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# Synthesis of a Novel Nanoencapsulated n-Eicosane Phase Change Material with Inorganic Silica Shell Material for Enhanced Thermal Properties through Sol-Gel Route

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# Abstract

A novel nanoencapsulated phase change material (PCM) based on an n-eicosane core and an inorganic silica shell was synthesized through sol-gel route by using tetraethyl-orthosilicate (TEOS) and sodium silicate as an inorganic silica-precursor at different conditions for enhanced thermal stability and phase change properties. Fourier transform infrared spectra confirm the chemical composition of synthesized nanocapsules. Scanning electronic microscopic images show that the nanocapsules consist of spherical morphology. Furthermore, nanocapsules present different particle size range between 250-550 nm with respect to their pH values; the optimum pH for n-eicosane/TEOS nanocapsules is 2.20, and 2.94 for n-eicosane/sodium silicate, respectively. In addition to this, capsules synthesized by using TEOS show small particle size distributions as compared to the ones integrated by using sodium silicate as a silica-precursor. Differential scanning calorimetry suggests that by controlling the acidity of the reaction solution nanoencapsulated n-eicosane/silica can achieve good phase change properties and high encapsulation efficiency. Thermogravimetric analysis (TGA) shows that silica-nanocapsules have good thermal stability and phase change performance. Synthesis of nanoencapsulated n-eicosane (PCM) with the silica shell material through sol-gel process can be a perspective technique to prepare the nano-PCMs with enhanced thermal transfer and phase change properties for potential applications to thermal-regulating textiles and fibers.

**Keywords:** N-eicosane; Sol-gel process; Nanoencapsulation; Silicaprecursors; Thermal and phase-change performance

# Introduction

In the past two centuries the industrial development has produced remarkable wealth and brought prosperity to the whole world. However, it has also triggered a series of environmental issues [1]. Therefore, the development of new energy storage materials has been drawing huge attention in both academic and industrial communities all around the globe [2]. Phase change materials (PCMs) are considered as a good candidate with efficient utilization of energy to reduce the dependence on traditional fossil energy sources [3]. PCMs can also be used for thermal-regulating fiber and textiles [4]. When PCMs are integrated into fibers or textile materials, they can change their phase from solid to liquid to absorb the access heat as the temperature increases above the human body temperature. Otherwise, when the temperature decreases below the human body comfortable temperature these PCMs change their phase from liquid to solid by desorbing heat [5]. During this phase-change process these PCMs can actually bring the human body to the comfortable feel [6].

The organic n-alkanes (paraffin waxes), fatty alcohols, fatty acids, neopentyl glycol, eutectic mixtures, and some inorganic substances like salt hydrates are most usually applied PCMs to the thermal regulating fiber and textiles, which have high phase change enthalpies between 150 and 240 J/g [7]. Especially paraffin waxes (n-alkanes), are one of the most promising organic PCMs, can be generally applied in textiles like garments and home furnishing products [8,9]. These linear hydrocarbons have suitable melting–freezing temperature range between 18°C and 36°C, making humans feel comfortable [10,11].

However, these paraffin PCMs are mobile when molten to low viscous liquids and may diffuse throughout other materials which leads to a decrease in their lifespan [12]. Hence, the use of pristine PCMs is usually not endorsed in most cases. Therefore the encapsulation of PCMs has been considered as a vital solution for the problems

mentioned above. The encapsulated PCMs cannot only maintain their microscopic solid form during the phase change processes to improve the ease of handling but also provide a large heat transfer area [13]. Most of the literatures indicated that both organic polymers and inorganic materials could be employed as shell materials to encapsulate PCMs through chemical processes; such as suspension polymerization [14], interfacial polycondensation [15], *in situ* polycondensation [16], *in situ* precipitation [17] and other special *in situ* processes [18]. These shell materials covered polyurea-formaldehyde resin [19], melamine-formaldehyde resin, poly(methyl methacrylate) (PMMA) [20], polystyrene [21], CaCO<sub>3</sub> [22], SiO<sub>2</sub> [23], TiO<sub>2</sub> [24], Al<sub>2</sub>O<sub>3</sub> [25], and so more.

