FATTY ACID BASED PHASE CHANGE MATERIALS FOR THERMAL STORAGE APPLICATIONS

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ABSTRACT

A novel phase change material (PCM) made from fatty acids is proposed for usage in domestic water heating applications in tropical countries. The PCM is made from a binary mixture of myristic acid (MA) and palmitic acid (PA), having a range of phase transition temperature between 40 to 45 °C. Acid based surfactant such as sodium stearate (SS), sodium laurate (SL), sodium myristate (SM), and sodium palmitate (SP) was also proposed as additives to improve the latent heat capacity and depress the phase transition temperature of the MA/PA mixture. The thermal properties and thermal conductivity of both MA/PA and MA/PA+ surfactants were measured using differential scanning calorimetry (DSC) thermal analysis and KD2Pro thermal conductivity analysis. The results have shown that the addition of 5 wt.% SS, 10 wt.% SL, 5 wt.% SM, and 5 wt.% SP to MA/PA binary mixture was effective in depressing the phase transition temperature and reducing the undercooling problem, while increasing the latent heat capacity and thermal conductivity of the eutectic PCM. Cyclic thermal tests have also shown good retainments of thermo-physical properties in the MA/PA+surfactants samples, with only a small change in phase transition temperature and latent heat capacity, and have good chemical structure stability and small volume changes, even after long periods of thermal cyclic tests. To further improve the thermal conductivity of the MA/PA and MA/PA+surfactants, a porous material addition into the mixture was subsequently proposed. The proposed material, in the form of *shorea javanica* derived from purified damar gum trees, was impregnated into the mixtures to form a eutectic composite phase change materials (CPCMs). The thermal properties, thermal conductivity, and thermal stability of CPCM were measured using Differential Scanning Calorimetry (DSC) thermal analysis, hot disc thermal conductivity analyzer, and Simultaneous Thermal Analyzer (STA), respectively. In addition, a Fourier Transform Infra-Red (FT-IR) spectrophotometer was used to evaluate the occurrence of a chemical reaction between the fatty acid binary mixture and *shorea javanica* in the CPCM. The results shown that the addition of 2 to 3 wt.% of *shorea javanica* into the fatty acid eutectic mixture has improved the thermal conductivity of the CPCM without major changes on its thermo-physical properties and occurrence of chemical reactions. The prepared CPCMs have also shown good thermal performance and thermal stability. Finally, the compatibility of the CPCMs to container materials of stainless steel and carbon steel was evaluated using gravimetric analysis. The results shown that both metals have good corrosion resistance against the prepared eutectic CPCMs for an extended period of use. Thus, this comprehensive study has successfully developed a novel thermal energy storage materials based on fatty acids which meet the standards of thermal properties, physical, and chemical properties requirement for thermal energy storage application in particular to domestic solar water heating system.

ABSTRAK

Bahan perubahan fasa (PCM) yang novel diperbuat daripada asid lemak telah dicadangkan untuk digunakan di dalam aplikasi pemanasan air domestik di negara-negara tropika. PCM diperbuat daripada campuran penduaan asid miristik (MA) dan asid palmitik (PA), yang mempunyai julat fasa peralihan suhu antara 40 hingga 45 °C. Asid berasaskan surfaktan seperti sodium stearat (SS), sodium laurate (SL), natrium miristat (SM), sodium palmitat (SP) juga telah dicadangkan sebagai bahan tambahan untuk meningkatkan kapasiti haba pendam dan menurunkan suhu peralihan fasa campuran MA/PA. Sifat-sifat terma dan keberkondukan haba kedua-dua MA / PA dan MA / PA + surfaktan diukur menggunakan pemetaran kalori pengimbasan perbezaan (DSC), analisis terma dan KD2Pro analisis keberkondukan haba. Keputusan telah menunjukkan bahawa penambahan 5 wt.% SS, 10 wt.% SL, 5 wt.% SM, dan 5 wt.% SP kepada campuran perduaan MA / PA berkesan menurunkan suhu peralihan fasa dan mengurangkan masalah pendinginan kurang, di samping meningkatkan kapasiti haba pendam dan keberkondukan haba PCM eutektik. Ujian haba berkitar juga telah menunjukkan sampel MA / PA + surfaktan mengekalkan sifat termo-fizikal yang baik, dengan hanya perubahan yang kecil pada suhu peralihan fasa dan muatan haba pendam, dan mempunyai kestabilan struktur kimia yang baik dan perubahan isipadu kecil, walaupun selepas tempoh ujian kitaran haba yang lama. Bagi meningkatkan lagi keberkondukan haba MA / PA dan MA / PA + surfaktan, dicadangkan seterusnya bahan berliang ditambahkan ke dalam campuran. Bahan yang dicadangkan, didalam bentuk *shorea javanica* yang diperolehi daripada getah pokok damar yang telah dibersihkan, diresapi ke dalam campuran untuk membentuk komposit bahan perubahan fasa eutektik (CPCMs). Sifat-sifat haba, keberkondukan haba, dan kestabilan haba CPCM diukur menggunakan pemetaran kalori pengimbasan perbezaan (DSC) analisis terma, cakera panas penganalisis keberkondukan haba, dan penganalisis haba serentak (STA), masing-

masing. Selain itu, Jelmaan Fourier Infra-Merah (FT-IR) spektrofotometer telah digunakan untuk menilai kejadian tindak balas kimia antara asid lemak campuran penduaan asid lemak dan *shorea javanica* didalam CPCM itu. Keputusan telah menunjukkan bahawa penambahan 2 hingga 3 wt.% *shorea javanica* ke dalam campuran eutektik asid lemak telah menambah baik keberkondukan haba CPCM tanpa perubahan besar ke atas sifat termo-fizikal dan kejadian tindak balas kimia. CPCMs yang telah disediakan juga telah menunjukkan prestasi haba dan kestabilan haba yang baik. Akhir sekali, keserasian CPCMs dengan bahan bekas keluli tahan karat dan keluli karbon yang telah dinilai menggunakan analisis gravitian. Keputusan telah menunjukkan bahawa kedua-dua logam mempunyai ketahanan kakisan yang baik terhadap CPCMs eutektik yang disediakan untuk tempoh penggunaan yang panjang. Oleh itu, kajian menyeluruh ini telah berjaya menghasilkan bahan penyimpanan tenaga haba yang novel berasaskan asid lemak yang menepati piawaian sifat haba, fizikal, dan sifat-sifat kimia yang diperlukan untuk penyimpanan tenaga haba khususnya untuk penggunaan sistem pemanasan air solar domestik.

