Prediction of Phase Change Material (PCM) Degradation

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ABSTRACT

Phase change materials (PCMs) are now well-known as potential additives to building insulation to provide a thermal mass effect to help conserve energy and maintain comfortable temperatures. There are many PCMs available, with phase change temperatures covering a wide range of applications; however, the performance envelope of most PCMs over time is not well known. For example, PCMs may lose energy storage capacity at temperatures at which phase transitions occur or may change due to chemical and physical transformations over many cycles of use. In this paper we are simulating long–term use of selected PCMs by laboratory testing in a thermal cycling chamber where temperatures are varied over the PCM samples' transition temperature ranges every 90 minutes. PCM samples being tested include: (1) encapsulated octodecane, (2) un-encapsulated mixtures of palm-oil and soy oil, and (3) samples of core materials excised from PCM panels. PCMs samples are removed from thermal cycling at two week intervals and differential scanning calorimetry (DSC) analysis is conducted to determine any degradation in thermophysical properties including melting point, heat of fusion, specific heat capacity, melting onset, and melting peak transition range. All PCM samples tested will be subjected to 5,400 cycles during the one-year long experiment to simulate 20 years of use in buildings. This research is expected to result in an accelerated aging methodology that allows reliable prediction of long-term PCM performance.

INTRODUCTION

Phase change materials (PCMs) are materials with a high capacity to absorb and release energy in the form of latent heat over a short temperature range at ambient conditions (Mondal 2008). The phase changes involved may be solid-liquid or solid-solid. Incorporation of the PCMs and their performance in building cooling and heating applications have been reviewed by several researchers (Sharma at al. 2009; Tyagi and Buddhi 2007; Farid et al. 2004; Kosny et al. 2012). These materials and concepts are being evaluated with renewed interest due to the increased costs associated with energy and the environment. In particular, applications of PCMs for building envelopes for heating and cooling are considered very promising applications as the market for cooling of buildings is expanding rapidly and free cooling systems can be retrofitted in existing buildings. The design of a thermal storage system within this narrow temperature range must be founded on reliable and high resolution material data. The accurate determination of the PCM's heat storage capability as a function of temperature is crucial. Another very important factor in the design of free cooling applications is the heat transfer between storage material and ambient air. There have been several research articles on simulation and modeling of the PCM based materials; often the stability of the PCMs over extended periods of time and the effect of thermal cycling have not been extensively studied. Experimental measurements on PCMs are needed to confirm calculations. In this paper we report experimental measurements on changes in the latent heat, melting and freezing points, heat of fusion, specific heat capacity (C_p), melting and freezing onset, and peak transition ranges of four commercial PCMs to assess their stability over 5,400 thermal cycles representing a duration of 20 years.

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EXPERIMENTAL

Materials

In this research, four commercially available PCM materials were selected. These materials represent different chemical natures, including two encapsulated octadecane mixtures with different melting and freezing points (designated as MA and MB in this paper, respectively), one un-encapsulated mixture of palm oil and soy oil (designated as POSO), and one sample of paraffin wax extracted from a PCM panel (designated as PWAX). The micro-encapsulated PCMs (Figure 1a and 1b), have the consistency of free-flowing powders and are generally mixed in with loose fill insulation. The POSO samples were extracted from one of the polymeric pouches of a PCM blanket (Figure 1c). In practice, the PWAX materials are used as the core materials of a PCM wall or ceiling panel with the wax and elastomer binder sandwiched in between two aluminum sheets (Figure 1d). The purpose of the elastomer binder is to hold the paraffin in place to prevent sagging and dripping as it melts. For this research, the PCM samples were extracted from one of the panels and subjected to thermal cycling.

Sample Preparation

Samples of the four types of PCM materials (MA, MB, POSO, and PWAX) were placed in aluminum pans for DSC measurements, which were then hermetically sealed. Three DSC pans were prepared for each material. In order to reduce the variation in measurements of the heat storage capacity with respect to temperature, all samples weighed approximately between 5 mg and 6 mg. The DSC pans and lids were obtained from TA instrument, Inc. (New Castle, DE). Baseline DSC measurements for each sample were conducted prior to thermal cycling.

