

Thermal cycling test of PCM to ensure long-term performance of domestic hot water systems

Camila Barreneche^{1,2}, Aran Solé¹, Gerard Ferrer¹, Ingrid Martorell¹, Luisa F. Cabeza^{1,*}

1 GREA Innovació Concurrent, Universitat de Lleida, Lleida, Spain. Edifici CREA, Pere de Cabrera s/n, 25001-Lleida (Spain).

Phone: +34-973 003576, Fax: +34-973 003575; *Corresponding author e-mail: lcabeza@diei.udl.cat

2 Department of Materials Science & Metallurgical Engineering, Universitat de Barcelona, Barcelona, Spain. Martí i Franqués

1-11, 08028-Barcelona (Spain). Phone: +34-93 4021298; Email: c.barreneche@ub.edu

Abstract

The successful use of thermal energy storage systems relies on the stability of the phase change materials (PCM). The thermal stability of these materials can be determined by measuring its thermophysical properties after a number of repeated thermal cycles. In this paper, results when three different PCM for domestic hot water applications (fatty acid, paraffin and salt hydrate) are thermally-cycled 0, 100, 1000 and 3650 times, are presented. Thermophysical characterization before and after those cycles was performed in differential scanning calorimeter (DSC) and chemical degradation was evaluated by FT-IR. Results show that there is no degradation after cycling, therefore the three PCM retain their thermophysical properties after 3650 cycles.

1. Introduction

Thermal energy storage (TES) through phase change materials (PCM) is one of the most fruitful ways to store thermal energy [1,2] being the most implemented one at this moment and with better performance in real applications for domestic hot water [3], heating/cooling systems [4], solar cooling [5], concentrated solar power plants [6], etc. However, this method to store heat presents several drawbacks from an overall system energy efficiency point of view.

One of the most mentioned issues is the cyclability or the durability of PCM, but it is also one of the less studied factors at the moment. The successful use of thermal energy storage systems relies on the stability of the phase change materials (PCM). The thermal stability of these materials can be determined by measuring its thermophysical properties after a number of repeated thermal cycles and it is of great importance to ensure the long-term performance of latent heat storage systems. This study must be performed before the implementation of the PCM in the final system/application [7,8].

However, no methodology standards explaining the best method, equipment and times to cycle each PCM type can be found. Therefore, important differences on the thermophysical properties of a same PCM are generally found on literature after cycling as every author applies their own methodology.

This study presents the results obtained when three potential PCM (fatty acid, paraffin and salt hydrate) for domestic hot water applications (DHW) are thermally-cycled 0, 100, 1000 and 3650 times. These PCM were cycled in a GENE Q Hangzhou Bioer TC18/H(b) and they were analysed by differential scanning calorimetry (DSC) and infrared spectroscopy (FT-IR).

2. Materials

The PCM listed in Table 1 are the ones thermal-cycled in this study. Their thermophysical properties were analyzed before and after thermal cycling.

Note that all these PCM are suitable for DHW as their melting point is around 60 °C.

Table 1. PCM under study and their thermophysical properties [9]

Material	Type	Melting temperature [°C]	Heat of Fusion [kJ/kg]	Density [kg/m ³]	Energy density [GJ/m ³]
Palmitic acid	Organic (fatty acid)	61	203	847 (liquid, 80°C)	0.17
Na(CH ₃ COO) · 3H ₂ O	Inorganic (salt hydrate)	58	226-264	1280 (liquid)	0.31
RT-54	Organic (paraffin)	58-60	189	795 (liquid, 70°C) 920 (solid, 20°C)	0.16

3. Methodology

PCM samples under study (Table 1) were cycled 100, 1000, and 3650 times using a GENE Q Hangzhou Bioer TC18/H(b) Technology thermocycler. This simulates the degradation after the charge and discharge processes during several years of operation depending on the times the charge process is given per day (if it is accounted one charge per day, it'll be considered that these PCM were cycled during 10 years).

The thermal cycling method used is shown in Figure 1: it considers two isothermal steps at two different temperatures (35 °C and 75 °C) during 1.5 minutes.