Though, these polymeric wall materials have some drawbacks, such as flammability, low mechanical strength and poor thermal and chemical stability [26,27]. Most of inorganic materials show a better rigidity and strength than the polymeric ones, and therefore, a high-strength inorganic shell material not only improves the thermal transfer performance of a PCM system but also increases the durability and working reliability of encapsulated PCMs [27,28]. Recently, silica materials as carriers in controlled drug release, has gained growing interest due to their several attractive features such as stable structure, high surface area, tunable pore sizes, well-defined surface properties,

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nontoxic nature [29], and good biocompatibility [29]. Moreover, these silica spheres expedite a high storage capacity, chemical, thermal, excellent thermal conductivity, and environmentally inert characteristics [30].

As cited in many articles, the inorganic silica was most employed as a wall material for the encapsulation of PCMs. Wang et al. [31] first reported the encapsulation mechanism of PCMs with silica through *in situ* polycondensation in an oil-in-water emulsion. Li et al. [32] and Fang et al. [33] reported the synthetic method of the silica/paraffin phase-change composites through interfacial polycondensation and found that these phase change composites exhibited a good heat storage performance and also had a form-stable feature. Jin et al. [34] developed a one-step synthetic method for the microencapsulated PCMs with the silica wall in dispersant free condition.

In this article, we attempted to nano-encapsulate the n-eicosane PCM with silica wall, n-eicosane is an important member of the paraffin family, it has been used as a thermal-regulating functional PCM for clothing application due to its appropriate phase-change temperature around 37°C, comfortable for the human body as well as its high latent heat of around 248 J/g. Nanocapsules were prepared by sol-gel method through an oil-in-water (O/W) emulsion route due to its easy control over size and morphology of the capsules and size distributions. The PCM material first dispersed in an aqueous solution to form droplets with the aid of surfactant, which resulted in a stable O/W emulsion. Low-temperature hydrolysis and condensation reactions occurred to accomplish the gelation of the solution. In this study we extract silica wall material by using two different precursors; Tetraethyl-orthosilicate (TEOS) and sodium silicate, though both are inorganic materials with their own advantages and disadvantages, generally TEOS is more often used in laboratory-scale work due to its high cost as a raw material on other hand sodium silicate consider to be easy available and of low cost as compared to TEOS. The aim of this work to develop a novel inorganic encapsulation technique for PCMs to enhance their performance in heat energy storage and thermal regulation, and to investigate the formation mechanism of these silica nanocapsules, influence of pH range and comparison of two different precursors.

# **Experimental section**

# Materials

Tetraethyl orthosilicate (TEOS), Sodium silicate and hydrochloric acid (HCl 36.46 wt%) were purchased from Sinopharm Chemical Reagents Company, China. N-eicosane with the purity of (99 wt%) and Poly (ethylene oxide-b-propylene oxide-b-ethylene oxide) triblock copolymer (PEO-PPO-PEO, Pluronic P123) were commercially obtained from Shanghai Vita chemical Reagents Company, China. All chemicals were of reagent quality and used without further purification.

# Synthesis of capsules

A series of nanoencapsulated n-eicosane with silica shell were synthesized at various pH values through a sol-gel route by using two different silica-precursors. The nanoencapsulation of n-eicosane was derived from the hydrolysis and condensation reactions of TEOS/ sodium silicate in an O/W emulsion and HCL was used as a catalyst. A synthetic procedure for TEOS derived n-eicosane/silica capsules is described as follows: In one beaker, PEO-PPO-PEO (0.25 g) was dissolved in 150 ml deionized water at 55°C. When the emulsifier completely agitates in water and the temperature become stable then, n-eicosane (15.0 g) was added into this solution and continuously stirred for 3 h to form a stable emulsion. In another beaker, the mixture of TEOS (15.0 g) was taken and to get the desired pH value, HCl aqueous solution was added dropwised and stirred at 35°C until a homogeneous solution was obtained, indicating that the hydrolysis of the TEOS was completed and the silica-sol solution as encapsulation precursors was formed. Subsequently, the silica-sol solution was added drop wise into the prepared emulsion and kept it stirring for 24 h to complete the gel process.