Differential Scanning Calorimetry (DSC)

The thermal characterization of samples including melting and freezing points, heat of fusion, specific heat capacity (C_p), melting and freezing onset, and peak transition range were determined by the DSC (Model Q20 from TA instrument, Inc., New Castle, DE), which is shown in Figure 2. All DSC measurements were carried out at constant heating and cooling rate of 1°C min^{-1} and were repeated three times for each sample. The beginning and ending temperatures of the DSC scans depended on the physical properties of each PCM being evaluated in order to ensure complete melting and solidification.

Thermal Cycling Chamber and Thermal Cycling Profile

The DSC pans containing PCM samples were placed in Model EC127 temperature test chambers (Sun Electronic Systems, Inc., Titusville, FL), as shown in Figure 3 (left), where thermal cycling was performed under controlled thermal and humidity conditions. The thermal cycle begins at –10°C and the heating rate proceeds at 3.5°C min^{-1} up to 60°C. The samples are held at 60°C for 25 minutes and then cooled back to –10°C with a cooling rate of 3.5°C min^{-1}. The samples are held at –10°C for another 25 minutes, and the thermal cycle is repeated, as shown in Figure 3 (right). Each complete cycle requires 90 minutes. The thermal cycling chamber was outfitted with a small battery operated thermometer to provide an independent verification of the chamber temperatures. Samples were taken out of thermal cycling chamber at two week intervals, and they were subjected to DSC measurements to determine any changes in thermal properties. Each thermal cycle represents approximately one day of actual use in a building envelope. Since PCMs used in building envelopes would likely only undergo phase changes during 75% of a year, it is reasonable to assume that PCM materials would undergo 270 complete phase change cycles per year. As the duration of each cycle in the test chamber was 90 minutes, one year of use can be simulated in these cham-

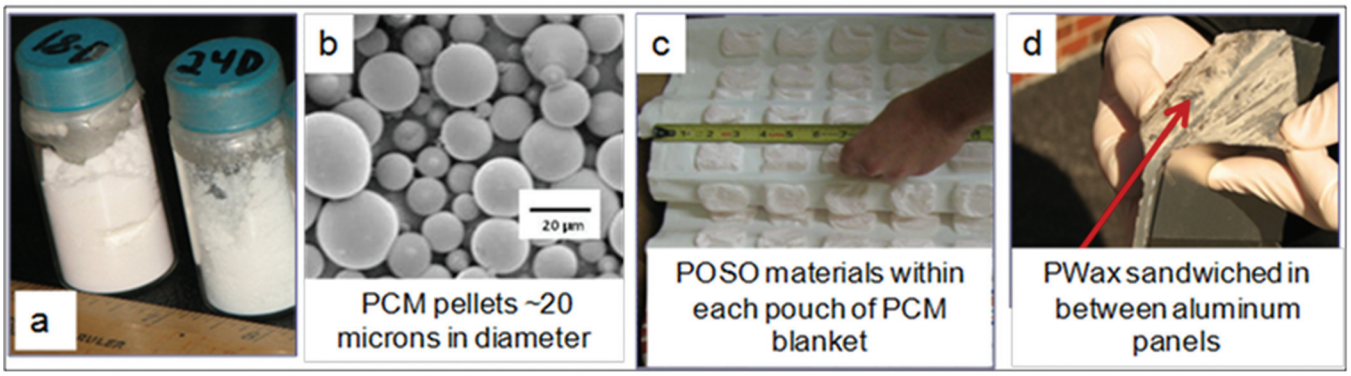

Figure 1 *(a) Vials containing micro-encapsulated octadecane mixtures with two different melting and freezing points; (b) Scanning electron micrograph of microencapsulated PCM pellets shown in (a); (c) blanket with pouches of mixture of palm-oil and soy oil; (d) paraffin wax with elastomer binder sandwiched in between aluminum panels.*