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NOMENCLATURES

Q	Quality of heat stored	(J)
T_i	Initial temperature	(^oC)
T_f	Final temperature	(^oC)
m	Mass of heat storage medium	(kg)
C_p	Specific heat	($Jkg^{-1}K^{-1}$)
C_{ap}	Average specific heat between T_i and T_f	($Jkg^{-1}K^{-1}$)
W_{int}	Initial weight before contact with eutectic CPCM	(g)
W_{fin}	Final weight after thermal cycles	(g)
k	Unit conversion constant	
T	Time of explosures	(min)
A	Area	(cm^2)
ΔW	Weight loss	(g)
D	Density of metal	(gcm^{-3})
a_m	Fraction melted	
Δh_m	Heat of melting per unit mass	Jkg^{-1}
T_m	Melting temperature	(^oC)
ΔH_f	Latent heat heat fusion	Jkg^{-1}

Abbreviations

US	The United State
IEA	The International Energy Agency
kWh	Kilo Watt hours
GHG	Greenhouse gasses
BP	British Petroleum
CO_2	Carbon dioxide
PV	Photovoltaic
TES	Thermal energy storage
CSP	Concentrating solar power
PCM	Phase change material
TCS	Thermos-chemical storage
LHTES	Latent heat thermal energy storage
SHTES	Sensible heat thermal energy storage

SHS	Sensible heat storage
LHS	Latent heat storage
TES	Thermal energy storage
r	Radius of the nucleus

CHAPTER I

INTRODUCTION

Energy is defined as a property of objects which can be transferred to other objects or converted into a different form (Kroemer & Kittel, 1980). Human has been harnessing energy for work, heating, transportation, food production, manufacturing of products, and electricity. Energy in its classical term appears in many forms in our daily life in the form of gravitational energy, kinetic or mechanical energy, electrical energy, heat radiation energy, wave energy, chemical energy, and nuclear energy. The Law of Conservation of energy states that the form of energy may change in time such as conversion of electrical energy into mechanical energy, but the total amount of energy does not change.

1.1 The world energy problem

The state of the world today is based on the capability of a human to convert energy from one form to another. The world population is rapidly growing, with a predicted global population increase from 7 billion people living today to 9 billion people in 2040. The global citizens will need energy for living, thus, the overall global energy demand will exponentially increase. The world energy problem is that of the unbalanced supply-demand situation, with the most prosperous and developed countries are the ones having good access to and use the most amount of energy. Thus, the biggest challenge for humankind in this century will be tackling the problem of energy.

The energy consumption per capita is usually linked to the living standard of a country. In 2010, in the United State (US) has registered a daily use of around 230 kWh of the energy per capita. In contrast, countries in Africa, such as Nigeria, only uses onetenth of this amount, around 23 kWh per day per capita. As shown in Fig 1.1, the living standard expressed in human development index can be illustrated on a global scale. As can be seen, large consumption of energy usually corresponds to the high living standards of the country.

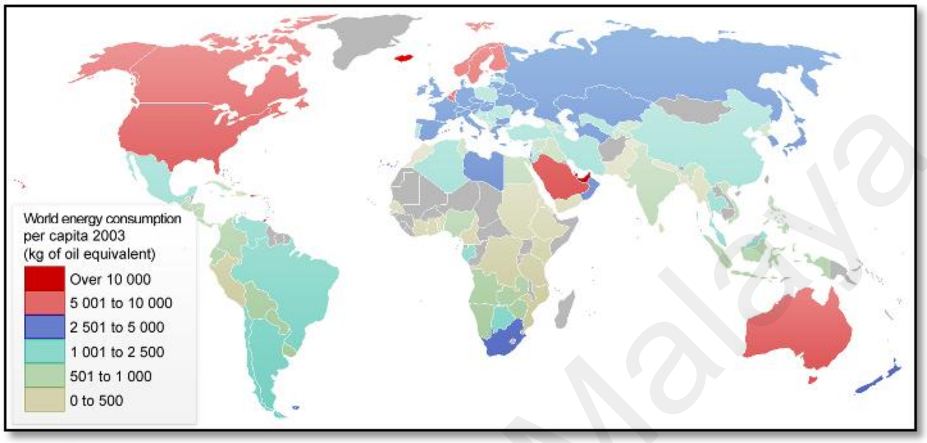


Figure 1.1. A map depicting world energy consumption per capita based on 2003 data from International Energy Agency

In recent years, the living standard is rapidly increasing in many emerging economies such as China and India. With a combined population of almost 2.5 billion people, the population of these two countries represent almost a third of the world population. The increasing population and the expectation of high standard of living will put a large demand on the requirement of energy. The International Energy Agency (IEA) Outlook 2013 predicts that the energy consumption will increase by 56% from the year 2010 to 2040. The increase in energy demand will have a chain effect on the economy, elevating the prices of goods and services.

Refer to annual average oil prices in USD/barrel BP workbook of historical data in 2012 which is reported that the price of oil peaked in the 1970s due to the oil crisis, when oil-producing countries had imposed a halt on the trade of oil. The second peak of oil is seen in the beginning of the millennium when there is an increase in energy demand from newly emerging economies.

