Preparation and Properties of Phase Change Material by Microencapsulation of Lauric Acid for Thermal Regulation

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Abstract. Lauric acid, the phase change material (PCM) in this study, is encapsulated in a silica shell using a modified sol-gel method. Encapsulation was done at varying pH, mixing ratio, drying temperature and drying time. Analysis of variance revealed that all these parameters and their interactions affect the PCM yield and encapsulation ratio. FT-IR and DSC Analysis showed that the microencapsulated PCM (μPCM) formed using 1:1:2 mixing ratio of Tetraethyl orthosilicate: Ethanol: Water, with pH ~1.92 and drying condition of 100°C for 7hr had a latent heat of fusion (207.65 J/g) similar to that of pure PCM with latent heat of fusion of 212.47 J/g ). SEM Analysis and DSC were utilized to confirm the efficiency of encapsulation of PCM. The glass sheet with μPCM and binder was found to have a latent heat of 182.14 J/g and a thermal conductivity of 0.0537 W/mK. The glass with silica microencapsulated lauric acid exhibited potential application for energy conservation.

1. Introduction
The phase change material is a new class of construction material that increases the thermal mass of a structure by reducing the load of an equipment. The term “phase change material” (PCM) is used to describe material that use phase transitions to absorb or release large amounts of latent heat at relatively constant temperature. Phase change materials influence the natural property of latent heat to help maintain products temperature for extended periods of time.

Microencapsulation is defined as a process in which tiny particles or droplets are surrounded by a coating, or embedded in a homogeneous or heterogeneous matrix, to give small capsules [1]. The material being encapsulated is called core material while the material from which the capsule is formed is called shell material. The volume of phase change materials (PCMs) in encapsulating shells changes during melting and crystallization. Breakage of shell occurs as the liquefied PCM leaks out because of mismatch of thermal expansion of the core and the shell materials at high temperature. Microencapsulation isolates and protects enclosed particles from external environment. A good design for the PCM requires a container that acts as a barrier preventing interaction with the environment, providing a stable structure and sufficient surface for heat transfer, and ease in process handling.
Fatty acids are carboxylic acids with long hydrocarbon chains. These are soluble in solvents such as hexane. Among the most common and relatively abundant in the local setting is Lauric acid, a fatty acid PCM derived from coconut oil. It’s crystallization and melting behavior has been studied in a test cell showing its viability as phase change material [2].

Development of Microencapsulated PCM
There are two approaches to create a microencapsulated phase change material (μPCM): in emulsion and in solid matrix. Emulsion containing μPCMs can be used as thermal exchange medium to enhance the efficiency of thermal exchangers. While, the μPCMs in solid matrix are used in smart thermal-regulation composites, such as fibers, construction materials, blood temperature controlling materials and anti-icing coats [3].

The sol-gel process has been widely used to create organic-inorganic composite materials, which were termed “ormosils” or “ormocers” [4]. Sol-gel reaction in the presence of organic molecules are typically polymeric and contain functional groups to improve their bonding to the ceramic-like phase. The molecular sol-gel encapsulation phenomenon results in pronounced physical and chemical protection deriving from isolation of dopant molecule, while the matrix offers better tightness and resistance to extraction forces than polymer or waxes. The sol-gel process can be viewed as a two-step network-forming process, the first step being the hydrolysis of a metal alkoxide and the second consisting of a polycondensation reaction.

\[
\begin{align*}
Si - OR + H_2O & \rightarrow Si - OH + ROH \\
Si - OH + RO - Si & \rightarrow Si - O - Si + ROH \\
Si(OR)_4 + 2H_2O & \rightarrow SiO_2 + 4ROH
\end{align*}
\]