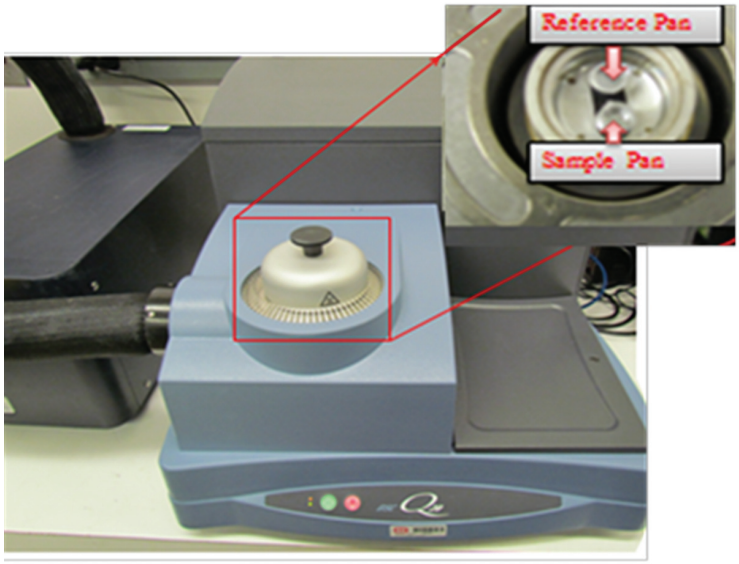

Figure 2 *Differential scanning calorimetry (DSC) model Q20 from TA instrument, Inc. with inset showing the sample and reference pans.*

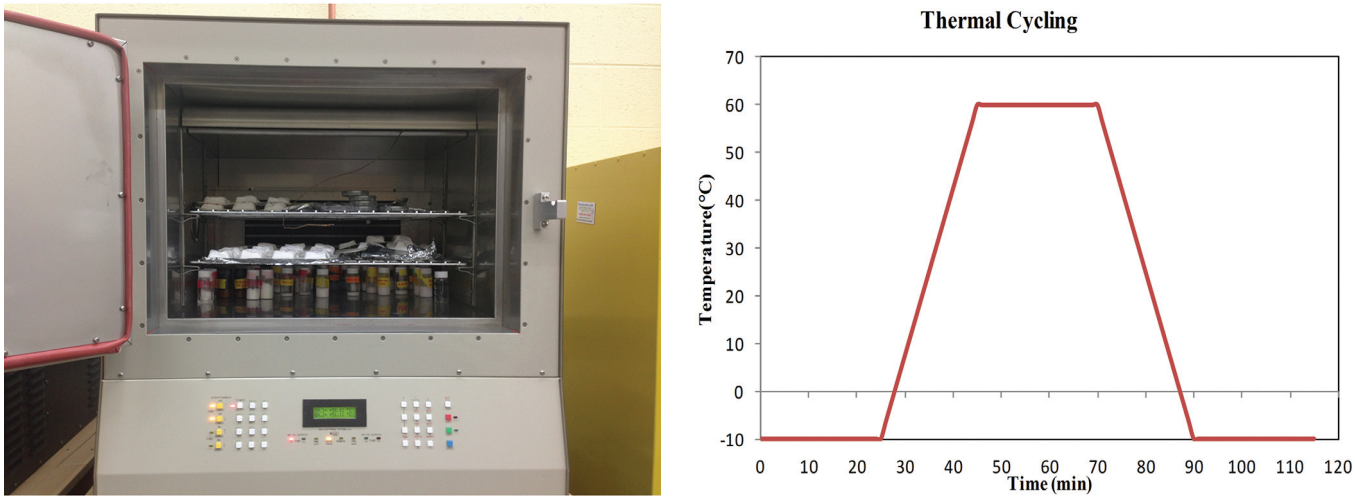

Figure 3 *Left: EC127 thermal cycling chamber (Sun Electronic Systems). Right: Thermal cycling profile used for the thermal cycling experiments.*

bers in 17 days. All the PCM samples are subjected to 5,400 thermal cycles during this one-year long research effort to simulate 20 years of use in building envelopes.

RESULTS

Changes in latent heat capacity were determined for each sample using DSC. The results of melting point on-set, average melting point, freezing point, and latent heats for all the four PCMs at different cycles are included in Tables 1–4 and the results are also presented in Figures 4–7.The same DSC pan sample was periodically removed from the chamber (after approximately 200 cycles), analyzed with the DSC and then replaced into the test chamber.

