-sonication. Also, encapsulation efficiency was equal to 86.7 which showed a significant increase compared to encapsulation with ultrasound waves (40.9).

SEM images of microcapsules obtained from ultra-sonication and magnetic stirring can be seen in Figs. 3C and D. By using ultrasonic waves, the temperature

**Table 3: Thermal properties of microcapsules with different core/shell weight ratios (MW: 52,000 g/mol, emulsification method: magnetic stirring).**

| Core/shell weight ratio | Encapsulation efficiency (%) | Melting   |                        |                        | Crystallization |                        |
|-------------------------|------------------------------|-----------|------------------------|------------------------|-----------------|------------------------|
|                         |                              | T (°C)    | $\Delta H_{DSC}$ (J/g) | $\Delta H_{cal}$ (J/g) | T (°C)          | $\Delta H_{DSC}$ (J/g) |
| 3:1                     | 29.2±0.7                     | 25.59±0.7 | 50.13±1.5              | 171.63±2.0             | 24.19±0.7       | 22.51±0.7              |
| 2:1                     | 86.7±2.0                     | 26.41±0.7 | 132.33±2.5             | 152.56±2.0             | 26.41±1.0       | 91.24±1.2              |
| 1:1                     | 87±2.0                       | 25.36±0.7 | 99.54±1.0              | 114.42±1.7             | 23.36±0.7       | 65.20±1.0              |

**Fig. 3: DSC curves and SEM images of n-octadecane/cellulose acetate core/shell microcapsules prepared by A, C: ultra-sonication and B, D: magnetic stirring (weight ratio of core/shell: 2:1, MW: 52,000 g/mol)**

in the emulsification process rose quickly so that, rapid evaporation of solvent occurred and as a result, rapid deposition of polymer. This phenomenon caused the polymer chains to have insufficient time for proper alignment and thus, a fair number of cellulose acetate shells were perfectly formed (Fig. 3C). On the other hand, n-octadecane encapsulation with high efficiency took place when magnetic stirring was utilized, as shown in Fig. 3D. It was obvious that polymeric shells were completely created without defects. In addition, emulsification by magnetic stirring was associated with a noticeable and significant increase in the size of resulting microcapsules. In the literature, emulsification efficiency by ultrasonic waves was compared with other mechanical methods. Gaikwad and Pandit showed that by using ultra-sonication, the size of droplets in the emulsion was much smaller,

compared to mechanical stirring under similar conditions [30]. Abismail et al. showed that the size of droplets becomes smaller when the ultrasonic device is utilized instead of a mechanical stirrer, and also, less energy was required to achieve a specific diameter, compared to emulsions prepared by mechanical stirring [31].

#### Effects of core/shell weight ratio

To study the effect of core/shell weight ratio on n-octadecane encapsulation, three core/shell weight ratios were utilized, i.e. 1:1, 2:1 and 3:1. DSC curves obtained for these weight ratios of core/shell microcapsules are presented in Figs. 4A-C. Results for the capsulation efficiency in the samples and parameters of thermal analysis were calculated and reported in Table 3. Microcapsules that were produced with a core/shell ratio of 3:1 demonstrated



