Research paper

Thermal characteristic reliability of fatty acid binary mixtures as phase change materials (PCMs) for thermal energy storage applications

Hadi Fauzi [a, c, *], Hendrik S.C. Metselaar [a, *], T.M.I. Mahlia [b], Mahyar Silakhori [a], Hwai Chyuan Ong [a]

[a] Department of Mechanical Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia
[b] Department of Mechanical Engineering, Universiti Tenaga Nasional, Kajang 43000, Selangor, Malaysia
[c] Department of Chemical Engineering, Syiah Kuala University, Banda Aceh 23111, Indonesia

HIGHLIGHTS

- The MA/PA/SM and MA/PA/SP were used as eutectic phase change materials (PCM).
- Thermal reliability of eutectic PCMs evaluated using a thermal cycling test.
- MA/PA/SP has a great thermal characteristic than MA/PA/SM after 3600 thermal cycles.
- The eutectic PCMs did not show change of appearance after 3600 thermal cycles.

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ABSTRACT

The thermal characteristic reliability of two binary mixtures of fatty acid, myristic acid/palmitic acid/sodium myristate (MA/PA/SM) and myristic acid/palmitic acid/sodium palmitate (MA/PA/SP), were investigated using a thermal cycling test setup for 0, 1000, 2000, 3000, and 3600 heating/cooling cycles. The changes in thermal properties and chemical bonding of both eutectic PCMs were measured using Differential Scanning Calorimetric (DSC) and Fourier Transform Infrared Spectroscopy (FT-IR) analyzer, respectively. MA/PA/SM and MA/PA/SP eutectic mixtures shows only minor changes in phase transition temperature (T_m, T_s) and in latent heat of fusion (ΔH_f). Moreover, the chemical bonding structures of these eutectic PCMs show no degradation and the thermal performance of those PCMs shows a good stability after 3600 thermal cycles. Therefore, it is found that the thermal characteristic stability of prepared MA/PA/SM and MA/PA/SP eutectic mixtures were acceptable for long term performance and economic feasibilities used as a phase change material (PCM) for thermal energy storage (TES) application.

1. Introduction

The ideal phase change material (PCM) for thermal energy storage (TES) application must have the following features: appropriate phase change temperature, high latent heat, low cost, non-toxicity, non-flammability, and uniform phase change characteristics, such as no undercooling or phase separation. Beside these features, it must have a high thermal reliability to allow a long life performance [1].

Phase change materials (PCMs) typically used for TES, such as paraffin and salt hydrates, can absorb a large amount of heat as they melt. But these materials have the disadvantage of phase segregation during heating/cooling cycles, which makes them unsuitable for application as heat storage materials [2]. Fatty acids have been reported as a most promising PCM because of the following advantages: suitable phase change temperature, high latent heat of fusion, ready availability, non-toxicity, non-flammability, non-undercooling, no or little volume change, good thermal reliability after a large number of melting/solidification cycles, as well as compatible with many holding materials, and easy production from common vegetable and animal oil that provide an assurance of continuous supply despite the shortage of fuel sources [3–7].

* Corresponding authors. Department of Mechanical Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia. Tel.: +60 3 79674451; fax: +60 3 796744.
E-mail addresses: hadidoank@gmail.com (H. Fauzi), h.metselaar@um.edu.my (H.S.C. Metselaar).

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Every latent heat thermal energy storage (LHTES) system requires a suitable PCM. The assessment of latent heat storage material for an LHTES system should consider the feasibilities of economic, thermodynamic, kinetic and chemical properties [8]. Therefore, comprehensive knowledge of the thermal reliability of the PCMs as a function of repeated heating/cooling cycles is essential to assure a long term performance and economic feasibility of a latent heat storage system [1].

The economic feasibility of employing a latent heat storage material in a system depends on the life time of the storage material, i.e. there should not be major changes in the melting temperature and latent heat of fusion with increasing number of thermal cycles of the storage material [8,9]. As a thermal energy storage system undergoes at least one thermal cycle in a day, an accelerated thermal cycling test can be conducted to study the behavior of a PCM after a repeated number of thermal cycles [8,9]. The changes of phase change transition temperature and latent heat of fusion values of a PCM after a large number of melting and solidification processes must be as low as possible before using it in an actual energy storage system [1].