Studies on sol-gel method is concentrated on metal-organic alkoxides, especially silica which can form an oxide network in organic matrices. In silica-based preparations the tetraethyl orthosilicate (TEOS) is often dissolved in ethanol or a similar alcohol, and then hydrolyzed to silicic acid, which eventually condenses to give a silica gel network. Gelation of the sol is accomplished through low-temperature hydrolysis and condensation reactions. A major key of this method is the self-assembly of the silica precursor on the organic droplets under elaborate conditions, which is required for a reasonably rapid hydrolysis reaction to eventually form the silica shell. Taking the Stöber process on the synthesis of micro spherical particles by means of hydrolysis of TEOS and condensation of silicic acid in alcoholic solution:

\[
TEOS + alcohol + water + catalyst + dopant \rightarrow silicaPCM
\]

2. Experimental Method

Materials
The reagents used in preparation of microencapsulated Phase Change Material (PCM) were purchased and acquired locally. Two amber bottled 500-mL Tetraethyl silicate (Aldrich) was used as precursor, 2.5-L of absolute Ethanol (Scharlau) was used as solvent, 500-g of 99% Lauric acid (Sigma) was used as PCM, Polyvinyl alcohol, Span 80 (Sigma) and Tween 80 (Haryana) completed the set. The first batch use of 500-g of 99% Lauric acid (Sigma), 2.5M Sodium chloride solution, 10% Acetic acid and 6M Hydrochloric acid and 98% Sulfuric Acid were obtained from the University.

Microencapsulation of Lauric Acid
Preparation of Sol. Microencapsulation of Lauric acid was based on the sol-gel method used by Fang, et al in microencapsulating palmitic acid. [5]. To form the microcapsule shell, forty-three (43) mL of the alkoxide tetraethyl orthosilicate (TEOS) was dissolved in 50 mL absolute ethanol and then poured into a beaker containing 50 mL distilled water while briskly agitating at 300 rpm. For complete hydrolysis, an acid catalyst prepared from concentrated HCl and 30 mL distilled
water is added to the mixture while agitation is increased to 600 rpm at 65 °C for 90 minutes using a Corning PC4200 hotplate. Solution pH was varied between 1 and 2 for different microencapsulation trials.

Lauric acid encapsulation in Silica Network. Twenty-four grams of lauric acid weighed in a Mettler Toledo AB204-S analytical balance was added into the sol. The mixture was then stirred at 800 rpm for 40 min for uniform dispersion while the temperature of the mixture was maintained at 80°C. The sol is poured into glass Petri dish slightly uncovered. It was placed in Precision Scientific TS -31477 AU2 gravity convection oven at 100°C for 5hrs. The samples are removed from oven and stored in a desiccator according to their gel time. It was recommended in a paper published by University of Oslo that the gel time changes according to the catalyst used [6]. The resulting product is an encapsulated PCM in the form of soft solid or hard gel. The samples were stored in desiccator for aging.

Fabrication of PCM Glass Sheet. The μPCM prepared using the optimized encapsulation procedure was applied to different surfaces wood, aluminium and glass. To promote adhesion to the glass surface, ample amounts (<5mL) of acrylic solution was mixed with the μPCM while the temperature of mixture is still 80°C. Finally, the sol-gel mixture was poured onto a 3mm glass sheet over a Pyrex pan. The sample was dried at 90°C for 7 hr partially uncovered. It was stored in a desiccator for 106 hrs for aging.

It is important to compare the thickness of coating and thermal conductivity test of ordinary glass and microencapsulated PCM integrated in glass surface (glass PCM). The items with given thickness were tested using Anacon / TCA 12 thermal conductivity analyser with cold plate temperature of 10.2°C and hot plate temperature of 37.9°C. The environmental condition was accounted with 21-25°C and relative humidity of 50-60%.

Analytical Test Methods. The method of testing the Fourier-Transform Infrared was patterned using ASTM E168, ASTM E1252 and the spectrum in each run was treated using Kubelka-Munk conversion and the result was reported in transmittance versus wavenumber. The method of using the Differential Scanning Calorimeter was according to ASTM D3947-80, ASTM D3418-15. Finally, the ASTM used for Scanning Electron Microscopy is ASTM E1508.