The second challenge facing the global community is the fact that the world energy infrastructure is heavily dependent on fossil fuel such as oil, coal and gas. Fossil fuels are essentially solar energy from million of years ago stored in the form of chemical energy. Fossil fuels are non-sustainable energy sources and are being depleted at an exponential rate. In the coming century, if the consumptions continue at the present rate, it is predicted that the global oil and gas reserve will run out. Oil companies and governments are taking greater risks in oil explorations, and several technological mishaps have occurred in the course of extracting from the depths of the current oil reserves, as can be seen from the Gulf of Mexico oil spill in 2010.

The third challenge is the production of greenhouse gasses (GHG), such as carbon dioxide, as a byproduct from the burning of oil. Scientists have postulated that the increase in carbon dioxide is responsible for the global warming and climate change, which can have drastic consequences of the habitats of people and animals (IRENA, 2013). Various technologies have been proposed to reduce the consumption of oil, such as the use of hydroelectric, wind and solar power.

1.2 Renewable energy carriers

Renewable energy carriers, such as hydro, wind and solar, are replenished by natural processes at a rate comparable or faster than its rate of consumption. For example, hydroelectricity is an energy conversion technology that is not based on heat generated by fossil or nuclear fuels. The potential energy of rain falling in mountainous areas or elevated plateaus is converted into electrical energy via a water turbine. Similarly, with tidal pools placed on the ocean beach, the potential energy stored in tides can also be converted to mechanical energy and subsequently electricity. The kinetic energy of wind can be converted into mechanical energy using windmills. Likewise, the energy contained in sunlight called solar energy, can be converted into electricity directly using devices based on photovoltaic (PV) semiconductor materials. In solar thermal energy applications, the solar light is converted into heat (Jager et al., 2014).

1.3 Solar thermal energy

Photovoltaic technology is based on the principles of electrodynamics and solid-state physics to convert solar energy into electricity directly, whereas solar thermal energy is mainly based on the laws of thermodynamics (Jager et al., 2014).

Thermal energy storage (TES) is a technology that stocks thermal energy by heating or cooling a storage medium to be later used for heating and cooling applications and power generation. Thermal energy storage systems are particularly used in low temperature and high-temperature applications such as building and power generation. In the application, generally, half of total energy consumption that used for a living is thermal energy and the demand for which may vary in different time of days. Therefore, the utilization of thermal energy storage will possible to help to balance the energy demand and supply on a daily even seasonal basis applications. They also can improve the energy efficiency by reducing peak demand, energy consumption, CO_2 emissions and costs of energy systems. Furthermore, the conversion and storage of thermal energy as a variable renewable energy also would help to increase the share of renewables in the total energy supply. The development of thermal energy storage now is highlighted for power generation systems in applications of concentrating solar power (CSP) plants by utilized the solar heat for electricity production when sunlight is not available (IEA-ETSAP & IRENA, 2013).

Thermal energy storage (TES) commonly divided into three types in different applications, namely: 1) sensible heat storage which is absorbed and release the heat by using a liquid or solid storage medium (e.g. water, sand, molten salts, rocks); 2) latent heat storage, absorb and store the heat by using thermal energy storage medium or known as phase change materials (PCMs); 3) thermochemical storage (TCS) that store and release the thermal by using chemical reactions as a medium (IEA-ETSAP & IRENA, 2013).

In economic feasibility aspect, the sensible heat storage medium relatively serves an inexpensive cost compared to latent heat storage and thermos-chemical storage mediums as well as it is applicable to domestic heating systems and industrial needs (IEA-ETSAP & IRENA, 2013). However, the sensible heat storage medium have a problem with a low energy density that makes them requires large volumes approximately three and five times compared to latent heat storage and thermos-chemical mediums to store a same amount of energy, respectively. Furthermore, a sensible heat storage systems come with an appropriate design to able discharge thermal energy at constant temperatures. In general, latent heat storage medium or phase change material (PCM) and thermos-chemical storage (TCS) systems are more costly than sensible heat systems and are economically feasible for systems with a large number of cycles application (IEA-ETSAP & IRENA, 2013).

A latent heat thermal energy storage (LHTES) systems can be applied either in low and high temperature as distributed and centralized systems, respectively. The LHTES distributed system mostly used in domestic heating and cooling application by capturing the solar thermal and using it for water and space heating or cooling. Furthermore, The LHTES centralized systems use to be designed for district heating or cooling, large industrial plants, combined heat and power plants, or in renewable power plants known as centralizing solar power (CSP) plants. In both cases, LHTES systems may reduce energy demand at peak times (IEA-ETSAP & IRENA, 2013). An LHTES system's economic feature performance depends essentially on its particular application and operational needs, including the lifetime of the systems. Developers in Germany, Slovenia, Japan, Russia and the Netherlands are working actively on new materials and techniques for all LHTES systems, including their integration into building walls (e.g. by encapsulating phase change materials into plaster or air vents) and transportation of thermal energy from one place to another (IEA-ETSAP & IRENA, 2013). These new applications are now being commercialized, even though their cost, performance, and reliability have yet to be verified.

Research and development of new storage materials for thermal energy storage (TES) integration in buildings, industrial application, and variable renewable power generation are essential to foster its commercial deployment and mass adoption. In this study, we develop the thermal storage materials in the form of a fatty acid based phase change materials (PCMs) for domestic water heating applications.

1.4 Research objectives

The overall objective of this study is to develop a phase change materials (PCMs) suitable for the thermal energy storage in solar water heating applications. The PCM developed in this work should have an appropriate phase transition temperature within the range 40-45 ^{o}C, high amount of latent heat of fusion and thermal conductivity, have a long life stability, and compatible with other construction materials. To achieve this, the following detailed objectives are addressed:

1. To prepare the eutectic phase change material (PCM) and to study the effect of surfactants on the thermal properties of eutectic PCM.
2. To investigate the thermal reliability of prepared eutectic PCMs subjected to a large number of thermal cycles.