Based on previous experiments, it was observed that 1.5 minutes are required to melt and solidify the amount of sample used. For that reason, each step accounts 1.5 minutes.

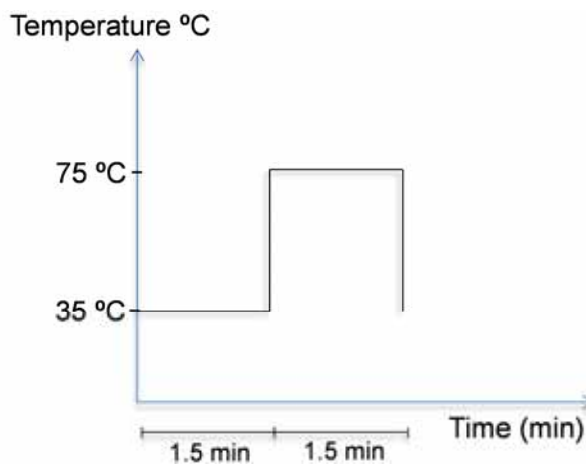


Figure 1. Thermal cycle method used in the cycling test of the PCM under study

Thermophysical properties were analyzed by differential scanning calorimetry (DSC). The equipment used was a Mettler Toledo 822e DSC and one measurement was performed after 0, 100, 1000, and 3650 cycles.

The measurements were performed in a 40 μl aluminum crucible filled with around 10 mg of each PCM, with a heating rate of 0.5 K/min and 80 ml/min N₂ flow.

On the other hand, their chemical structures were evaluated by infrared spectroscopy (FT-IR). The FT-IR instrument used was Spectrum Two™ from Perkin Elmer and supported by Dynascan™ interferometer and Optics Guard with ATR. Thereby, chemical degradation was evaluated along with the stability of the thermophysical properties over the PCM cycles.

4. Results and discussion

From the thermophysical point of view and as results listed in Table 2 show, there are not consistent differences between the non-cycled samples and the ones cycled 3650 times.

Both melting and solidification point changes for organic PCM (Palmitic acid and paraffin RT-54) are near 0%. Moreover, the melting enthalpy changes for organic PCM are between 1.5-5%, which are within the equipment error (around 8%).

However, for the salt hydrate ($\text{Na}(\text{CH}_3\text{COO}) \cdot 3\text{H}_2\text{O}$) the melting point difference between 0-3650 cycles is around 5%, which is a small difference. Solidification results were not obtained because of the high subcooling this PCM presents.

Table 2. Thermophysical results obtained with DSC before and after thermal cycling

		H_m (kJ/kg)	T_m (°C)	H_s (kJ/kg)	T_s (°C)
Palmitic acid	0 cycles	199	63	201	60
	3650 cycles	202	63	200	61
	Percent change (0-3650 cycles)	1.5%	0%	0.5%	2%
$\text{Na}(\text{CH}_3\text{COO}) \cdot 3\text{H}_2\text{O}$	0 cycles	263	57	n.d.	n.d.
	3650 cycles	247	60	n.d.	n.d.
	Percent change (0-3650 cycles)	6%	5%	n.d.	n.d.
RT-54	0 cycles	140	51	141	53
	3650 cycles	147	51	147	53
	Percent change (0-3650 cycles)	5%	0%	4%	0%

*n.d. stands for not determined

where m stands for melting and s for solidification.

The structural degradation of one substance or material is noted when the IR-characteristic peaks disappear or other peaks appear instead.

Results obtained with FT-IR spectroscopy show that there is no degradation in any of the studied materials because FT-IR characteristic signals remain constant over cycles as it is shown in Figure 2, Figure 3 and Figure 4.

FT-IR signals are characteristics of each material/substance and they are highlighted in these figures. The signals will depend on the vibration of the chemical bonds of the chemical structure.