As can be seen in Tables 1–4,the measured melting point temperatures and latent heat values for baseline samples were generally in accordance with the manufacturer's stated values. Thus far, the samples have been exposed to 848 heating/cooling cycles, which represents about 3.1 years of PCM use, based on 5,400 cycles for 20 years. It is readily apparent that all PCM materials tend to lose latent heat capacity as they undergo thermal cycling.

PCM samples comprised of micro- encapsulated octadecane mixture samples with low melting point (T_m ~ 18°C), desig-

Table 1. Differential Scanning Calorimetry Data (Melting and Freezing) for PCM Comprised of Paraffin Wax and Binder Elastomer

Samples	Cycles	Melting			Freezing		
		Onset (°C) Average	Melting Point (°C) Average	Latent Heat (J/g) Average	Onset (°C) Average	Freezing Point (°C) Average	Latent Heat (J/g) Average
PWAX 1*	0	16.56	22.27	68.50	21.20	16.82	68.22
	212	17.37	23.11	64.29	20.54	17.58	67.95
	424	18.75	24.17	57.73	21.57	18.31	64.10
PWAX 2	0	16.94	22.47	72.31	20.43	17.74	76.29
	212	18.32	23.17	69.05	20.56	17.45	76.15
	424	18.72	23.97	67.17	21.27	18.13	74.63
	636	19.40	24.53	62.76	21.94	18.71	70.44
	848	19.24	24.87	56.48	20.56	18.72	67.18
PWAX 3	0	16.40	22.36	69.82	21.97	16.87	74.16
	212	17.27	23.21	67.71	20.91	17.26	74.80
	424	18.22	24.19	61.46	21.68	18.02	70.74
	636	19.40	24.53	62.76	21.94	18.71	70.44
	848	19.11	24.81	50.07	25.12	18.57	61.71

* PWAX: mixture of paraffin wax and elastomer binder

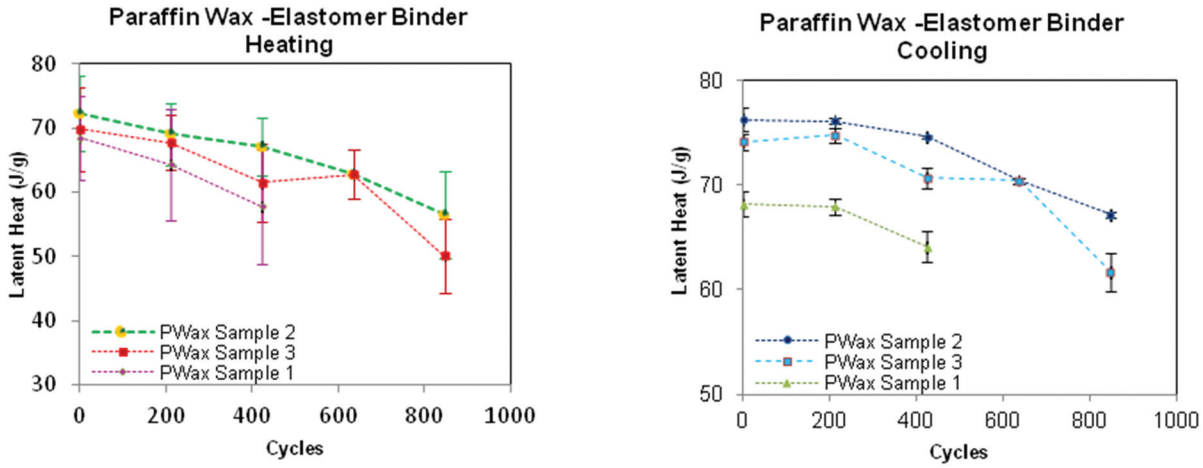

Figure 4 *Latent heat versus number of cycles for PCM comprised of paraffin wax and elastomer binder.*

nated as MA, showed the greatest decrease of latent heat for both heating and cooling curves, at rates of about –0.040 J/g/cycle. PCM samples comprised of micro-encapsulated octadecane mixture samples with high melting point (T_m ~ 24°C), designated as MB, showed the least degradation in terms of loss of latent heat capacity in both heating and cooling curves, at rates of about –0.10 J/g/cycle. PCM samples comprised of palm oil and soy oils (POSO) showed latent heat degradation rates for both heating and cooling curves of –0.30 J/g/cycle and –0.020 J/g/cycle, respectively, except for one sample which showed anomalous behavior, with approximately five times higher degradation rates. PCM samples comprised of paraffin wax and binder (POSO), showed latent heat degradation rates of –0.025 J/g/cycle and –0.014 J/g/cycle, for heating and cooling curves, respectively.