Therefore, in our current work the thermal properties, chemical structure and thermal performance stabilities of myristic acid/palmitic acid/sodium myristate (MA/PA/SM) and myristic acid/palmitic acid/sodium palmitate (MA/PA/SP) eutectic mixtures subjected to 0, 1000, 2000, 3000, and 3600 heating/cooling cycles were evaluated. This study was conducted to establish the economic feasibility and thermal characteristic performance of PCM before applying it in LHTES applications particularly in domestic water heating application.

2. Material and methods

2.1. Materials

Two kinds of fatty acid binary mixtures, myristic acid/palmitic acid/sodium myristate (MA/PA/SM) and myristic acid/palmitic acid/sodium palmitate (MA/PA/SP) were prepared as the tested phase change materials (PCMs). These binary mixtures were proposed by Fauzi et al. [10] in a previous work by blending the MA (Acros Organic) and PA (Acros Organic) with the composition of 70 wt.% and 30 wt.%, respectively. 5% sodium myristate (SM) (Sigma Aldrich) and sodium palmitate (SP) (Sigma Aldrich) were added separately as the surfactants in order to improve the thermal properties of the MA/PA binary mixture [10]. The eutectic composition MA/PA in 70/30 wt.% selected due to its phase transition temperature which is near to suitable range temperature compared to other compositions [10,11]. Hence, the addition of SM and SP as surfactant proposed to decreased the phase transition temperature and in the same time enhanced the latent heat capacity of MA/PA (70/30, wt.%) [10].

2.2. Methods of experiment and analysis

Fig. 1 shows the thermal cycling test set-up as described by Fauzi et al. [12] was used to evaluate the reliability of fatty acid binary mixtures after 1000, 2000, 3000, and 3600 heating/cooling cycles. 5 g of binary mixture was put in a glass cylindrical capsule inside the chamber separately and submersed in the heat transfer fluid (HTF). The temperature of the HTF was cycled between 30 °C and 55 °C, for using the samples to change phase as melting temperature of 41.36 °C and 41.58 °C, respectively [10]. Moreover, the thermal performance of both binary mixtures was evaluated to compare endothermic and exothermic characteristics of samples before and after 3600 thermal cycles.

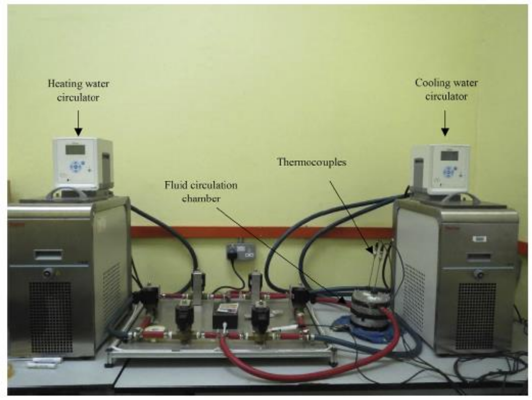

Fig. 1. Thermal cycling test setup.

The melting temperature, T_m, and latent heat of fusion, ΔH_f, of both binary mixtures were measured using a Differential Scanning Calorimeter (DSC, Perkin Elmer DSC 8000) subjected to 1000, 2000, 3000 and 3600 thermal cycles. The samples were put in a sealed aluminum crucible pan and analyzed under heating and cooling rate 5 °C/min under flowing of Nitrogen (N_2) gas at a temperature range of 0–70 °C.