Procedure for sodium silicate derived n-eicosane/silica capsules is described as follows: PEO-PPO-PEO (0.5 g) was dissolved in one beaker with 250 mL of deionized water at 70°C. Then, n-octadecane (10.0 g) was added into this solution, and to get a stable emulsion continually stirred it for 1 h to form a stable emulsion. In another beaker, sodium silicate (5.0 g) was dissolved in 50 mL of deionized water at 35°C, and the HCl aqueous solution was added to obtain a desired pH value under a vigorous stirring until a homogeneous solution was obtained. Which indicated that the silica-sol solution was formed as silica monomers and oligomers and hydrolysis of sodium silicate was completed. Afterwards, this silica sol solution was added dropwise into the prepared n-eicosane emulsion under continuous stirring. This mixture was heated to 70°C with agitation for 24 h to complete the silicate condensation.

After filtration and washed with deionized water some white powders were collected. Finally, the silica-nanoencapsulated n-eicosane was obtained after being washed with ethanol to effectively remove the residual surfactants and drying at 50°C overnight.

#### Characterization

Morphologies of nanocapsules were obtained by using scanning electron microscope (SEM, SU1510). During the synthetic process before filtration, the status of the nanocapsules was monitored by Moritex ML-Z07545D optical microscope equipped with JVC TK-C9201EC digital camera. The size of nanocapsules was detected using NanoBrook Omni (280039) a laser particle size analyzer, and the mean diameters of the silica-nanoencapsulated n-eicosane were determined.

Fourier transform infrared (FTIR) spectra of the sample were obtained by using a Nicolet iS10 FT-IR spectrometer (Thermo Fisher Scientific), which were recorded in the range of 400-4000 cm<sup>-1</sup>.

PCMs were measured through differential scanning calorimetry instrument (DSC-Q200) with the scanning rate of 10°C/min in nitrogen atmosphere. DSC curves were recorded with the temperature ranging from 5 to 50°C with a scanning rate of 10°C/min. The precisions of measurements were  $\pm 2.0\%$  and  $\pm 2.0$ °C for calorimeter and temperature, respectively.

Thermogravimetric analysis (TGA) for the nanocapsules was carried out at a heating rate of 10°C/min under a nitrogen atmosphere from room temperature to 550°C by using a TA thermal gravimetric analyzer.

# **Results and Discussions**

#### Synthesis mechanism of nanocapsules with silica wall

Nano-encapsulation of n-eicosane PCM with inorganic silica was achieved via sol-gel process through *in situ* condensation. Figure 1 shows the schematic route of this sol-gel synthesis. This encapsulation mechanism is described as follows: Firstly the oily n-eicosane was dispersed in an aqueous solution including a nonionic emulsifier. To obtain the stable O/W emulsion, vigorous agitation was carried out. During this period, the hydrophilic segments of the emulsifier alternatively arrange along its hydrophobic chains, and thus are linked with the water molecules and trimly cover the surface of the oil droplets of n-eicosane with hydrophobic chains oriented into the oil droplets and hydrophilic groups out of the oil droplets. One the other hand, the silica sol was prepared by dissolving TEOS/sodium silicate in water under acidic conditions. The reaction can be explained as the hydrolysis and condensation processes of the silica source. In case of TEOS, hydrolysis reaction occurs in the presence of an acidic catalyst with a controlled pH around 1.9-2.5. The hydrolysis rate of TEOS is significantly higher than the condensation rate of the silica precursors at pH around 2.0. When the silica-sol solution is added drop wise into the emulsion containing n-eicosane micelles, these silica precursors are attracted onto the surfaces of the micelles through a hydrogen-bonding interaction between the silanol groups and the hydrophilic PEO segments of the surfactant, and by mixing the silica-sol solution with the emulsion reduces the concentration of hydrogen ions, which results in a rise in pH values. This leads to an acceleration of the condensation rate of the silica precursors, while an opposite trend occurs for the hydrolysis rate as long as the pH value is below 7. Here, the alcoholysis and oxolation reactions become dominant, and consequently, though this sol-gel process a silica shell is successfully fabricated onto the surface of the n-eicosane droplets.

# Microstructure and particle size and distribution of nanocapsules

Images were taken by using optical microscope, when the reaction was completed in the solution before the filtration of nanocapsules. Figure 2a and 2b displays the formation of n-eicosane/TEOS nanocapsules in the solution and Figure 2b and 2d shows n-eicosane/ sodium silicate, respectively. Growth of nanocapsules can be seen in all images, which illustrates the successful encapsulation of PCM in silica wall material.