DISCUSSION

Thermal performance models of the building envelopes that include the dynamics of phase change materials must depend on the materials properties of the PCMs employed;

Table 2. Differential Scanning Calorimetry Data (Melting and Freezing) for PCM Comprised of Palm-Oil and Soy-Oil Mixture

Samples	Cycles	Melting			Freezing		
		Onset (°C) Average	Melting Point (°C) Average	Latent Heat (J/g) Average	Onset (°C) Average	Freezing Point (°C) Average	Latent Heat (J/g) Average
POSO 1*	0	22.46	26.37	130.55	22.19	21.04	131.25
	212	23.01	24.61	92.85	22.33	21.24	97.44
	424	22.71	24.70	63.43	22.41	21.49	69.09
	636	22.40	24.42	45.78	22.23	21.56	47.11
POSO 2	0	22.87	26.46	136.30	22.01	21.23	137.25
	212	24.36	26.37	136.47	21.81	21.39	137.70
	424	24.30	26.16	130.93	21.67	20.99	133.83
	636	24.11	26.04	117.27	21.56	21.06	125.13
	848	24.13	25.93	110.33	21.55	21.07	120.67
POSO 3	0	22.81	26.59	136.03	22.04	21.12	137.43
	212	24.12	26.22	136.93	21.82	21.00	138.53
	424	24.16	26.08	130.83	21.73	21.11	136.77
	636	24.05	25.96	124.03	21.65	21.16	135.47
	848	23.20	25.90	119.90	21.55	21.18	133.60

* POSO: PCM containing palm-oil and soy-oil mixture

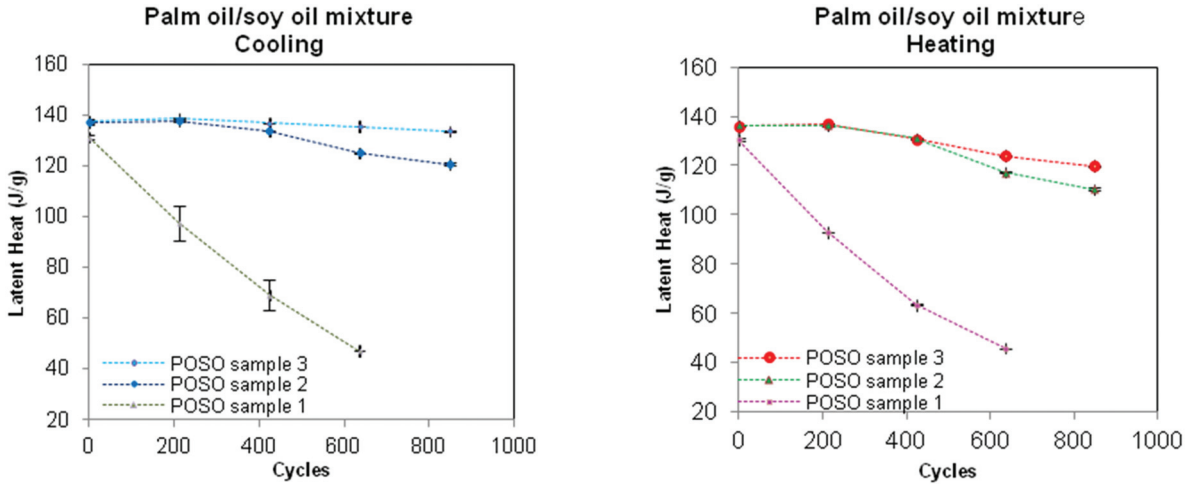

Figure 5 *Latent heat versus number of cycles for PCM comprised of palm-oil and soy-oil mixture* T_m *~ 25°C).*

however, if those properties change over time, the long term performance expectations and service life may be reduced. For example, if the transition temperatures drift or if latent heat values have degraded over time, the expected savings in energy due to installation of the PCM will not be achieved.