Fourier transform infrared spectroscopy (FT-IR, Bruker Tensor 27) was used to identify the chemical structure bounds of MA/PA/SM and MA/PA/SP binary mixtures at 0 thermal cycles and after 3600 thermal cycles. The prepared fatty acid binary mixtures were analyzed by ATR sample compartment with MIR spectra in the wavenumber range of 4000–400 cm^{-1}.
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3. Results and discussion

3.1. Thermal properties stability

The thermal properties of fatty acid binary mixtures, MA/PA/SM and MA/PA/SP subjected to a large number of thermal cycles were measured in order to evaluate the thermal properties stability of eutectic PCMs subjected to 1000, 2000, 3000, and 3600 thermal cycles corresponding to a utilization period of about 10 years. The results are tabulated in Table 1 and show the changes of thermal properties (phase transition temperature T_m, T_s and latent heat of fusion ΔH_f) of MA/PA/SM and MA/PA/SP binary mixtures. The value of phase transition temperature and latent heat of fusion both eutectic PCMs were obtained from the onset temperature and numerical integration of area under peak [1,13] from DSC curves shown in Figs. 2 and 3, respectively.

As shown in Table 1, the melting temperature of MA/PA/SM and MA/PA/SP after 1000 thermal cycles increase by 1.54 and 1.39 °C while their solidification temperature decreased by −0.64 and −0.70 °C. Subsequently, the T_m of MA/PA/SM and MA/PA/SP was more stable and only small irregular changes of 1.61, 1.54, 1.46 °C and 1.31, 1.29, 1.42 °C after 2000, 3000, and 3600 thermal cycles were observed. The same trend occurred in the T_s of those binary PCMs which is only small irregular decrease of −0.78, −0.64, −0.69 °C and −0.82, −0.77, −0.73 °C after 2000, 3000, and 3600 thermal cycles. The results in Table 1 also show that the changes of latent heat of fusion (ΔH_f) of MA/PA/SM which was decreased by 5.27% and 5.29% after 1000 and 2000 thermal cycles, while the reduction of its ΔH_f was the smallest after 3000 and 3600

Table 1
Thermal properties of fatty acids binary mixtures.

No. of cycles	MA/PA/SM				MA/PA/SP			
	T_m (°C)	ΔH_{fsm} (J/g)	T_s (°C)	ΔH_{fss} (J/g)	T_m (°C)	ΔH_{fsm} (J/g)	T_s (°C)	ΔH_{fss} (J/g)
0	41.36[1]	179.12[10]	41.70[10]	176.26[10]	41.58[10]	184.14[10]	41.98[10]	184.06[10]
1000	42.90	169.67	41.06	172.22	42.97	173.62	41.28	177.37
2000	42.97	169.64	40.92	175.47	42.89	172.03	41.16	176.28
3000	42.90	174.00	41.06	175.85	42.87	173.13	41.21	177.21
3600	42.82	172.23	41.01	173.99	43.00	171.80	41.25	176.325

thermal cycles with 2.86% and 2.84%. A different phenomenon occurred for MA/PA/SP binary mixture, the ΔH_f these binary PCM consistently decreased by 5.71%, 6.57%, 5.98%, and 6.70% for 1000, 2000, 3000, and 3600 cycles, respectively.

The stability of thermal properties fatty acid has been studied by others previously. Sari et al. [1] in their work of thermal reliability of stearic acid (SA), palmitic acid (PA) myristic acid (MA) and lauric acid (LA) reported that the T_m of these fatty acids were constant up to 120 thermal cycles, but that they decreased by 5.04, 2.52, 2.21, 0.26 °C and 7.87, 5.84, 6.78, and 1.38 °C after 560 and 1200 thermal cycles, respectively. Furthermore, the changes of ΔH_f of SA, PA, MA, and LA were −4.8% to 3.9%, −17.3%, −27.7%, and −12.9% to 11.3% after 10, 560 and 1200 thermal cycles, respectively. In another work Sari [14] also evaluated the change of T_m and ΔH_f of lauric acid/myristic acid (LA/MA), lauric acid/palmitic acid (LA/PA), and myristic acid/stearic acid (MA/SA) binary mixtures and reported that the T_m and ΔH_f of those binary mixtures were irregular decreased with increasing number of thermal cycles. In addition, Karaipekli et al. [15,16] also evaluated the thermal reliability of capric acid/stearic acid (CA/SA), capric acid/lauric acid (CA/LA), and capric acid/myristic acid (CA/MA) binary mixtures and found that the T_m value of CA/SA, CA/LA, and CA/MA were irregularly changed by 0.27–0.48 °C, 0.58–1.50 °C and 0.50–1.36 °C after 1000 to 5000 thermal cycles. The changes in ΔH_f of CA/SA, CA/LA, and CA/MA binary mixtures were between −10 and 6.4%, 6.5–20.3%, and 3.3–14.4% after 1000 to 5000 thermal cycling numbers. Therefore, considering these previous studies it can be noted that the changes of thermal properties of prepared binary mixtures fatty acid were in reliable level to apply as PCMs for thermal energy storage system in range temperature between 40 and 45 °C.