3. To enhance the thermal conductivity of the prepared eutectic PCMs by impregnation of high conductive materials to form a eutectic composite phase change material (CPCMs).
4. To measure of the compatibility of the CPCMs with metallic container materials to evaluate weight losses and corrosion rate of the metal.

1.5 Scope of the research

Latent heat thermal energy storage (LHTES) system development should include three basic components: (a) a thermal storage material to absorb and release the heat, (b) a container for holding the storage materials and (c) a heat collector to transfer the heat from heat source to PCM. Figure in Appendix A.1 shows the scope of development of an LHTES system that can be divided into two areas, which are material investigation and heat exchanger development. For this study, the scope of work is limited to the investigation on the appropriate phase change material (PCM) suitable for use in an LHTES in domestic water heating applications.

References

IEA-ETSAP, & IRENA. (2013). Thermal Energy Storage, Technology Brief. 18.

IRENA, I.-E. a. (2013). Thermal Energy Storage, Technology Brief.

Jager, K., Isabella, O., Smets, A. H. M., Swaaij, R. A. C. M. M. v., & Zeman, M. (2014). Solar Energy - Fundamentals, Technology, and Systems. *Delf University of Technology*.

Kroemer, H., & Kittel, C. (1980). *Thermal physics*: WH Freeman.

CHAPTER 2

LITERATURE REVIEW

The development of a latent heat thermal energy storage (LHTES) material involves understanding four diverse subjects: consideration of the phase change materials (PCMs) temperature, evaluation of the thermal reliability of PCMs, improvement of the thermal conductivity, and identification of the compatibility of the PCMs with container materials. This chapter will discuss the past and ongoing developments of phase change materials (PCMs) of latent heat thermal energy storage (LHTES) system for heating and cooling applications.

2.1 Thermal energy storage (TES) methods

The mechanism of a thermal energy storage (TES) system involves cooling, heating, melting, solidifying, or evaporating a material with the energy becoming available as heat when the process is reversed. TES methods are classified as sensible heat thermal energy storage (SHTES) and latent heat thermal energy storage (LHTES) (Mehling & Cabeza, 2008; Pielichowska & Pielichowski, 2014). SHTES involves increasing or decreasing the temperature of a material and its effectiveness depends on the specific heat capacity and the volume of the material. On the other hand, LHTES depends on the material's ability to accumulate energy densities at almost isothermal conditions and over a narrow temperature range. LHTES materials, known as phase change materials (PCMs), offer a significant advantage over SHTES media, particularly on the small temperature difference between melting and solidifying points, small volume requirement, and low weight per unit of storage capacity. PCMs absorb heat as storage energy during the heating process and releases it during cooling (Pielichowska & Pielichowski, 2014).

2.1.1 Sensible TES

Sensible heat storage involves storing thermal energy by raising the temperature of a solid or liquid. The principle is based on the material's change of heat capacity and temperature during the process of charging and discharging. Heat storage as sensible heat is transferred to increase the temperature of the storage medium. The ratio of stored heat to temperature rise is the heat capacity of the storage medium. The temperature increase can be easily measured using a thermometer sensor and the heat stored is called as sensible heat (Mehling & Cabeza, 2008). The amount of heat stored is a function of the specific heat of the medium, the temperature change and the mass of storage medium, as shown in equation 1 (Pielichowska & Pielichowski, 2014; Sharma et al., 2009).

$$Q = \int_{T_i}^{T_f} mc_p dt = mc_{ap}(T_f - T_i) \tag{2.1}$$

Where, Q: quantity of heat stored (J), T_i: initial temperature (^{o}C), T_f: final temperature (^{o}C), m: mass of heat storage medium (kg), C_p: specific heat (Jkg^{-1}K^{-1}), C_{ap}: average specific heat between T_i and T_f (Jkg^{-1}K^{-1}).

The storage material absorbs heat by conventional heat transfer mechanisms of radiation, conduction, and convection. As the material cools at night or during a cloudy day, the stored heat is released by the same modes. In an active space heating system, a tank of water or rock buns is usually used as the storage medium. Water is the best sensible heat storage (SHS) material due to its low cost and high specific heat (Pielichowska & Pielichowski, 2014), although oils, molten salts, and liquid metals are used for temperatures above 100 ^{o}C. Similarly, for air heating applications, rock bed type storage materials are utilized (Sharma et al., 2009).

2.1.2 Latent TES

Latent heat storage is the most efficient method of storing thermal energy. Latent heat storage (LHS) relies on the storage material absorbing or releasing heat as it undergoes a solid to solid, solid to liquid or liquid to gas phase change or vice versa. The storage capacity of LHS system with PCMs is given by (Sharma et al., 2009; Pielichowska & Pielichowski, 2014) as:

$$Q = \int_{T_i}^{T_m} mC_p\,dt + ma_m\Delta h_n + \int_{T_m}^{T_f} mC_p\,dt \qquad (2.2)$$

$$Q = m\left[C_{sp}(T_m - T_i) + a_m\Delta h_n + C_{lp}\left(T_f - T_m\right)\right] \qquad (2.3)$$

Where, a_m: fraction melted, Δh_m: heat of melting per unit mass (Jkg^{-1}) (Sharma et al., 2009).