3. Results and Discussion

Physical Data
Preparation of microcapsules involved balance of pH of the mixture, substituent, solvent and water ratio. It was observed that the TEOS: EtOH: H2O mixture vary in miscibility at different concentrations while the process commences. The preparation factors were observed during the sol-gel process. Initial mix ratio is 1:1:4 (A) and higher water in the mix increases the condensation of the sol-gel which results to lower yield. The mix ratio is then adjusted to 1:1:2 (B).

The gel time changes according to the type of catalyst used. On a hydrochloric acid, gel time is 4 days and on sulfuric acid, gel time takes 5 days. This is not a thermodynamic event rather it indicates how much network was formed.

Drying condition involves temperature and time. Sample 5 did not undergo drying which resulted to low enthalpy and melt temperature. If temperature was taken as constant in the case of sample 4 and 3, while changing drying time, the enthalpy has huge difference. If the time is taken constant in the case of Sample 3 and 2, and changing drying temperature, there is still a change in enthalpy. Sample 1’s condition is based on research of Fang. The drying temperature is below the evaporation temperature of ethanol which is not enough to create a stable form of shell to hold the lauric acid in the core.
Table 1. Variation in parameters during synthesis of PCM

| Sample   | Precursor Mix | LA: precursor (wt. ratio) | Oven Drying Time | Temperature °C | Produced wt. | Encapsulation Ratio |
|----------|---------------|---------------------------|------------------|----------------|--------------|---------------------|
| Sample 1 | A             | 1.86                      | 12 hr.           | 75             | 33           | 41 %                |
| Sample 2 | A             | 2.24                      | 7 hr.            | 90             | 31           | 54 %                |
| Sample 3 | A             | 1.92                      | 7 hr.            | 100            | 31           | 98 %                |
| Sample 4 | A             | 1.73                      | 5 hr.            | 100            | 34           | 28 %                |
| Sample 5 | B             | 1.50                      | -                | -              | 74           | 24 %                |
| Sample 6 | B             | 2.00                      | 5 hr.            | 100            | 20           | -                   |
| Sample 7 | A             | 2.00                      | 4 hr.            | 125            | 35           | -                   |

The pH was plotted with enthalpy change and weight. It can be observed that the increase in pH value below 1.92 will increase the thermal properties of the samples. However, increasing it further to 2.24 creates a different effect. It is therefore considered that this experiment’s optimum pH is 1.92 which is below the point of zero charge of the shell. The point of zero charge or PZC is the pH when the particle is neutral which is 2.5 for Silica. This means the reaction rate is proportional to the acid catalysts effect.

![Effect of pH](image)

The Point of Zero Charge (PZC) is also called the isoelectric point. It predicts the rates of gelation and the effect of syneresis. The rate of shrinkage during syneresis is slower for larger gels. As the gel network contracts, it subjects the pore liquid to a compressive load that forces it out of the body. If the gel is small enough, the liquid escapes easily; but if it is large, a steep pressure gradient is needed to drive the liquid to the surface. When the liquid in the gel is replaced by air, major changes to the network structure may occur. Normal drying of the gel leads to structural collapse due to capillary forces drawing the walls of the pores together and reducing the pore size [7].

Freshly prepared silica gels contain an appreciable amount of solvent which must be eliminated. The solid silica network formed by hydrolysis and polycondensation of Si alkoxides is made up by Silica species in micro sizes. Capillary stress appears when the liquid moves inside the pores during drying and form a liquid-gas curve interface. There were samples that shattered immediately. This phenomenon can be associated to the rapid exodus of water affecting the surface of the gel to contract while the interior was still swollen with water; the differential shrinkage caused stress and cracking during drying.