Figure 3 shows the SEM images of the nanoencapsulated n-eicosane/ silica synthesized at different pH values and silica-precursors. It can be observed from these micrographs that the nanocapsules obtained by n-eicosane/TEOS at pH 2.20 demonstrate some regular spheres with the diameter of about 330 nm, and these well-defined nanocapsules have very compact and even surfaces (Figure 3a and 3b). However, in case of TEOS when the pH was under 2 (Figure 3c and 3d), it is observed that the condensation rate of the silica precursors is so slow in the solution at pH 1.88 in this case, the shell is so thin that it can easily be cracked by brisk agitation, and then the subsequent silica oligomers continuously accumulate on the surface of the nanocapsules. As a result, the nanocapsules synthesized at pH below 2 have a thin and porous silica shell with a rough surface. However, when the acidity of the reaction solution increases the surface structure becomes finer. Figure 3e and 3f shows the morphologies of n-eicosane/sodium silicate nanocapsules, these capsules also shows spherical morphologies but it is found that they have bigger diameters about 528 nm at pH 2.94. Thus the most important factor along with temperature and agitation is pH, the capsules synthesized at pH values (2.9-3) have shown good spheres for sodium silicate but in case of TEOS best morphologies were obtained in the range of (pH 1.9-2.3).

The particle size and distribution of the silica nanocapsules synthesized at different pH values and silica-precursors were determined by using a laser particle size analyzer. The obtained mean diameters are listed in Table 1, and the size distribution plots are displayed in Figure 4, which indicates a multidispersed particle size distribution. Though there is a uniform Gaussian distribution for these nanocapsules, it can also be noted that there are small differences in the mean particle sizes and size distributions of the nanocapsules obtained under different conditions. It is obvious that the acidity of the reaction affects the particle size and size distribution with great impression. For the sample (a) synthesized with n-eicosane/TEOS at pH 2.20 exhibit a greater mean particle size and broader distributions than sample (b and c) which were synthesis under different pH values, whereas (b and c) showed wider size distributions than sample (a). The nanocapsules synthesized with n-eicosane/sodium silicate at pH 2.94 (Figure 4e) exhibit large mean particle size of 528 nm compared to the sample obtained at pH 2.50 (Figure 4d).

Evidently, the acidity plays an important role in the formation of the shell materials, and silica condensation can be conducted continuously and steadily with the proper acidity of the reaction solution. Figure 4d and 4e, when the acidity of the reaction increases to pH 2.94 from pH 2.50 the silica condensation also accelerates and more original n-eicosane micelles are encapsulated and we can see the wider particle size distribution. The effect of different silica-precursors on particle size and size distribution of nanocapsules is also illustrated in Figure



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Figure 2: Optical microscope images of the n-eicosane nanocapsules after completeion of 24 h reaction in solution before filtration and washing; (a and b) n-eicosane/TEOS at pH 2.20, (c and d) n-eicosane/sodium silicate at pH 2.94.





4 and Table 1. It is found that the nanocapsules synthesized with n-eicosane/TEOS have a small mean particle size as compared to the n-eicosane/sodium silicate. As it can be seen, the mean particle size of the sample (b) is 274 nm and when the pH value decreases to pH 1.88,

the mean particle size also increases. And the samples (d, e) prepared with n-eicosane/sodium silicate showed large mean particle sizes. This result indicates that the size of silica-encapsulated n-eicosane is strictly dependent on the pH values, which determines the ultimate particles size of the nanocapsules.

# **Chemical composition**

In Figure 5a displays the FTIR spectra of the bulk n-eicosane and n-eicosane/TEOS nanocapsules synthesis at different pH values and Figure 5b shows the FTIR spectra of bulk n-eicosane and n-eicosane/ sodium silicate nanocapsules prepared at different pH values respectively. In the spectrum of pure n-eicosane and n-eicosane/ TEOS the C-H bonding vibrations at 1471 and 1376 cm<sup>-1</sup> are due to methylene brides and the alkyl C-H stretching vibrations of methyl and methylene groups can be seen at 2921 and 2851 cm-1, respectively. (Figure 5a). It is found that the spectra of all the silica nanocapsules prepared by TEOS are quite similar, in which the peaks at 1082 and 457cm<sup>-1</sup> are respectively attributed to asymmetric and symmetric Si-O-Si stretching vibrations of the silica shells. However, n-eicosane/sodium silicate nanocapsules displayed only one Si-O-Si vibration at 1064 cm<sup>-</sup> <sup>1</sup>(Figure 2a). In Figure 2a an intense absorption band at 954 cm-1 and a weak one is at 3385 cm-1 assigned to Si-OH bending and stretching vibrations as in Figure 5b at 958 cm-1 and at 3390 cm-1, respectively. It is noteworthy that all the characteristic peaks of n-eicosane can be distinguished in the spectra of the nanocapsules, which confirms the successful encapsulation of n-eicosane within the silica shell. As the nanocapsules were synthesized through the condensation of the silica precursors via a so-gel route, it is expected that a large number of silanol groups could be detected on their silica shells.