Phase change materials (PCMs) are latent heat storage materials. Studies conducted in comparing the performance of PCMs and sensible heat storages material have shown that a significant reduction in storage volume can be achieved using PCM as compared to SHS materials (Agyenim et al., 2010). As the source temperature rises, the chemical bonds within the PCM break up as the material transitions from solid to liquid (Sharma & Sagara, 2005). The phase change is a heat seeking (endothermic) process and, therefore, the PCM absorb heat. As the heat is stored, the PCM will undergo a change from a solid to a liquid phase as the temperature reaches the phase transition temperature. The temperature will be constant as the material undergoes homogeneous melting, and the heat stored during the phase transition process of PCM is called latent heat (Sharma & Sagara, 2005)

2.2 Criteria for phase change materials (PCMs)

LHS offers a much higher storage density with a narrower temperature range between storing and releasing heat than SHS (Pielichowska & Pielichowski, 2014). As shown in

Table 2.1, the ideal PCM should meet several criteria related to the desired thermo-physical, kinetic and chemical properties (Pielichowska & Pielichowski, 2014; Sharma et al., 2009),

Table 2.1. The ideal characteristic of phase change materials (PCMs)

Thermal properties
• A melting temperature in the desire operating range • A high phase transition latent heat per unit volume • A high specific heat, to provide significant additional LHS • High thermal conductivity of both phase • No subcooling
Physical properties
• A small volume changes on phase transition • A low vapor pressure at the operating temperature • Favorable phase equilibrium • Congruent melting of the PCM • A high density
Chemical properties
• Long term chemical stability • A completely reversible freeze/melt cycle • Compatibility with the construction material • No corrosion influence on the construction material • It should be non-toxic, non-flammable and non-explosive to ensure safety

A number of latent heat storage materials have been proposed in the past which are suitable for TES applications within the desired temperature range for heating and cooling (Abhat, 1983; Lane, 1980; Lane, 1983). Several review articles on thermal energy storage materials describing the thermal properties and thermal reliability of materials, suitability of various applications, and merits and demerits have been reported by various authors (Lane, 1983; Farid et al., 2004; Lane, 1980; Lane, 1983). A large number of organic and inorganic substances have been identified having a high heat of fusion in any required temperature range, e.g. 0-80 ^{o}C. However, for use as heat storage materials in LHTES system, these phase change materials must exhibit certain desirable thermodynamic, kinetic and chemical properties. In addition, economic considerations of cost and large-scale availability of the materials must also be considered. Thus, several researchers have outlined various criteria that govern the selection of thermal energy storage materials (Farid et al., 2004; Mehling & Cabeza, 2008; Sarier & Onder, 2012). The two prominent requirements of a PCM for most applications are the suitability of the phase change temperature to the application and a large melting enthalpy. These requirements have to be fulfilled in order for the material to store and release heat effectively.

2.3 Classification and properties of PCMs

Over the last four decades, the developments of phase change materials have included utilizing inorganic and organic materials, and the eutectics of organic and inorganic compounds. PCM can be classified into three common group base on their phase transition range temperatures, which are: i) low phase transition temperature PCM (< 15^{o}C); ii) mid phase transition temperature PCM (15 – 90^{o}C) and iii) high phase transition temperature PCM (>90^{o}C). PCMs can be divided by their phase transition modes of solid-solid, solid-liquid, or liquid-gas systems as described in Fig. 2.1 (Farid et al., 2004; Pielichowska & Pielichowski, 2014).

A comprehensive list of several possible PCMs based on their phase transition temperature range for use in TES applications is summarized in Appendix A.2.a-e (Farid et al., 2004). The usage of PCMs with a liquid-gas phase transition has limited applications in TES due to its large volume changes, even if they possess a high latent heat of fusion value (Abhat, 1983; Pielichowska & Pielichowski, 2014). In practical applications, the solid-liquid and solid-solid system materials are preferred for TES due to their low volume changes, which are usually less than 10% (Sharma et al., 2009). Solid-solid PCMs store the heat in the transition process from one crystalline form to another, and can be considered as an alternative to solid-liquid PCMs (Chandra et al., 2005). Generally, the heat of phase transition for solid-solid PCMs is lower than solid-liquid PCMs, although solid-solid systems will not face the leakage problems which may be encountered in solid-liquid PCMs (Sharma et al., 2009Abhat, 1983; Pillai & Brinkworth, 1976).

