PHILIPPINE ENGINEERING JOURNAL
PEJ 2012; Vol. 33, No. 1: 69-75

# SYNTHESIS AND CHARACTERIZATION OF MICRO-ENCAPSULATED N-OCTADECANE IN UREA-MELAMINE-FORMALDEHYDE SHELL FOR THERMAL REGULATION

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## ABSTRACT

*Phase change materials (PCMs) have the ability to maintain a steady temperature upon changing phase. These materials are currently used for heat storage and space cooling. This research conducted preliminary observations on the surface cooling of polyurethane foams using PCM technology. Polyurethane foam is used in car seats and pillows which can reach 60-70°C when exposed to the sun for a certain period of time. A modified microencapsulation technique was used to synthesize a PCM with n-octadecane and urea-melamine-formaldehyde as shell and core materials, respectively. The modified technique was designed to adapt to the availability of reagents, including the time and equipment constraints in the Philippines. Differential Scanning Calorimetry revealed that the product obtained a peak melting temperature and latent heat of fusion at 34.9˚C and 190.8 J/g, respectively. A thin layer of the product was then manually applied to cover the surface of the polyurethane foam. Finally, using a Data Logger, temperature profiling of the surfaces was done as they were exposed to a heated environment. Results showed that the temperature profiles of the pure microencapsulated PCM were lower than the foam surface and ambient temperature by margins of 3.56˚C and 1.00˚C, respectively.*

## 1. RATIONALE AND SIGNIFICANCE

PCMs are able to reversibly store and release heat without undergoing a significant change in temperature by taking advantage of their high heat of fusion (Mehling et al, 2008). They have been extensively studied for the past 30 years. The researchers intend to apply this technology to the cooling of polyurethane foams used in car seats and pillows. PCM space cooling applications are well documented for buildings, food and pharmaceutical transport containers, clothing technology, and electronic gadgets. Aside from space cooling, latent heat storage is also heavily researched. However, studies focused only on solid-liquid PCMs, because it is difficult to set the boundary conditions and heat transfer calculations for gases.

Usually, PCMs must be microencapsulated prior to application to prevent the loss of sample and to rigidly contain the core material even when changing phase. Microencapsulation is very well documented for a wide array of paraffin wax cores and polymeric shells. The choice of core material is based on high latent heats and melting temperatures within the working temperature range.

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*Received: April 17, 2012*
*Accepted: May 31, 2012*

N-octadecane has a melting point of 28-30˚C, which is still comfortable for humans. Urea-melamine-formaldehyde (UMF) is the polymer shell of choice because of an established microencapsulation technique by Zhang et al (2005). Thus, this research adapted and modified the approach to the Philippine setting, paving the way for relatively new possibilities of PCM application to polyurethane foams subjected to heated conditions when cars are parked for long periods under the sun.

## 2. OBJECTIVES

The study aims: (1) To develop a modified methodology for microencapsulation adapted from Zhang et al (2005); (2) To synthesize a microencapsulated PCM with n-octadecane as the core material and urea-melamine-formaldehyde (UMF) as the shell material; (3) To characterize the microencapsulated PCM according to its phase change temperature and latent heat of fusion, and; (4) To determine the magnitude of reduction in the temperature profiles of PCM-covered polyurethane foams exposed to a heated environment.

## 3. PROBLEM STATEMENT AND DESCRIPTION

N-octadecane, in its pure and unencapsulated form, has very limited thermal regulation applications due to the volume changes associated to its transition from the solid to the liquid state. Phase transitions of unencapsulated phase change materials (PCMs) could lead to loss of material and contamination. The research aims to microencapsulate n-octadecane within a polymer shell made out of urea, melamine and formaldehyde through *in situ* polymerization, and to determine the thermal properties of the resulting microencapsulated PCM. The research also aims to determine the magnitude of reduction in the temperature profiles of PCM-covered polyurethane foams exposed to a heated environment. Knowing the reduction magnitude of these materials may serve as a basis for the potential application of the microencapsulated PCM as seat covering for automobiles.