# Phase-change performance

Dynamic DSC scans were performed to examine the phase

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Sample code	n-Eicosane/Silica precursor ratio (wt/wt)	Acidity (pH)	Mean diameter (nm)	T <sub>c</sub> (°C)	T <sub>m</sub> (°C)	Encapsulation ratio (%)	Encapsulation efficiency (%)	Char yield at 500°C (wt%)
1	100/0	-	-	33.6	38.6	-	-	-
2	50/50 (TEOS).	2.25	298	32.1	39.8	79.5	77.8	14.45
3	50/50 (TEOS)	1.88	274	33.1	40.8	70.2	70.5	17.42
4	50/50 (TEOS)	2.2	348	33.3	39.8	74	72.4	13.1
5	50/50 (S.S)	2.94	528	30.5	38.5	56.6	60.6	14.1
6	50/50 (S.S)	2.5	472	29.4	41	21.3	21.5	23.41

Table 1: The mean particle sizes, melting and crystallization temperatures and thermal performances of nanoencapsulated n-eicosane/silica.



change behavior and latent heat storage performance of nanocapsules synthesized at different pH values and by using two different silicaprecursors. The DSC curves and phase change temperatures is presented in Figure 6 and Table 1, respectively. It is noteworthy in Figure 6a that pure n-eicosane exhibits a bimodal phase transition behavior with two exothermic peaks during its crystallization process. A number of studies have indicated that normal alkanes like n-eicosane usually present a rotator phase above the bulk crystallization temperature during the phase transition from liquid to solid [35]. Such a metastable rotator phase is considered as the orthorhombic rotator phase with molecules untitled with respect to the layers. As a result, pure n-eicosane has to undergo twice phase transitions between the isotropic liquid and stable orthorhombic phases. The first transition is from the homogeneously nucleated liquid to the rotator phase, and the second one is from the heterogeneously nucleated rotator phase to the crystalline phase. This leads to the presence of rotator-phase-transition peak at a temperature higher than the crystallization temperature in the DSC thermogram. However, pure n-eicosane only exhibits a single endothermic peak at 38.6°C in the melting process. It is noteworthy in Figure 6a and 6b that pure n-eicosane generates phase change enthalpies of 240 and 235 J/g during the crystallization and melting processes, respectively. This indicates the excellent latent-heat storage–release performance for pure n-eicosane as an organic PCM. It can be found that the melting curves of nano-encpsulated n-eicosane are become wider which shows their melting points are improved.

It can also be observed from Figure 6a and 6b that the encapsulation of n-eicosane into silica wall significantly influences the phase change performance of the n-eicosane core, although the nanocapsule samples synthesized by using TEOS as a silica-precursor demonstrate a phase change behavior similar to pure n-eicosane at different pH values, But sample (6) which was prepared by using sodium silicate as a silica precursor at pH 2.50 found to have the lowest enthalpies, probably due to the worst encapsulation ratio, though sample (5) at pH 2.94 showed quite superior phase change properties and enthalpies.

Encapsulation ratio and encapsulation efficiencies are two important parameters in describing the phase-change properties of the nanoencapsulated n-eicosane, and can be determined by the results from the DSC measurements. As one of the most important phasechange performance affecting the working effect of the nano-PCM, the phase-change enthalpy strongly depends on the encapsulation ratio and encapsulation efficiency of the silica nanoencapsulated n-eicosane. The values can be found in Table 1. The actual encapsulation efficiency (E) of nanocapsules was calculated by the following equation 1.