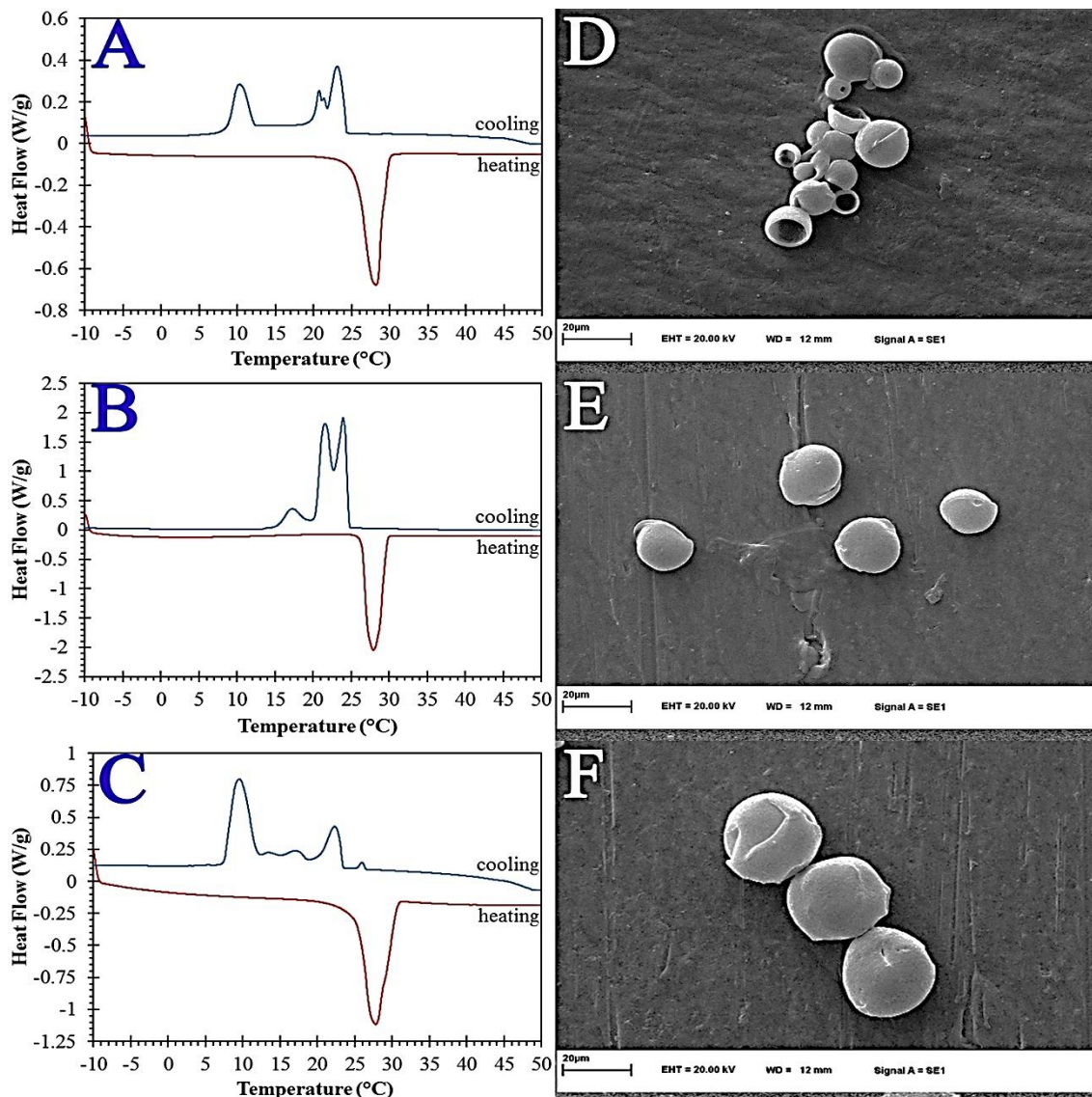


Fig. 4: DSC curves and SEM images of microcapsules composed of *n*-octadecane/cellulose acetate core/shell with weight ratios of A, D: 3:1, B, E: 2:1 and C, F: 1:1 (MW: 52,000 g/mol, magnetic stirring as emulsification method).

low enthalpy of melting and crystallization, i.e. 50.13 and 22.51 J/g, respectively (Fig. 4A). Encapsulation Efficiency (EE) in this ratio was also found to be very low (29.2%). A high core/shell weight ratio resulted in a low concentration of cellulose acetate in the organic phase, leading to the formation of imperfect capsules. The incomplete formation of capsules caused *n*-octadecane to leak out of the final product, thereby reducing the enthalpy of phase change and microencapsulation efficiency. By raising the core/shell weight ratio up to 2:1 with sufficient concentration of polymer, complete shell formation and increment of *n*-octadecane in the system occurred (Fig. 4B). Both melting enthalpy and encapsulation

efficiency increased to 132.33 J/g and 86.7%, respectively. By reducing the core/shell weight ratio to 1:1 and thus, further increase in cellulose acetate concentration in the organic phase with sufficient concentration, complete polymer shells were formed (Fig. 4C). Thus, leakage of *n*-octadecane was prevented and efficiency of microencapsulation increased to a significant amount, i.e. 87%. Despite high encapsulation efficiency in the core/shell weight ratio of 1:1 (87%), melting enthalpy of microcapsules fell to 99.54 J/g, compared to the core/shell weight ratio of 2:1 (132.33 J/g). This phenomenon is due to a reduction in *n*-octadecane concentration during the initial organic phase which reduces the amount of *n*-octadecane in the final capsules.