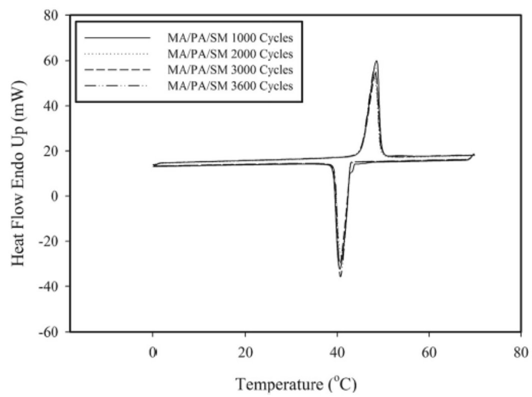

Fig. 2. DSC curves of thermal properties MA/PA/SM binary mixture subjected to 1000, 2000, 3000, and 3600 thermal cycles.

3.2. Chemical structure stability

The analysis of the chemical structure of MA/PA/SM and MA/PA/SP eutectic mixtures was necessary in order to validate the reason of thermal properties changing of those eutectic samples. It has been noted that a chemical degradation and presence of impurities lead to a change of thermal properties after a large number of thermal cycles [17–19]. The FT-IR spectra of MA/PA/SM and MA/PA/SP eutectic mixtures before and after 3600 thermal cycles are shown in Figs. 4 and 5 and indicate that all peak positions of MA/PA/SM and MA/PA/SP remained at the same frequency

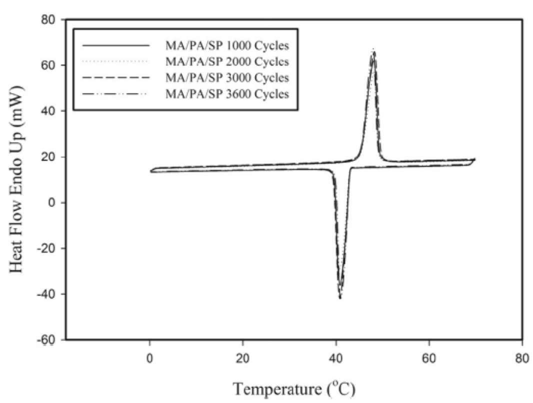

Fig. 3. DSC curves of thermal properties MA/PA/SP binary mixture subjected to 1000, 2000, 3000, and 3600 thermal cycles.

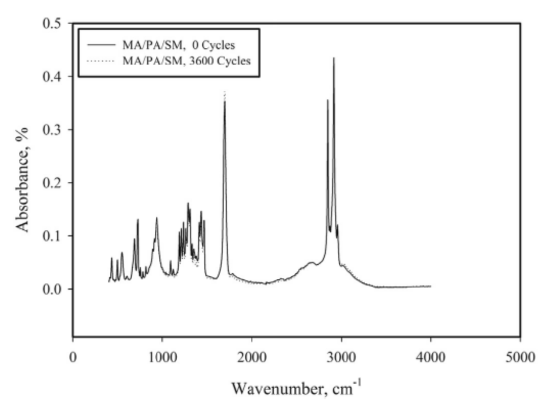

Fig. 4. FT-IR curves of un-cycled MA/PA/SM and MA/PA/SM after 3600 heating/cooling cycling test.

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