$$\mathcal{R} = \frac{nano \ (\Delta Hm)}{PCM \ (\Delta Hm)} \times 100\%$$

Nano  $(\Delta H_m + \Delta H_c)$  in the equation represented the plus of melting and crystallizing enthalpy from nanocapsules. PCM  $(H_m + H_c)$  was the plus of melting and crystallizing enthalpy from PCM. The encapsulation ratio (R) can be calculated by following equation 2.

$$\mathcal{R} = \frac{nano \ (\Delta Hm)}{PCM \ (\Delta Hm)} \times 100\%$$

Where  $\Delta$ Hm is the fusion heat of nano-PCM and bulk n-eicosanen respectively. Encapsulation ratio describes the effective encapsulation of n-eicosane within the nanocapsules while the loading content is considered as dry weight percent of the core material. Melting and crystallization enthalpies of silica-nanocapsules are shown in Figure 7.

# Thermal stability

Figure 8a shows the digital photographs of the n-eicosane/silica nanocapsules and Figure 8b of pure n-eicosane respectively, while heating at 60°C on a hot stage. These photographs were taken at different melting stages so as to record the change of shape for two specimens; n-eicosane/silica nanocapsules and pure n-eicosane, during melting process. It is witnessed that pure n-eicosane gradually lost its original shape due to a transformation from solid to liquid state while melting, and it cannot be recovered to its original shape when cooling. However, the n-eicosane/silica nanocapsules were kept its original triangle shape during long-term heating at a temperature above the melting point of n-eicosane. There is no difference in shape between the original sample and the recovered one, and it appears that no liquid n-eicosane is found to leak out of the capsules. These results indicate that the n-eicosane core is well encapsulated within the silica material and isolated it from the outside environment. In this case, the silica layer could not only maintain the original shape of PCMs but also could provide a good protection for the encapsulated PCMs, preventing the molten n-eicosane from leakage accordingly.

For the applications of nanoencapsulated n-eicosane/silica in heat energy storage and thermal regulation, thermal stability is a significant factor to be evaluated. The thermal stability of the silica nanocapsules synthesized under different pH values and silica precursors was investigated by means of TGA, which presents the mass loss of samples and corresponding temperature. The thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) curves are represented in Figure 9a and 9b, respectively and obtained char yield (wt%) is also presented in Table 1. It is observed that the weight loss profiles of all



Figure 5: FTIR spectra of bulk and nanoencapsulated n-eicosane synthesized at different pH values and silica-precursors: (a) n-eicosane/TEOS; (b) n-eicosane/sodium silicate.





Figure 7: Phase change enthalpies of bulk n-eicosane and silica nanocapsules synthesized at different conditions.

the nanocapsules are quite similar, and their thermal decompositions performed in the temperature range off 35-500°C and occur through two-step decomposition. It can be easily found that silica nanocapsules, which were synthesized at optimum pH values, they start loosing their weight after reaching at higher temperatures, due to high encapsulation ratios and well defined thick silica walls, which indicates that they can withstand against high temperatures for more time. As Figure 9a clearly depicts that sample 2 and 5 lost their maximum weight in the range between 180-270°C, while on the other hand all other samples starts loosing their weight at around 120°C to onwards.

The DTG curves also display a narrow peak corresponding to the

Photographs taken after an equal time interval 0 to 15 min when heating at 60°C | After recovery |

Figure 8: Digital photographs: (a) n-eicosane/silica nanopasules; (b) pure n-eicosane heated at hot stage from room temperature to  $60^{\circ}$ C.



temperature at the rapid weight loss of the n-eicosane when leaking from the nanocapsules. As comprehended in Figure 9b, the nanocapsules synthesized at the n-eicosane/TEOS at pH 2.25 and n-eicosane/sodium silicate at pH 2.94 resist to the highest temperature while rapid weight lose, which is attributed to the greatest thickness of their shells as a result of the highest silica loading. It is comprehensible that the compact and thick shell material prevents the leaking of the core material. However, the sample synthesized at pH 2.5 by using sodium silicate as a precursor has a loose shell due to the fast condensation rate as well as has the lowest encapsulation efficiency, resulting in a lower temperature at the rapid weight loss. Furthermore, the broad peaks of samples suggest a slower process of the further condensation of the silica shell material at high temperatures.