Obviously, all PCM products should exhibit high stability of the thermal properties over time (i.e., withstand thousands of cycles without degradation). Builders that use PCMs with unknown or unreliable thermal performance are taking some risk, especially if cyclic testing does not indicate long-term stability. We have presented an experimental approach to evaluate long-term thermal stability of PCMs. The laboratory-based cyclic testing described in this work provides a means of screening and comparing candidate PCM materials performance in a simulated relevant environment. The information obtained from these studies is expected to assist in selection of the optimum PCM for a given application.

Table 3. Differential Scanning Calorimetry Data (Melting and Freezing) for PCM Comprised of Micro-Encapsulated Octadecane Mixtures with Low Melting Point (18°C)

Samples	Cycles	Melting			Freezing		
		Onset (°C) Average	Melting Point (°C) Average	Latent Heat (J/g) Average	Onset (°C) Average	Freezing Point (°C) Average	Latent Heat (J/g) Average
MA 1*	0	14.39	17.21	164.88	14.43	12.95	167.75
	212	14.22	17.25	160.13	14.49	13.25	157.33
MA 2	0	14.40	17.21	170.70	14.54	12.97	175.65
	212	14.15	17.34	162.60	14.74	13.09	166.93
	424	13.60	17.14	153.47	14.82	13.74	156.43
	636	13.28	17.07	144.27	14.88	13.77	146.60
	848	13.30	17.05	136.17	14.95	13.77	138.37
MA 3	0	14.49	17.29	174.25	14.60	13.18	177.05
	212	14.53	17.19	169.93	14.73	13.60	172.93
	424	14.32	17.17	162.30	14.74	13.67	165.73
	636	13.52	17.07	156.17	14.80	13.76	158.63
	848	13.12	16.99	148.30	14.86	13.84	146.80

* MA: encapsulated octadecane mixture sample with low melting point
* Sample MA1 failed the test after 424 cycles because the pan and lid fell apart.

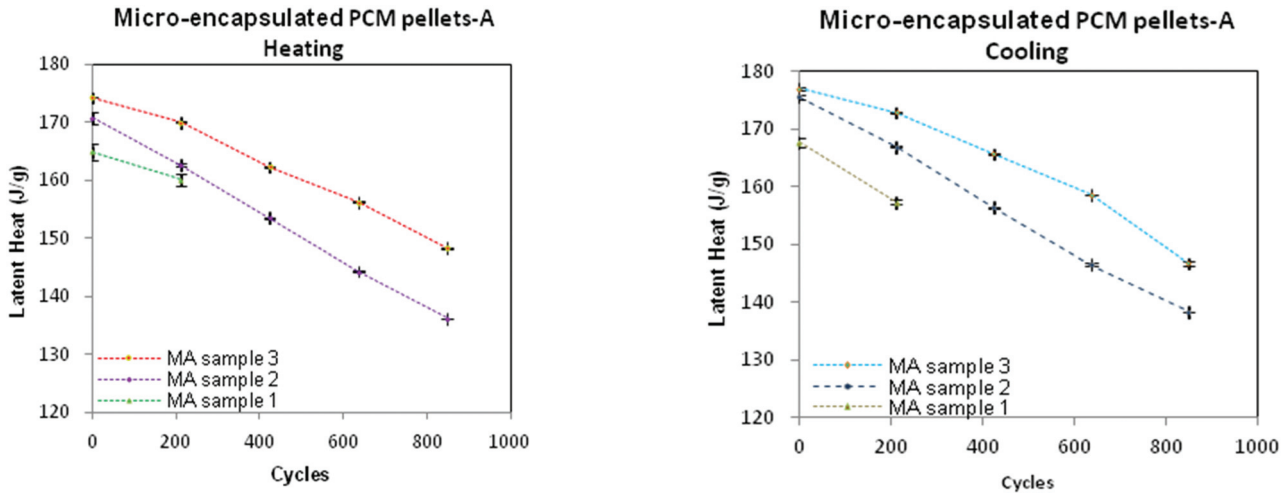

Figure 6 *Latent heat versus number of cycles for PCM comprised of micro-encapsulated encapsulated octadecane mixtures with low melting point (18°C).*