**Thermal Properties**

The Differential Scanning Calorimeter (DSC) was used to determine the specific heat, melting point and latent heat of fusion of lauric acid. In this study the reference used to get the actual value is Indium.
(25.1256e+03 1/mW). The DSC equipment used was a Mettler Toledo DSC 822E attached with immersion cooler Haake EK90. The samples weighing 5-8 mg were placed in hermetically sealed 40μl aluminum standard pans. The temperature program used an isothermal segment 0°C for 5min followed by a heating segment from 0 to 60°C at a heating rate of 5°C/min. Then a cooling segment from 60 to 0°C at a cooling rate of –5°C/min was performed. The DSC software used does not have latent heat determination at that time, therefore Boole’s rule of numerical integration was utilized to determine the area under the curve, \( I \). Boole’s rule is an approximation to the integral of \( f(x) \) over \([x0,x4]\). Boole’s rule is being derived by putting \( n = 4 \) in the general quadrature formula which can be approximated by a polynomial of 4th degree.

\[
I = \frac{2h}{45} [7f_0 + 32f_1 + 12f_2 + 32f_3 + 7f_4]
\]

The thermal properties of the samples were compared with the core material lauric acid (LA). Since only the melting phase was reported, the encapsulation ratio was computed on formula below. It is important to compute for the encapsulation efficiency, \( \varepsilon \) to determine if a reasonable amount of PCM was encapsulated. It is observed that Sample 3 has a high encapsulation ratio, \( R \). This means the synthesis parameters applied in this method was effective.

\[
R = \frac{\Delta H_{m,\mu PCM}}{\Delta H_{m,PCM}} \times 100\%
\]

\[
\varepsilon = \frac{\Delta H_{m,\mu PCM} + \Delta H_{c,\mu PCM}}{\Delta H_{m,PCM} + \Delta H_{c,PCM}} \times 100\%
\]

**Chemical Structure**

The chemical structural analysis of the \( \mu \)PCM was conducted by using Fourier transformation infrared spectroscope. FT-IR is utilized to compare the chemical structures of lauric acid and silica and to confirm the encapsulation of core material in its shell. The FTIR spectra were recorded on a Shimadzu Prestige 21, Perkin Elmer Spectrum 100 and Thermo Scientific Nicolet 6700 from 400 to 3500cm\(^{-1}\) with a resolution of 1/cm. The samples were pulverized and dispersed in KBr. The FTIR scans were acquired using a diffuse reflectance spectrometry (DRS) accessory.

It was found that there is no shift in the FTIR absorption peaks of the microcapsules when compared with the spectra of the LA. This result indicates that there is no chemical interaction between the LA and precursors. The -OH groups on opposite sides may react and form new bonds by condensation. Cracking occurs if the tension in the gel is so large that it cannot shrink anymore. Gas will enter the pores with a thin film of liquid on the walls leaving isolated spaces with liquid. Figure 2 illustrates the spectra of silica shell and compared with the spectra of the samples. The 98% encapsulation ratio of Sample 3 was supported by this transmittance in which all peaks were present. This means all lauric acid was contained inside the shell.
Figure 2. Transmittance of TEOS with microencapsulated PCM

Morphology of Microencapsulated PCM

Controlling the morphology of particles is very important to identify the physicochemical properties. The following figure represents a multi core formation of microparticles. Figure 3 shows a micrograph of platinum coated microencapsulated lauric acid exposed in a 10kV electron beam with a magnification of x1000. The image shows the agglomeration of non-homogenized size microparticles or multicore structure. The average size of microparticles is 4.18μm. A lumping mass was observed in the middle of each particle which may be assumed to be the encapsulated lauric acid. The image at x6000 magnification was carried out at 3kV due to unavailability of sputter coater. It was observed that there was no breakage of shell of μPCM thus having no leakage.