**Table 4: Thermal properties of different microcapsules with different core/shell weight ratios**

| Core/shell weight ratio | AS               |          | ABS              |          | PC               |          |
|-------------------------|------------------|----------|------------------|----------|------------------|----------|
|                         | Heating enthalpy | EE (%)   | Heating enthalpy | EE (%)   | Heating enthalpy | EE (%)   |
| 2:1                     | 82.6±2.0         | 61.3±0.7 | 57.1±1.5         | 42.4±1.5 | 45.4±0.7         | 33.5±1.0 |
| 4:1                     | 113.5±2.1        | 70.2±1.0 | 107.1±2.0        | 66.3±1.5 | 49.5±1.0         | 30.6±0.7 |
| 5:1                     | 142.3±2.2        | 84.6±1.0 | 40.6±0.7         | 24.1±0.5 | 7.0±0.1          | 4.2±0.1  |

Yang et al investigated the effect of core/shell weight ratio in microencapsulation of n-tetradecane with acrylonitrile-butadiene-styrene (ABS) terpolymer, polycarbonate (PC) and acrylonitrile-styrene (AS) copolymer shell [14]. Microcapsules with different core/shell weight ratios were prepared to find the most stable and optimal condition for the greatest phase change enthalpy (Table 4).

SEM images of prepared microcapsules in different proportions of core/shell weight ratio are shown in Figs. 4D-F. In the weight ratio of 3:1 core/shell, polymer concentration in the organic phase was low, resulting in the inability polymer of forming a complete shell which was lack of defects (Fig. 4D). This was associated with the reduction of phase change enthalpy and encapsulation efficiency. According to Figs. 4E and F, the reduction of core/shell weight ratio was accompanied by an increase in the polymer concentration during the organic phase, resulting in an improvement of the shape of capsules, complete shell formation and overall enhancement of process efficiency. Additionally, Figs. 4D-F shows that with a reduction of core/shell weight ratio and an increase in the polymer concentration in the organic phase, the size of the capsule increased. As mentioned before, with an increase in polymer concentration, higher viscosity of the internal phase in the emulsion (organic phase) ensued [17]. The higher viscosity of the internal phase entailed greater energy/power for breaking droplets in this phase during emulsification [18, 29]. Increasing the size of capsules with phase change materials by reducing the core/shell weight ratio is consistent with the results of previous literature [18, 29, 32].

#### **Properties of optimal microcapsules**

Among variables considered in this study for the encapsulation of n-octadecane, the highest enthalpy of phase change was obtained using cellulose acetate with a molecular weight of 52,000 g/mol, core/shell weight ratio of 2:1 and magnetic stirring as an emulsification method (Fig. 4B). The results of the thermal analysis indicated that

encapsulation in this condition led to the formation of microcapsules such that the melting process of phase change material was started at 26.41°C along with the enthalpy of 132.33 J/g. n-Octadecane crystallization in these capsules was begun at 26.41°C, accompanied with the enthalpy of 91.24 J/g. The encapsulation efficiency in this condition was 86.7% (Table 3).

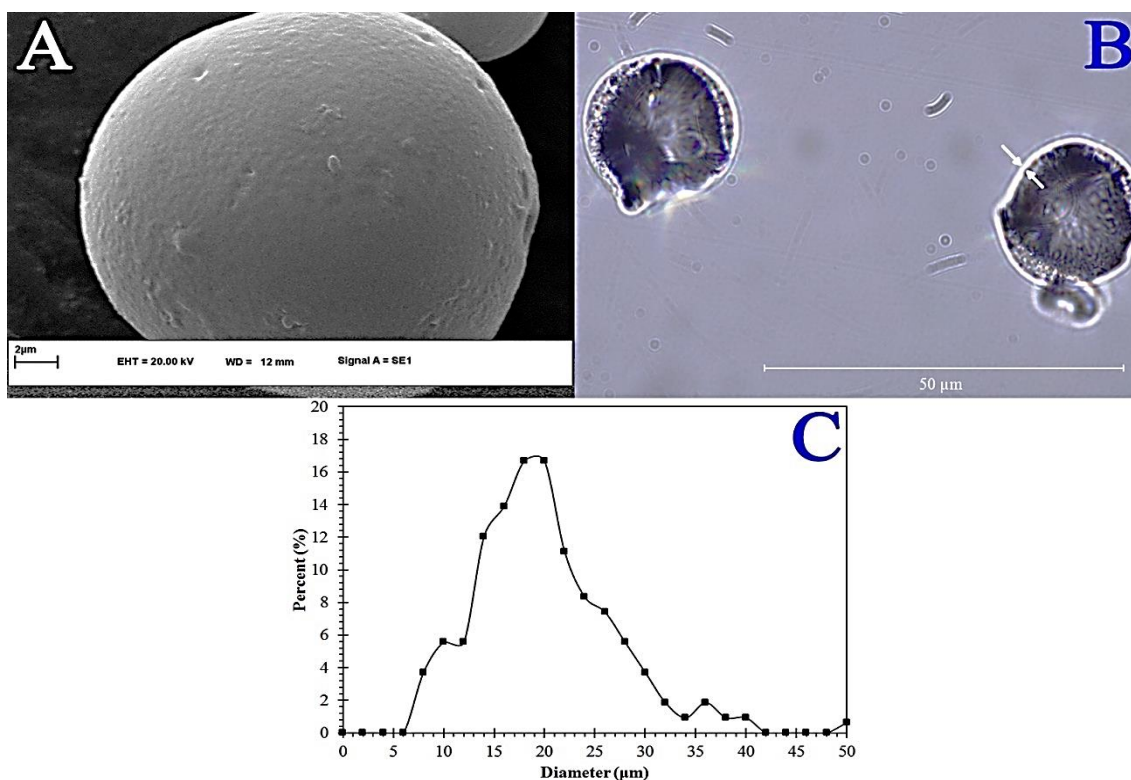
SEM image of prepared microcapsules is shown in Fig. 5A with high magnification. Surface morphology clearly indicated that the capsule shell was complete without structural defects, allowing the use of these capsules without n-octadecane leakage. Fig. 5B shows optical image of prepared microcapsules in the optimal condition. It was obvious that the capsule had core-shell morphology with a thin polymeric shell layer completely formed around capsule without flaws. The average wall thickness of polymeric capsules was 0.777 μm which was calculated by analyzing the image using image processing software. The type of refraction in the capsule indicated that the capsules were not empty, but contained n-octadecane. Particle size distribution of n-octadecane microcapsules is presented in Fig. 5C which revealed the average particle diameter was equal to 20.48 μm. Various different research studies indicated that microencapsulated PCM like ethyl cellulose/hexadecane (shell/core) with an average diameter of 85 μm [13] and 92 μm [2] and acrylonitrile-styrene/tetradecane (shell/core) with an average diameter of 0.7 μm, and acrylonitrile-butadiene-styrene/tetradecane (shell/core) with an average diameter of 0.4 μm [14] had been made by phase separation technique.