The research takes advantage of the polycondensation reaction of formaldehyde with urea and melamine to produce a solid polymer shell with an appreciably high melting point range. This polymerization reaction is also used in the industry to manufacture urea foams and other melamine products.

Zhang et al (2005) applied this polycondensation technique in the microencapsulation of alkanes for potential PCM applications. The technique used in this research is a modified methodology from the study of Zhang et al (2005). Changes were made to the type and concentration of the emulsifier to address surfactant availability issues. The researchers also included adjustments based on the theoretical mechanism in the operating pH and the order of reagent additions to ensure microencapsulation and reproducibility. Resorcinol was incorporated to the methodology to facilitate improved flexibility of the microcapsules.

Among the challenges to the research included the cost of the reagents for the encapsulation and their availability. These were aggravated by the limited number of local references on the topic. The development of a modified technique tailored to the availability of reagents and a more equipment-constrained condition will provide a reproducible methodology that can be implemented in the Philippines. This methodology may be used by researchers who desire to pursue PCM studies and applications.

 

## 4. METHODOLOGY

The research methodology is divided into two main parts: synthesis and characterization. Prior to these, the group conducted many trials on microencapsulation to come up with working modifications. These previous trials were inconclusive. The following procedure, however, produced PCM successfully:

For synthesis, thermocouples were first calibrated for accuracy. Two mixtures were prepared: the pre-polymer solution and the emulsion. The pre-polymer solution contained urea, melamine, and formaldehyde at established proportions, together with distilled water. The emulsion is a mixture of SDS surfactant, resorcinol, and n-octadecane homogenized for 1.6 hours. The two were then mixed and homogenized at 4400 rpm, including pH regulation to control polymerization. After two hours, microencapsulation was done, and samples were taken from different layers in the mixture. They were then filtered from unencapsulated core and excess shell materials. After vacuum filtration, the samples were dried for 8-10 hours in a gravity oven.

Characterization also has two parts: Differential Scanning Calorimetry with calibration, and temperature profiling using a Data Logger. Aside from the analysis of the different samples from different layers, samples of pure n-octadecane and of solidified urea-melamine-formaldehyde were prepared for comparison. The generated thermograms were plots of heat flux against the temperature of a sample. Inside the DSC, the sample was heated and cooled for two cycles, determining cycling stability. Phase change temperatures and latent heats were identified through TA Instruments Operating Software integrated into the DSC. After choosing the best sample (based on latent heat and melting temperature), temperature profiling began by creating a 1x1x2-ft. wooden box with a bulb on its hinged lid as heat source. The best sample was used and manually applied to completely cover the top surface of the foam. Together with the control/blank foam and a pure PCM sample, the covered foam was subjected to heating and cooling. Temperature probes were provided for each, as well as for the ambient temperature. Hydra Data Logger tabulated and profiled the temperatures for a period of 1.5 hours.

## 5. RESULTS AND RECOMMENDATION

To make PCM microencapsulation available and reproducible in the Philippines, modifications in the study were applied from the *in situ* polymerization technique done by Zhang et al to microencapsulate n-octadecane using urea-melamine-formaldehyde polymer shell.. Based on DSC results, n-octadecane was successfully microencapsulated in UMF shell. The best microcapsule samples had a peak melting temperature of 34.9˚C and a latent heat of fusion of 190.8 J/g. The generated peak melting temperature is 1.6˚C lower, and the latent heat of fusion is 23.8 J/g higher compared to the results obtained in the original study. This showed that the modified methodology yielded microencapsulated products with better thermal properties, since a lower peak temperature and higher latent heat of fusion would result to a more appealing environment for human comfort. Preliminary observations from comparing temperature responses of the microencapsulated product and polyurethane foam exposed to the same heating conditions showed that the former had temperatures lower by an average of 3.56˚C relative to the blank polyurethane foam sample, and by an average of 1˚C relative to the ambient temperature. Based on the temperature profiles generated, these results suggest that the product is thermally feasible for foam applications, like in car pillows and car seats.