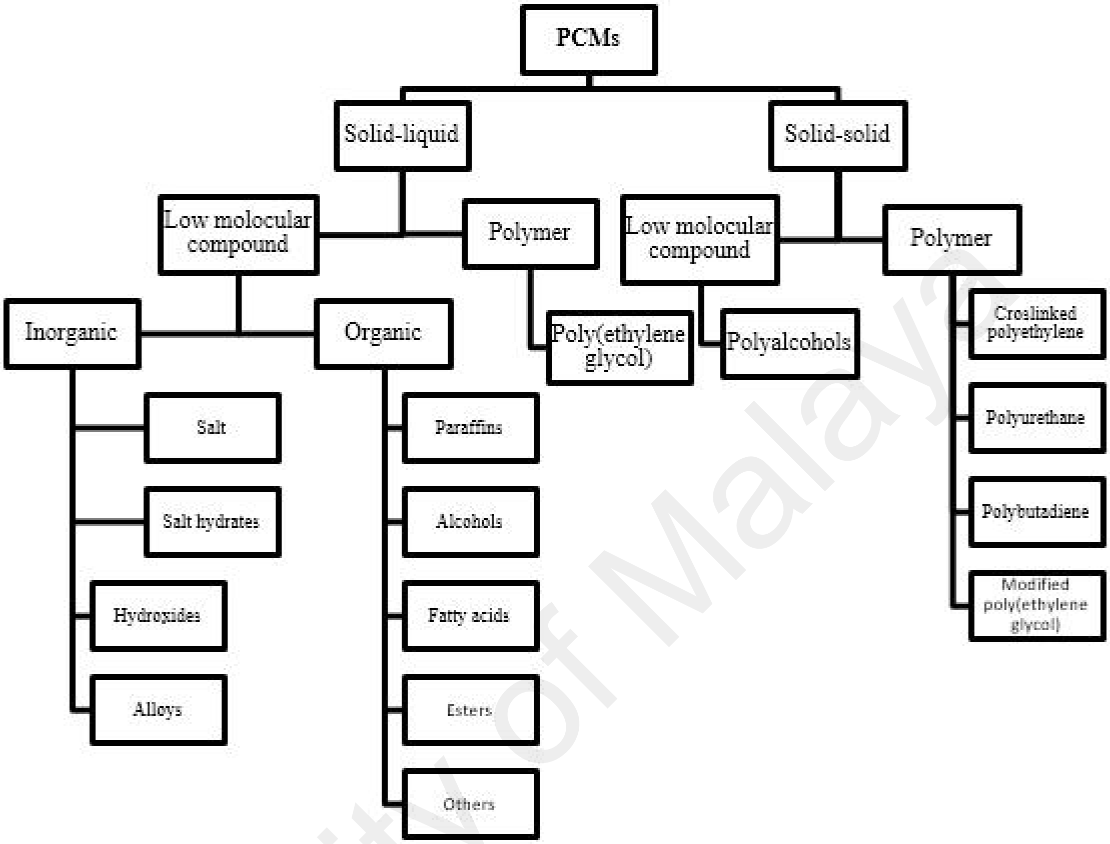


Figure 2.1. Classification of thermal energy storage materials

2.3.1 Solid-liquid PCMs

Many solid-liquid phase change materials (PCMs) have been developed for use in LHTES applications. Inorganic PCMs, shown in Appendix A.2.c and A.2.d, indicated that salt hydrate is the most preferred material, having high volumetric storage density (~ 350 kJ.kg^{-1}), relative high thermal conductivity (~ 0.5 W m^{-1}K^{-1}), and moderate cost (Biswas, 1977; Farid et al., 2004). However, the problems of phase segregation and subcooling have limited application. Biswas (1977) suggested the use of the extra water principle to prevent the formation of heavy anhydrous salt. Although this makes the system stable with cycling, it reduces the storage density and required the system to be operated with a large temperature swing. The use of some thickening agent, such as Bentonite clay with Glauber salt, has been suggested to overcome the problem of phase segregation. Unfortunately, this reduces the rates of crystallization and heat transfer to the salt due to the lower thermal conductivity of the mixture (Farid et al., 2004). Borax has been long suggested by Telkes (1952), as a nucleating agent to minimize subcooling, although a thickening agent is required to prevent settling of the high density of borax. Similarly, most other hydrated salts PCMs also share similar problems (Farid et al., 2004).

Paraffin wax has been proposed as an organic PCM, having a low price with moderate thermal storage densities (200 kJ.kg^{-1}). As can be seen in Appendix A.2.a, paraffin wax has a wide range of phase transition temperatures. They undergo negligible subcooling and are chemically inert and stable with no phase segregation. However, they have low thermal conductivity (0.2 Wm^{-1}K^{-1}). Metallic fillers, metal matrix structures, finned tubes and aluminum shavings have been used to improve their thermal conductivity (Farid et al., 2004; Hasnain, 1998). Although pure paraffin wax is expensive, technical grade paraffin can still be used (Farid & Husian, 1990; Farid & Kanzawa, 1989; Farid & Mohamed, 1987).

Table 2.2. Comparison of inorganic and organic PCMs for TES application

Organics	Inorganics
Advantages	Advantages
No corrosives, Low or none subcooling, Chemical and thermal stability.	Greater phase change enthalpy
Disadvantages	Disadvantages
Lower phase change enthalpy, Lower thermal conductivity, Inflammability.	Subcooling, Corrosion, Phase separation, Phase segregation, lack of the thermal stability.

(Zalba et al., 2003)

Another organic material that has been proposed for LHTES system is based on fatty acids. These acids are characterized by a large range phase transition temperature (18 - 65^{o}C) and high thermal storage density (210 kJ.kg^{-1}), which can cater for a wide range of

TES applications (Farid et al., 2004; Feldman et al., 1989). The advantages and disadvantages comparison between inorganic and organic PCMs is shown in Table 2.2.

2.3.1.1 Inorganic PCMs

Inorganic PCMs developed for TES applications include single compounds, salt hydrates, eutectic mixtures and non-eutectic mixtures. These PCMs can be used in various phase transition temperature for TES applications, as tabulated in Table 2.3 to 2.5.

Table 2.3. Inorganic compounds of PCMs with potential use for TES applications

Compounds	Melting point (T^m), ^oC	Latent heat of fusion (ΔH_f), Jg^{-1}
$AlCl_3$	192	280
$LiNO_3$	250	370
$NaNO_3$	307	172
KNO_3	333	266
Na_2O_2	360	314
KOH	380	150
$KClO_4$	527	1253
LiH	699	2678
$MgCl_2$	714	452
NaCl	800	492
Na_2CO_3	854	276
KF	857	452
LiF	868	932
K_2CO_3	897	235
NaF	993	750
MgF_2	1271	936

(Pielichowska & Pielichowski, 2014)

Table 2.4. Salt hydrates as potential PCMs for TES applications

Compounds	Melting point (T^m), ^oC	Latent heat of fusion (ΔH_f), Jg^{-1}
$LiClO_3.3H_2O$	8	253
$KF.\ 4H_2O$	18.5-19	231

Table 2.4, *continued*

$Na_2SO_4.10H_2O$	34	256
$Mn(NO_3)_2.6H_2O$	25.3	125.9
$CaCl_2.6H_2O$	28-30	190-200
$LiNO_3.3H_2O$	30	256
$CaBr_2.6H_2O$	34	115.5
$Na_2HPO_4.12H_2O$	35-45	279.6
$Zn(NO_3)_2.6H_2O$	36	146.9
$Zn(NO_3)_2.4H_2O$	45.5	
$Zn(NO_3)_2.2H_2O$	54	
$Na_2S_2O_3.5H_2O$	48-55	201
$Na(CH_3COO).3H_2O$	58	226
$Cd(NO_3)_2.4H_2O$	59.5	
$Na_2B_4O_7.10H_2O$	68.1	
$Na_3PO_4.12H_2O$	69	
$Na_2P_2O_7.10H_2O$	70	184
$Ba(OH)_2.8H_2O$	78	266
$(NH_4)Al(SO_4)_2.12H_2O$	95	269
$MgCL_2.6H_2O$	117	169
$Mg(NO_3)_2.6H_2O$	89.3	150