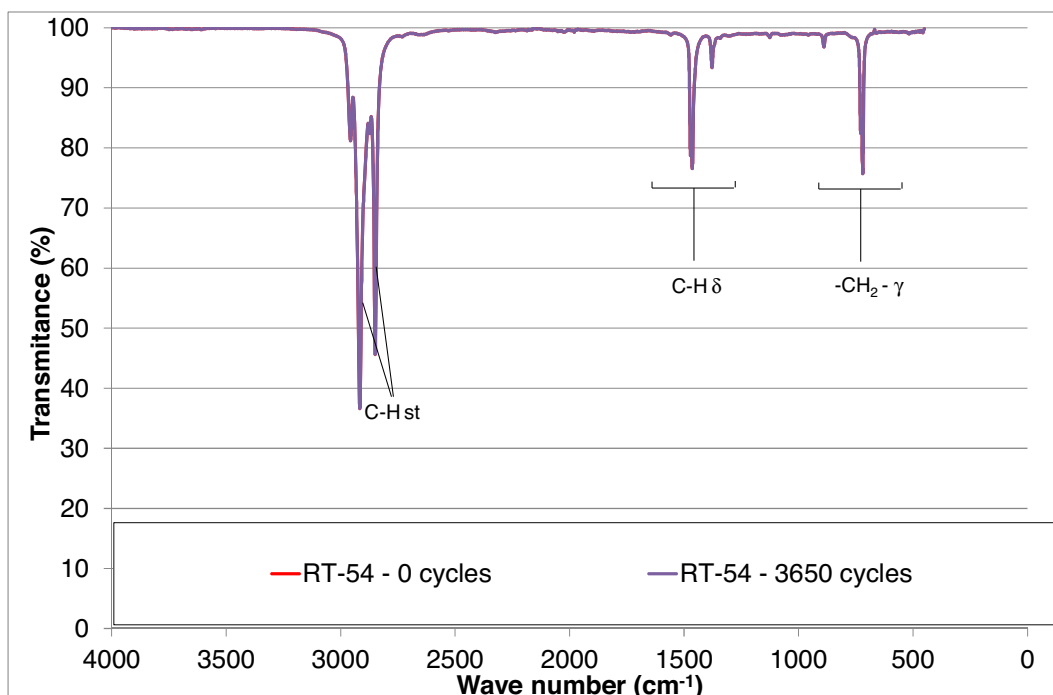


Figure 2. FT-IR spectrum for RT-54 before and after cycling

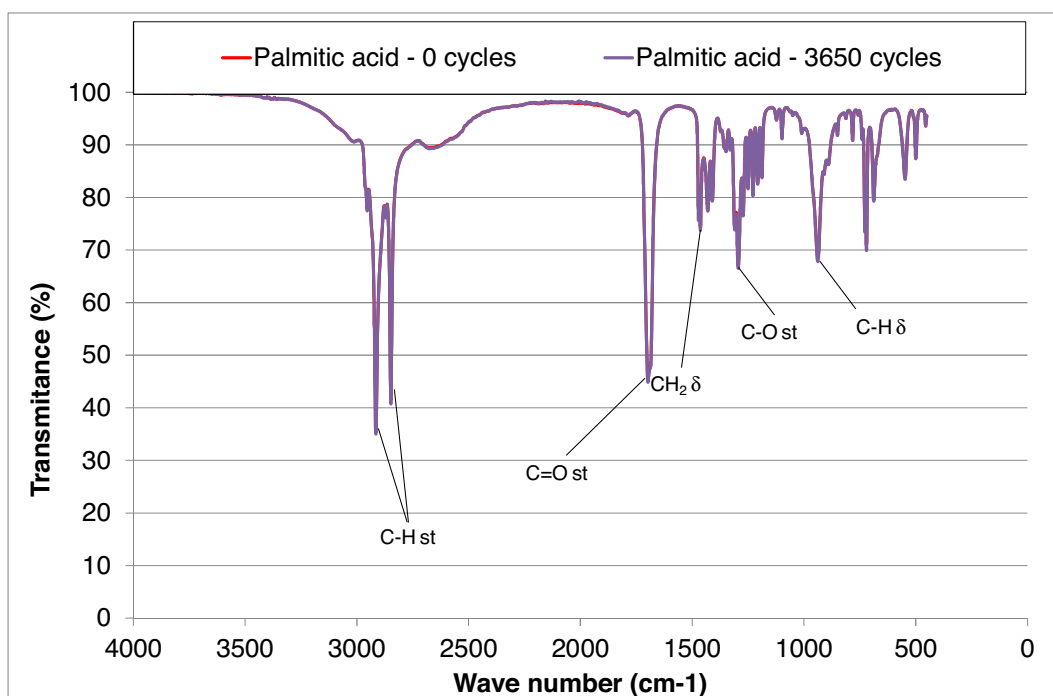


Figure 3. FT-IR spectrum for Palmitic acid before and after cycling

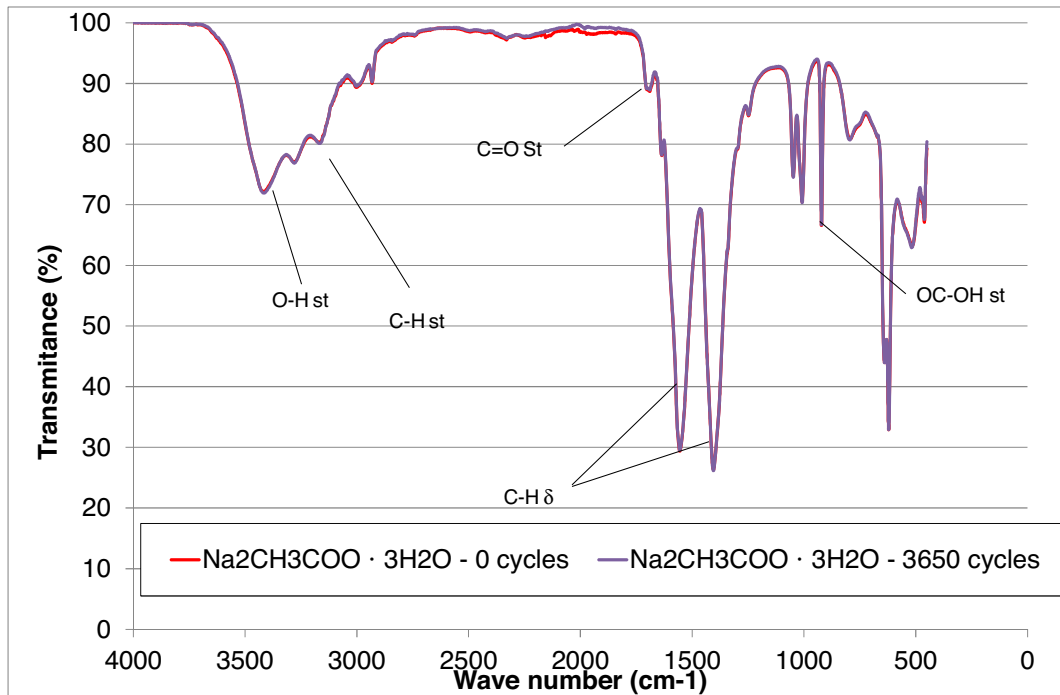


Figure 4. FT-IR spectrum for $\text{Na}(\text{CH}_3\text{COO}) \cdot 3\text{H}_2\text{O}$ before and after cycling

5. Conclusions

This study presents the thermophysical characterization of three potential PCM for DHW applications (a salt hydrate ($\text{Na}(\text{CH}_3\text{COO}) \cdot 3\text{H}_2\text{O}$), a paraffin wax (RT-54), and a fatty acid (palmitic acid) after a thermal cycling test (0, 3650 cycles which correspond to 10 years of service considering one charging/discharging process per day).

The thermophysical characterization results before and after cycling show that there are no significant changes on their thermophysical properties (less than 5% for the melting process and less than 6% for the solidification process). However, results for the solidification process were not obtained for the salt hydrate under study due to high subcooling.

Moreover, the chemical stability of these PCM was evaluated by FT-IR. Results showed that there is no degradation process acting through the cycles and the PCM retain their thermophysical properties after 3650 cycles.

-Summarizing, no degradation regarding neither chemical structure nor thermophysical properties of the PCM under study were obtained under a thermal cycling test, which means that these PCM are proper candidates to be implemented in DHW systems complemented with a TES system. However, the thermal cycling test stopped at 3650 cycles. Therefore, it is recommended to increase the number of thermal cycles in order to determine the thermal cycle limit.

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