 

The research can be further improved by exploring the possibility of adding other reagents that will enhance the properties of the microencapsulated product. Characterization of these properties, aside from the thermal features, is highly encouraged to obtain a more in-depth analysis of the samples. The temperature range of analysis for DSC characterization must be increased to fully complete the heating and cooling cycle. More repetitions of the heating and cooling cycles can further establish the cycling stability of the microcapsules. Lastly, devising an efficient method of incorporating the microencapsulated product to the foam surface, and performing cost analyses for the overall procedure (from product synthesis to application) are proposed for future research to obtain a more comprehensive study on the viability of using PCM in this application.

## Tables

**Table 1** List of samples to be examined under the DSC

| Sample No. | Filtered? | Source | Mass of Pan(mg) | Mass of Sample (mg) |
|---|---|---|---|---|
| **1** | N | Settled layer of the product solution | 41.1 | 5.7 |
| **2** | N | Unsettled layer of the product solution | 41.4 | 8.9 |
| **3** | N | Solids collected from the homogenizer blades | 41.1 | 6.2 |
| **4** | Y | Settled layer of the product solution | 41.3 | 6.3 |
| **5** | Y | Unsettled layer of the product solution | 41.4 | 9.3 |
| **6** | Y | Solids collected from the homogenizer blades | 41.5 | 5.2 |
| **7** | Y | Products from a Previous Trial* | 41.3 | 10.8 |
| **8** | N | Pure n-octadecane | 41.3 | 10.2 |
| **9** | N | Pure pre-polymer solution solidified through heating** | 41.3 | 6.5 |
| **Indium** | - | For calibration | 41.1 | 4.6 |

**Table 2** Onset Melting Temperatures and Latent Heats of the samples

| Sample No. | Average Onset Melting Temperature | Latent Heat of Fusion (J/g) |
|---|---|---|
| 1 | 27.695 ˚C | 1.617 |
| 2 | 28.4 ˚C | 137.75 |
| 3 | 28.84 ˚C | 135.7 |
| 4 | 27.225 ˚C | 60.875 |
| 5 **(Best)** | 28.305 ˚C | 190.8 |
| 6 | 28.075 ˚C | 113.1 |
| 8 | 29.12 ˚C* | 245 |

*Pure n-octadecane has a melting point of 28-30˚C

 