(Pielichowska & Pielichowski, 2014)

Table 2.5. Eutectic mixtures as potential PCMs for TES applications

Mixtures	**Melting point (T^m), °C**	**Latent heat of fusion (ΔH_f), Jg^{-1}**
45%$CaCl_2\cdot 6H_2O$+55% $CaBr_2\cdot 6H_2O$	14.7	140
66,6% $CaCl_2\cdot 6H_2O$ + 33,3% $MgCl_2\cdot 6H_2O$	25	127
50% $CaCl_2$ + 50% $MgCl_2\cdot 6H_2O$	25	95
48% $CaCl_2$ + 4.3% NaCl + 0.4% KCl + 47.3% H_2O	27	188
47% $Ca(NO_3)_2\cdot 4H_2O$ + 53% $Mg(NO_3)_2\cdot 6H_2O$	30	136
40% $CH_3COONa\cdot 3H_2O$ + 60% NH_2CONH_2	30	200.5
61.5% $Mg(NO_3)_2\cdot 6H_2O$ + 38.5% NH_4NO_3	52	125
58.7% $Mg(NO_3)_2\cdot 6H_2O$ + 41.3% $MgCl_2\cdot 6H_2O$	59	132
53% $Mg(NO_3)_2\cdot 6H_2O$ + 47% $Al(NO_3)_2\cdot 9H_2O$	61	148

Table 2.5, *continued*

66.6% urea + 33.4% NH_4Br	76	161
59% $Mg(NO_3)_2\cdot 6H_2O$ + 41% $MgBr_2\cdot 6H_2O$	66	168
14% $LiNO_3$ + 86% $Mg(NO_3)_2\cdot 6H_2O$	72	180
35.1% LiF + 38.4% NaF + 26.5% CaF_2	615	n.a
32.5% LiF+50.5% NaF+17.0% MgF_2	632	n.a
51.8% NaF + 34.0% CaF_2 + 14.2% MgF_2	645	n.a
48.1% LiF + 51.9% NaF	652	n.a
63.8% KF + 27.9% NaF + 8.3% MgF_2	685	n.a
45.8% LiF + 54.2% MgF_2	746	n.a
53.6% NaF + 28.6% MgF_2 + 17.8% KF	809	n.a
66.9% NaF + 33.1% MgF_2	832	n.a

(Pielichowska & Pielichowski, 2014)

i. Salt hydrates

Salt hydrates are inorganic salts containing the general chemical formula, $AB.nH_2O$ (Pielichowska & Pielichowski, 2014). The salt hydrates can be classified based on their melting behaviors, as outlined below:

a. Salt hydrates with congruent melting behavior. These types of salt hydrates are soluble in the hydration of water at melting temperatures of the salts.
b. Salt hydrates with incongruent melting behavior are the type of salt hydrates that are partially soluble in the hydration of water at melting temperatures of the salts.
c. Salt hydrates with semi-congruent melting, indicates that during the melting process, the equilibrium solid and liquid phases would have different compositions due to the transformation of the salt hydrate to a salt hydrate with a lesser amount of hydration water (Sharma et al., 2009, Pielichowska & Pielichowski, 2014).

A large number of salt hydrates melt incongruently and the amount of released water is insufficient to dissolve the crystalline salt formed during the dehydration process. This leads to density differences, phase separation and sedimentation in containers causing serious technical problems in practical applications (Pielichowska & Pielichowski, 2014). To minimize this situation, gelling or thickening agents are added to avoid the segregation and sedimentation in salt hydrates. The addition of a gelling (e.g. polymeric) material to the salt leads to the formation of a three-dimensional network to hinder salt sedimentation while the addition of a thickening agent increases the viscosity of the salt hydrate and helps to hold the salt hydrate molecules together (Cabeza et al., 2003). Another disadvantage of salt hydrates is their poor nucleating ability, which causes significant subcooling. To reduce this problem, either nucleating agents are added, or small amounts of crystals are retained in the system to act as nucleation sites (Sharma et al., 2009).

Several studies have also highlighted the possibility of corrosion problems when the salt hydrates come in contact with metallic components in energy storage installations (Cabeza et al., 2002; Farrell et al., 2006). Nevertheless, even with the limitations outlined, salt hydrates are still commonly utilized as PCMs for TES applications due to their large latent heat of fusion, appropriate phase transition temperature and are economically viable (Pielichowska & Pielichowski, 2014).

ii. Alloys

Metallic alloys are used as high-temperature PCMs as they offer high thermal reliability and repeatability (Liu et al., 2012). The largest phase transition heat, on a mass or volume basis, has been found for binary and ternary alloys of the relatively plentiful elements Al, Cu, Mg, and Zn, although not all of the potential materials are suitable for use in TES systems (Birchenall & Riechman, 1980). Aluminum alloys are usually investigated for use as PCMs in high-temperature TES systems because of their suitable phase change temperature, high latent heat density and good thermal stability (Sun & Zhang, 2005).

2.3.1.2 Organic PCMs

Organic PCMs consist of a wide range of materials such as paraffin, fatty acids and their eutectic mixtures, esters and other organic compounds. Several organic PCMs and their thermo-physical properties are shown in Tables 2.6 to 2.9.