# Conclusion

Nanoencapsulation of n-eicosane PCM with inorganic silica shell was carried out via sol-gel route by using two different inorganic silica-precursors. Capsules were synthesized at different pH values. FTIR spectra confirmed the chemical composition and crystallinity of the synthesized nanocapsules. The morphologies of the obtained nanocapsules strongly depend upon the pH value of the reaction solution. Nanoencapsulated n-eicosane derived from TEOS silicaprecursor exhibited spherical morphologies when synthesized at pH 2.20~2.30, in this pH range nanocapsules also demonstrate good phase change properties and higher encapsulation rates and efficiency. Whereas, n-eicosane/sodium silicate obtained nanocapsules presented good overall properties with high encapsulation rates and thermal stability, when prepared at pH 2.90~3.00, but showed very poor encapsulation efficiency and enthalpies when prepared under pH 2.9. In addition, thermogravimetric investigation presented that n-eicosane/ silica nanocapsules degrade in two steps and are resistant enough for usage at ambient temperatures. All of phase change properties with enhanced thermal performance make these nanocapsules a potential PCM for applications of thermal energy storage and thermal-regulating textiles and fibers.

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#### References

- Jiang F, Wang X, Wu D (2014) Design and synthesis of magnetic microcapsules based on n-eicosane core and Fe3O4/SiO2 hybrid shell for dual-functional phase change materials. Appl Energy 134: 456-468.
- Chai L, Wang X, Wu D (2015) Development of bifunctional microencapsulated phase change materials with crystalline titanium dioxide shell for latent-heat storage and photocatalytic effectiveness. Appl Energy 138: 661-674.
- Özonur Y, Mazman M, Paksoy HÖ, Evliya H (2006) Microencapsulation of coco fatty acid mixture for thermal energy storage with phase change material. Int J Energy Res 30: 741-749.
- Mondal S (2008) Phase change materials for smart textiles An overview. Appl Therm Eng 28: 1536-1550.
- Kara YA (2016) Diurnal performance analysis of phase change material walls. Appl Therm Eng 102: 1-8.
- Mohamed SA, Al-Sulaiman FA, Ibrahim NI, Zahir MH, Al-Ahmed A, et al. (2017) A review on current status and challenges of inorganic phase change materials for thermal energy storage systems 70: 1072-1089.
- Sun Z, Zhang Y, Zheng S, Park Y, Frost RL (2013) Preparation and thermal energy storage properties of paraffin/calcined diatomite composites as formstable phase change materials. Thermochim Acta 558: 16-21.
- Khudhair AM, Farid MM (2004) A review on energy conservation in building applications with thermal storage by latent heat using phase change materials. Energy Convers Manag 45: 263-275.
- Rao ZH, Zhang GQ (2017) Thermal Properties of Paraffin Wax-based Composites Containing Graphite Energy Sources Part A: Recovery 7: 587-593.
- Kim EY, Do KH (2005) Preparation and properties of microencapsulated octadecane with waterborne polyurethane. J Appl Polym Sci 96: 1596-1604.
- Delgado M, Lázaro A, Mazo J, Zalba B (2012) Review on phase change material emulsions and microencapsulated phase change material slurries: Materials, heat transfer studies and applications. Renew Sustain Energy Rev 16: 253-273.
- Su W, Darkwa J, Kokogiannakis G (2015) Review of solid-liquid phase change materials and their encapsulation technologies. Renew Sustain Energy Rev 48: 373-391.
- Borreguero AM, Carmona M, Sanchez ML, Valverde JL, Rodriguez JF (2010) Improvement of the thermal behaviour of gypsum blocks by the incorporation of microcapsules containing PCMS obtained by suspension polymerization with an optimal core/coating mass ratio. Appl Therm Eng 30: 1164-1169.
- 14. Zhan S, Chen S, Chen L, Hou W (2016) Preparation and characterization of polyurea microencapsulated phase change material by interfacial polycondensation method. Powder Technol 292: 217-222.
- 15. Zhang H, Wang X (2009) Fabrication and performances of microencapsulated phase change materials based on n-octadecane core and resorcinol-modified melamine-formaldehyde shell. Colloids Surfaces A Physicochem Eng Asp 332: 129-138.
- 16. Yu S, Wang X, Wu D (2014) Microencapsulation of n-octadecane phase change material with calcium carbonate shell for enhancement of thermal conductivity and serving durability: Synthesis, microstructure, and performance evaluation. Appl Energy114: 632-643.
- Zhao CY, Zhang GH (2011) Review on microencapsulated phase change materials (MEPCMs): Fabrication, characterization and applications. Renew Sustain Energy Rev 15: 3813-3832.
- Zhang H, Wang X (2009) Synthesis and properties of microencapsulated n-octadecane with polyurea shells containing different soft segments for heat energy storage and thermal regulation. Sol Energy Mater Sol Cells 93: 1366-1376.
- Sarı A, Alkan C, Karaipekli A (2010) Preparation, characterization and thermal properties of PMMA/n-heptadecane microcapsules as novel solid-liquid microPCM for thermal energy storage. Appl Energy 87: 1529-1534.
- 20. Fang Y, Liu X, Liang X, Liu H, Gao X, Zhang Z (2014) Ultrasonic synthesis and characterization of polystyrene/n-dotriacontane composite nanoencapsulated