The results of this study were compared with other research which are presented in Table 5. According to Table 5, the melting enthalpy of n-octadecane microcapsules obtained in the literature was in the range of 124-157 J/g. In this research, microcapsules with small particle sizes of 20.48 μm and high melting enthalpy (132.33 J/g) were obtained in this range. In addition,



**Table 5: Comparison of *n*-octadecane capsules with various polymer**

| Shell material                    | Mean particle size ( $\mu\text{m}$ ) | Melting temperature | Melting enthalpy | Ref.       |
|-----------------------------------|--------------------------------------|---------------------|------------------|------------|
| Cellulose acetate                 | 20.48                                | 26.41               | 132.33           | This study |
| Melamine-formaldehyde             | -                                    | -                   | 135              | [34]       |
| Melamine-formaldehyde             | 20.0                                 | 20                  | 135              | [12]       |
| Styrene                           | 0.1                                  | 35-23               | 124              | [35]       |
| Styrene-divinyl benzene Copolymer | 80.0                                 |                     | 125              | [36]       |
|                                   | -                                    | 31                  | 157              | [17]       |



**Fig. 5: A: SEM image, B: optical image and C: particle size distribution of *n*-octadecane/cellulose acetate core/shell with high magnification (MW: 52,000 g/mol, core/shell weight ratio: 2:1, magnetic stirring as emulsification method)**

the method used in this study was simple, fast and cost-effective [33]. It was also easy to scale up and did not require high temperatures or a phase change starter [13, 32]. All of these were conditions that could be best used for the preparation of microencapsulated phase change material at the industry level.

## CONCLUSIONS

Microcapsules containing *n*-octadecane/cellulose acetate (core/shell) were successfully prepared by phase separation technique. To acquire microcapsules with high heat and encapsulation efficiency, effects of polymer

molecular weight, emulsification method and core/shell weight ratio were studied. DSC analyses and SEM images confirmed that using shell polymer with molecular weight of 52,000 g/mol, 2:1 core/shell weight ratio and magnetic stirring for emulsification, microcapsules with high performance were prepared. In optimal condition, microcapsules showed onset of melting and crystallization temperature of 26.41 and 24.61 $^{\circ}\text{C}$  with enthalpy of melting and crystallization of 132.33 and 91.24 J/g along with encapsulation efficiency of 86.7%. Surface morphology in SEM images showed that the capsules shell was formed completely and without structural defects. Optical image

of prepared microcapsules in optimal condition revealed that the capsule has core-shell morphology with a thin polymeric shell layer completely formed without flaws. The average wall thickness of polymer capsules was 0.777  $\mu\text{m}$  and particle size distribution was equal to 20.48  $\mu\text{m}$ .

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