Although European standards for quality assurance of PCM performance (e.g., RAL-GZ-839), have been established, most US manufacturers rely on their own internal standards for quality assurance, and some US PCM manufacturers maintain limited data validating the cyclic performance of their products. Currently, one of the ASTM committees is working on developing a US standard for quality control/quality assurance of PCMs (Private Communication, 30 May 2013). In the meantime, most US manufacturers have focused on moisture transmission testing, based on the procedures of ASTM E96 (Method B) *Standard Test Methods for Water Vapor Transmission of Materials*, and fire resistance testing, as per ASTM E84-09 *Standard Test Method for Surface Burning Characteristics of Building Materials* results, rather than on tests simulating long-term thermal performance of their products. The industrial quality assurance standards used in Europe are well thought out, and US manufacturers would be well-advised to give them due consideration.

Table 4. Differential Scanning Calorimetry Data (Melting and Freezing) for PCM Comprised Micro-Encapsulated Octadecane Mixtures with High Melting Point (24°C)

Samples	Cycles	Melting			Freezing		
		Onset (°C) Average	Melting Point (°C) Average	Latent Heat (J/g) Average	Onset (°C) Average	Freezing Point (°C) Average	Latent Heat (J/g) Average
MB1	0	20.03	22.40	125.30	21.75	20.46	122.47
	212	19.33	22.54	121.88	22.29	20.78	120.60
	424	19.26	22.78	118.30	22.37	20.96	117.38
	636	19.53	22.89	118.15	22.52	21.40	115.80
MB2	0	19.84	22.20	127.28	21.91	20.68	123.08
	212	19.39	22.39	123.63	22.29	20.69	123.17
	424	19.22	22.68	120.10	22.34	20.85	118.67
	636	19.49	22.82	120.07	22.45	21.43	117.30
	848	19.72	22.94	118.13	22.59	21.64	114.47
MB 3	0	19.94	22.32	127.63	21.88	20.56	123.80
	212	18.99	22.68	120.83	22.26	20.44	121.77
	424	19.16	22.77	119.80	22.34	20.94	119.67
	636	19.48	22.88	120.67	22.45	21.37	119.10
	848	19.67	22.96	120.30	22.57	21.57	117.27

* MB: micro-encapsulated octadecane mixture sample with high melting point

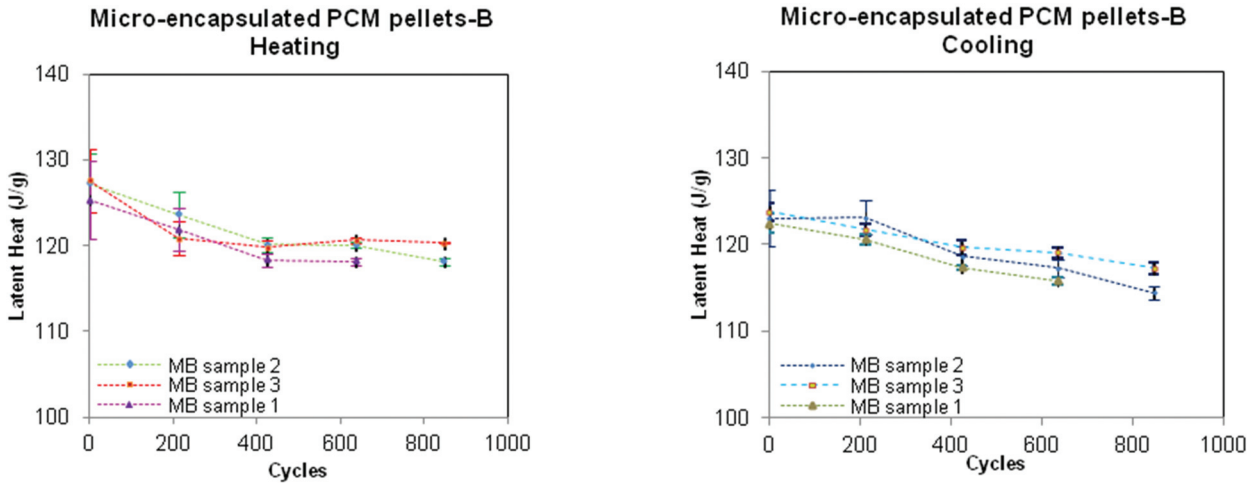

Figure 7 *Latent heat versus number of cycles for PCM comprised of micro-encapsulated octadecane mixtures sample with high melting point (24°C).*