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phase change material for thermal energy storage. Appl Energy 132: 551-556.

- Bayés-García L, Ventolà L, Cordobilla R, Benages R, Calvet T, et al. (2010) Phase Change Materials (PCM) microcapsules with different shell compositions: Preparation, characterization and thermal stability. Sol Energy Mater Sol Cells 94: 1235-1240.
- 22. Zhang X, Wang X, Wu D (2016) Design and synthesis of multifunctional microencapsulated phase change materials with silver/silica double-layered shell for thermal energy storage, electrical conduction and antimicrobial effectiveness. Energy 111: 498-512.
- 23. Chai L, Wang X, Wu D (2015) Development of bifunctional microencapsulated phase change materials with crystalline titanium dioxide shell for latent-heat storage and photocatalytic effectiveness. Appl Energy 138: 661-674.
- 24. Pan L, Tao Q, Zhang S, Wang S, Zhang J, et al. (2012) Preparation, characterization and thermal properties of micro-encapsulated phase change materials. Sol Energy Mater Sol Cells 98: 66-70.
- 25. Tyagi VV, Kaushik SC, Tyagi SK, Akiyama T (2011) Development of phase change materials based microencapsulated technology for buildings: A review. Renew Sustain Energy Rev 15: 1373-1391.
- Su J-F, Wang L-X, Ren L (2007) Synthesis of polyurethane microPCMs containing n-octadecane by interfacial polycondensation: Influence of styrenemaleic anhydride as a surfactant. Colloids Surfaces A Physicochem Eng Asp 299: 268-275.
- Sánchez-Silva L, Rodríguez JF, Romero A, Borreguero AM, Carmona M, et al. (2010) Microencapsulation of PCMs with a styrene-methyl methacrylate

copolymer shell by suspension-like polymerisation. Chem Eng J 157: 216-222.

- Tourné-Péteilh C, Lerner DA, Charnay C, Nicole L, Bégu S, Devoisselle JM (2003) The Potential of Ordered Mesoporous Silica for the Storage of Drugs: The Example of a Pentapeptide Encapsulated in a MSU-Tween 80. ChemPhysChem 4: 281-286.
- Ozalp VC, Eyidogan F, Oktem HA (2011) Aptamer-gated nanoparticles for smart drug delivery. Pharmaceuticals 4: 1137-1157.
- Rekuć A, Bryjak J, Szymańska K, Jarzebski AB (2009) Laccase immobilization on mesostructured cellular foams affords preparations with ultra high activity. Process Biochem 44: 191-198.
- Wang L-Y, Tsai P-S, Yang Y-M (2006) Preparation of silica microspheres encapsulating phase-change material by sol-gel method in O/W emulsion. J Microencapsul 23: 3-14.
- 32. Li B, Liu T, Hu L, Wang Y, Gao L (2013) Fabrication and Properties of Microencapsulated Paraffin@SiO 2 Phase Change Composite for Thermal Energy Storage. ACS Sustain Chem Eng 1: 374-380.
- Fang G, Chen Z, Li H (2010) Synthesis and properties of microencapsulated paraffin composites with SiO2 shell as thermal energy storage materials. Chem Eng J 163: 154-159.
- 34. Jin Y, Lee W, Musina Z, Ding Y (2010) A one-step method for producing microencapsulated phase change materials. Particuology 8: 588-590.
- Wang LP, Wang TB, Gao CF, Lan X, Lan XZ (2014) Phase behavior of dodecane--hexadecane mixtures in bulk and confined in SBA-15. J Therm Anal Calorim 116: 469-476.