## Figures

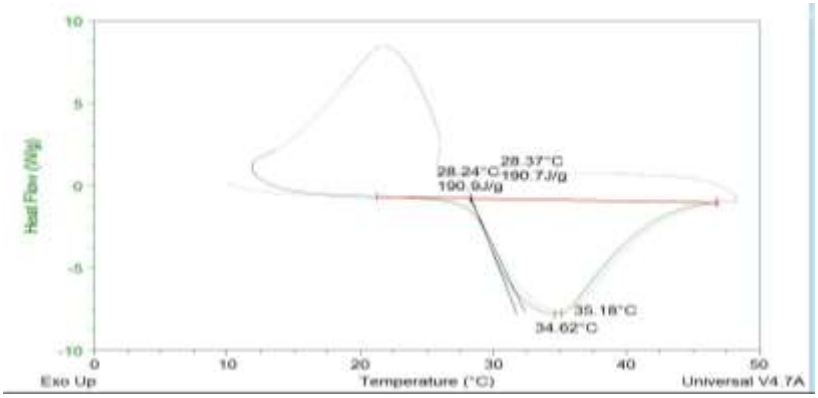


**Figure 1** Sample No. 5 Thermogram with Heating Cycle Analyzed

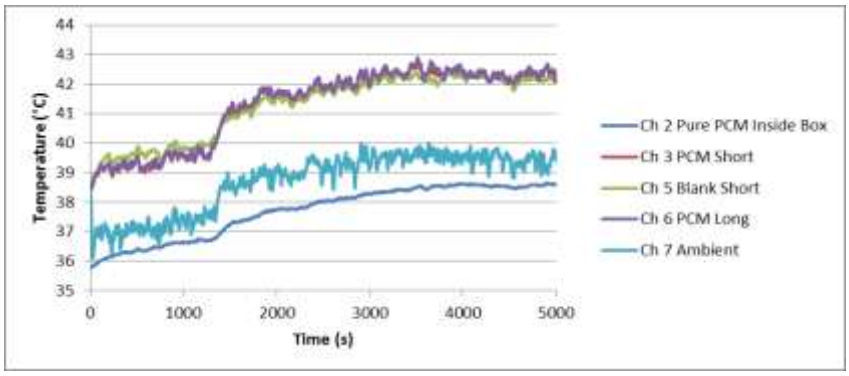


**Figure 2** Heating Profile of Setup (Channel 2 in contact with Pure PCM; Channel 7 on Ambient Temperature; Channels 3 and 6 on PCM-foam; Channel 5 on Blank foam)

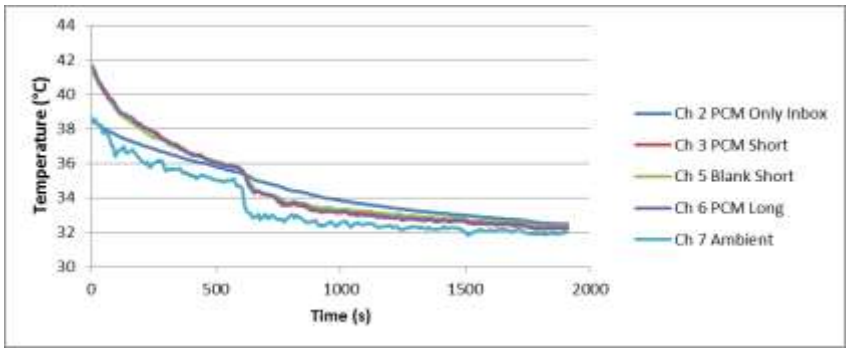


**Figure 3** Cooling Profile of Setup (Same Channel Assignements)

 

## Photos

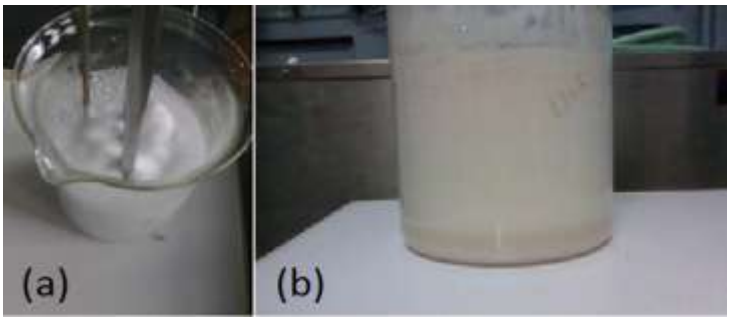


**Photo 1** Homogenized Mixture; (a) During homogenization, (b) after homogenization

**Photo 2** Microencapsulated PCM prior to Characterization

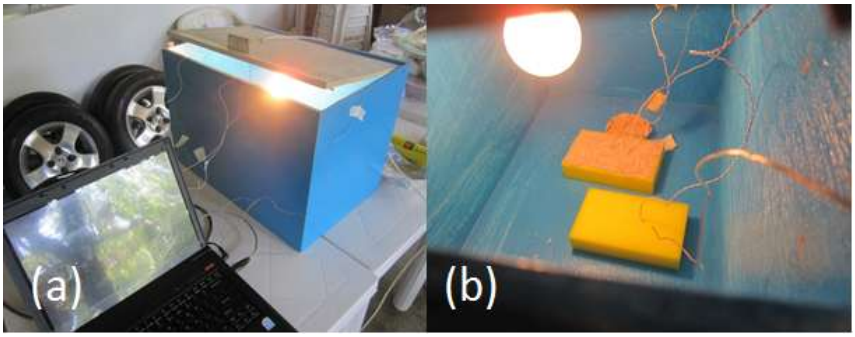


**Photo 3** Temperature Profiling Set-up; (a) Outside the box, (b) Inside the box

 

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