The motivation for evaluating change in performance of phase change materials as they are subjected to repeated cycling stems from the concern that the materials may undergo physical and chemical transformations, as well as changes in crystal structure. The materials may also absorb moisture, leading to chemical decomposition and degradation of the PCM material and degradation of its thermal properties. Such physical/chemical transformations are evident in all four PCM materials, however, the extent and rate of decrease in latent heat varies for different materials. The PCMs evaluated in this investigation have so far shown only slight degradation of latent heat during 848 repeated heating and cooling cycles, with no appreciable change in transition temperatures. It is also possible that flame retardants and other volatile components of the PCMs are released into the surroundings, contributing to the loss of latent heat. In the case of the PWAX

samples, it is possible that the elastomer binder had reacted with the paraffin wax, and contributed to latent heat loss. Also, other impurities in the PCM mixtures can interfere with bond breakage and formation, or (possibly by reacting with the primary PCM) causing this degradation over time.

While the PCMs in these experiments have only been subjected to 848 thermal cycles, simulating 3.1 year of use, this investigation is on-going and eventually the PCMs will be subjected to 5,400 cycles, in order to simulate 20 years of use. In future research, large samples of the PCMs will be collected in vials and will be subjected to thermal cycling, according to the same schedule as described for the samples in the DSC pans. The vial samples will allow visual examination of the PCM, bulk mass loss analysis and use of Fourier Transform Infrared (FTIR) spectroscopy to determine any chemical changes that may have occurred. The use of large samples in the vials will also circumvent the problems of loss of sample due to hermetic seal breaching during repeated cycles. However, it is noted that the process of evaluating the same sample each time, ensures that an accurate history of performance is attributed to changes in that particular sample. Both methods need to be evaluated in future experiments and compared. The anomalous behavior observed for sample 1 of the POSO samples, perhaps due to the breach of the hermitic seal during DSC measurements, will be further investigated. Overall, the maximum decrease in latent heat for each of the four materials over the 848 phase change cycles was as follows: (a) for PWAX (paraffin and elastomer binder), the decrease in latent heat was 22%–25% during heating, and ~15% during cooling; (b) for POSO (palm oil and soy oil mixture), the decrease in latent heat was 13%–19% during heating and 3%–12% during cooling; (c) for MA (low transition temperature microencapsulated octadecane mixtures samples, the decrease in latent heat during both heating and cooling was 15%–20%; for MB (high transition temperature microencapsulated octadecane mixture samples), the decrease in latent heat during both heating and cooling was 6%–7%. Both high temperature low temperature micro-encapsulated samples (MA and MB) exhibited the least variability in latent heat data.

CONCLUSIONS

Thermal cycling experiments are being conducted in order to establish a standard protocol for evaluation of the long-term performance of phase change materials, in a relatively short term tests. Thus far, samples of four types of PCM have been exposed to 848 heating/cooling cycles, which represents about 3.1 years of PCM use, based on 5,400 cycles for 20 years. The results have indicated that baseline latent heat values were generally in accordance with the manufacturer's stated values. All PCM materials evaluated tended to lose latent heat storage capacity as they underwent thermal cycling. PCM samples comprised of micro- encapsulated octadecane mixture samples with high melting point (T_m ~ 24°C), designated as MB, showed the least degradation in terms of loss of latent heat for both heating and cooling curves, at rates of about –0.10 J/g/cycle. PCM samples comprised of micro- encapsulated octadecane mixtures samples with low melting point (T_m ~ 18°C), designated as MA, showed the greatest loss of latent heat for both heating and cooling curves, at rates of about –0.040 J/g/cycle. Thermal cycling experiments are continuing to expose the four PCM materials to a total of 5,400 cycles.

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