Figure 3. SEM micrograph of microencapsulate LA in glass with binder (PCM4) in x50, x500, x1000 and x6000 magnification

Microencapsulated PCM on a Glass Sheet
A thin layer of microencapsulated PCM produced using the optimum parameters was applied onto a substrate. The substrates used were wood (PCM1), aluminum (PCM2) and glass (PCM3). To enhance the adhesion on glass, an ample amount (<1mL) of acrylic solution at 80°C was first mixed with μPCM mixture. The sol-gel mixture was then poured onto a 3mm glass sheet and then dried at 100°C for 7 hr partially uncovered and this was PCM4. It was then stored in a desiccator for 106 hr to let the ageing process commence. It was observed that adhesion was best in PCM4 followed by PCM3 with PCM2 having the weakest adhesion as shown in Table 2.

Table 2. Summary of melting profile of μPCM on various substrate

| Sample   | Substrate     | % Δwt | % PCM adhered | ΔTemp | Efficiency, ε |
|----------|---------------|-------|---------------|-------|---------------|
| Lauric Acid | none       |       |               | 10.4  |               |
| PCM 1    | Wood         | 2%    | 61%           | 7.1   | 39%           |
| PCM 2    | Aluminum     | 6%    | 28%           | 13.6  | 25%           |
| PCM 3    | Glass        | 0%    | 53%           | 7.2   | 70%           |
| PCM 4    | Glass + binder | 0%    | 86%           | 7.3   | 71%           |

Thermal Conductivity of μPCM in Glass Sheet

Thermal conductivity, $k$ is the property of a material’s ability to conduct heat which is measured in W/mK. The thermal conductivity predicts the rate of heat loss (J/s or W) through a piece of material. In the construction industry it is converted to thermal resistivity, $R$-value measured in English units. $R$-value determines the extent of insulation effect. The PCM4 shows increase in $R$-value signifying the effectivity of adhesion on glass sheet. Table 3 shows the comparison of the $R$-value and thermal conductivities of different PCM-on-glass preparations. It was observed that PCM4A with higher thickness resulted in higher thermal conductivity.

Table 3. Thermal Resistivity of μPCM on a glass sheet

| Sample   | Description     | Thermal Cond, $k$ (W/mK) | Thickness, $Δx$ (mm) | R-value (hr-ft²°F/BTU) | Latent Heat, J/g |
|----------|-----------------|--------------------------|----------------------|-----------------------|------------------|
| Control  | Glass           | 0.06538                  | 3                    | 0.26                  | -                |
| PCM 3    | Glass + PCM     | 0.06352                  | 3                    | 0.27                  | 112.00           |
| PCM 4A   | Glass + PCM+ Binder | 0.05536               | 4.7                  | 0.48                  | 182.14           |
| PCM 4B   | Glass + PCM+ Binder | 0.05178               | 2.5                  | 0.27                  | 182.14           |

4. Summary and Conclusion

Lauric acid was microencapsulated in a silica shell using acid catalyzed sol-gel process. This paper determined the most compatible parameters necessary for microencapsulation of lauric acid and defined the properties that contributed to its efficiency. In the preparation of microencapsulated lauric acid (μPCM), the highest encapsulation ratio of 98% was achieved using 1:2:1 precursor ratio of TEOS/H₂O/EtOH and a pH value of 1.92 using H₂SO₄. The best drying temperature and time was at 100°C for 7 hours which resulted in a steeper refined melting peak. The FTIR and DSC confirmed the presence of Lauric acid in the microencapsulated material. A 71% efficiency of microencapsulation was revealed by SEM and DSC. The adhesion of μPCm on the glass resulted to 182.14 J/g. The use of acrylic binder enhanced the adhesion of μPCM on glass, enabling a thicker μPCM coating and significantly improving the R-value.

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Acknowledgments

This work was supported by Department of Science and Technology - Engineering Research and Development for Technology in the Philippines. I would like to thank the people who have helped me through the experiments - sir John, Imee, J4, Carla, Khaye, Stephen and sir Rommel for sharing a conducive place.