Table 2.6. Paraffin as potential PCMs uses for TES applications

Paraffins	**Number of carbon atoms**	**Melting temperature (T_m), °C**	**Latent heat of fusion (ΔH_f), Jg^{-1}**
n-Tetradecane	14	5.8-6	227-229
n-Pentadecane	15	9.9-10	206
n-Hexadecane	16	18-20	216- 236
n-Heptadecane	17	22-22.6	164-214
n-Oktadecane	18	28-28.4	200-244
n-Nonadecane	19	32	222
n-Eicozane	20	36	247
n-Heneicozane	21	40	213
n-Docozane	22	44	249
n-Trikozane	23	47.5	234
n-Tetracozane	24	50.6	255
n-Pentacozane	25	53.5	238
n-Hexacozane	26	56.3	256
n-Heptacozane	27	58.8	235
n-Oktacozane	28	41.2	254
n-Nonacozane	29	63.4	239
n-Triacontane	30	65.4	252

(Pielichowska & Pielichowski, 2014)

Table 2.7. Fatty acids as potential PCMs uses for TES applications

Fatty acids	**Number of carbon atoms**	**Melting temperature (T_m), °C**	**Latent heat of fusion (ΔH_f), Jg^{-1}**
Caprylic acid	8	16.3	148
Capric acid (CA	10	31.3-31.6	163
Lauric acid (LA)	12	41–44	183-212

Table 2.7, *continued*

Myristic acid (MA)	14	51.5-53.6	190-204.5
Palmitic acid (PA)	16	61-63	203.4-212
Stearic acid (SA)	18	70	222
Arachidic acid	20	74	227
Undecylenic acid	22	24	141

(Pielichowska & Pielichowski, 2014)

Table 2.8. Eutectic fatty acids as potential PCMs uses for TES applications

Fatty acids	**Composition, wt.%**	**Melting temperature (T_m), ^oC**	**Latent heat of fusion (ΔH_f), Jg^{-1}**
CA/LA	45/55	17-21	143
CA/PA	76.5/23.5	21.8	171.2
LA/MA	66.0/34	34.2	166.8
LA/PA	69.0/31	35.2	166.3
LA/SA	75.5/24.5	37	182.7
MA/PA	58/42	42.6	169.7
MA/SA	64/36; 65.7/34.3	44.1; 50-52	182.4; 162
PA/SA	64.2/35.8	52.3	181.7

(Pielichowska & Pielichowski, 2014)

Table 2.9. Other organic compounds as potential PCMs uses for TES applications

Class of compounds	**Compounds**	**Melting temperature (T_m), ^oC**	**Latent heat of fusion (ΔH_f), Jg^{-1}**
Monohydroxy alcohols	1-dodecanol 1-tetradecanol	17.5-23.3 39.3	184-188.8 221.23
Ketones	Phorone	27	123.5
Ethers	Diphenyl ether	27.2	97
Esters of fatty acids	Methyl palmitate	27	163.2
	Allyl palmitate	23	173
	Propyl palmitate	16-20	186-190
	Methyl stearate	38-39	160.7
	Isopropyl palmitate	11	100
	Isopropyl stearate	14	142
	Butyl stearate	17-23	140-200

Table 2.9, *continued*

Esters of fatty acids	Ethylene glycole distearate	63.2	215.80
	Methyl-12-hydroxystearate	43	126
	Vinyl stearate	27	122
Halogen derivative	1-iodehexadecane	22.2	131
	Chlorobenzothiazole	18.6	65
	3-iodoaniline	23	64
Sulphur compounds	Octadecyl 3-mercaptopropionate	21	141
	Octadecyl thioglycolate	26	91
	Dilauryl thiopropionate	39	159
Amides	Acetamide	82	241
Sugars	Erythritol	117	344
	Mannitol	165	341
	Xylitol	93	280
	Sorbitol	97	110
	Granulated sugar	179	179
	White superior soft sugar	172	110
Dienes	Dicyclopentadiene	28.7	11.7
Oleo-chemical carbonates	Decyl carbonate	-2.2	144
	Dodecyl carbonate	19.3	200
	Tetradecyl carbonate	33.7	227
	Hexadecyl carbonate	44.9	219
	Octadecyl carbonate	51.6	223

(Pielichowska & Pielichowski, 2014)

i. Paraffins

Paraffin, with the chemical formula C_nH_{2n+2}, are a family of saturated hydrocarbons with similar properties. The paraffin between C_5 to C_{15} are in liquid forms, and the rest are waxy solids (Sharma & Sagara, 2005). Paraffin wax is mostly used as commercial organic phase change material (PCM) (Lane, 1983). It consists of mainly straight-chain hydrocarbons, with melting temperatures ranging from 23 to 67 ^{o}C (Abhat, 1983). Commercial grade paraffin wax is obtained from petroleum distillation. The wax obtained is not a pure substance, but a combination of different hydrocarbons (Sharma & Sagara, 2005). The thermal properties of paraffin are indicated by the average length of the hydrocarbon chain, a longer chain indicates a higher melting temperature and latent heat of fusion (Himran et al., 1994). In developing the PCM, various paraffin compositions can be physically mixed. In fact, most paraffin-based PCMs are mixtures of saturated hydrocarbons with different numbers of carbon atoms in the molecules (Pielichowska & Pielichowski, 2014).

Paraffin wax shows a tendency to segregate. Generally, they are chemically stable, although (Lane, 1983) have reported the occurrence of oxidation within paraffin as the materials interact with oxygen. The stability of the compound was evaluated by (Sharma et al., 2002; Sharma et al., 1999). They reported that the compound is thermally stable, with no regular degradation after 1500 number of thermal cycling test. Paraffin waxes are safe and non-reactive (Hasnain, 1998), thus making it suitable for use in metal containers and are easily incorporated into heat storage systems (Lane, 1983).

However, as shown in Table 2.10, paraffins have a relatively low thermal conductivity, reducing the rate of heat charging and discharging during the melting and solidification cycles (Bugaje, 1997; Gong & Mujumdar, 1996; Kaygusuz & Sari, 2007; Pielichowska & Pielichowski, 2014; Velraj et al., 1999). Velraj et al. (1999), proposed that the thermal conductivity limitations of paraffin can be solved using finned container and metallic fillers. Another disadvantage of paraffin is the large volumetric change during the phase transition, which will pose a challenge on the design and development of the containers (Hasnain, 1998).

Table 2.10. Thermal properties of paraffin

Name	No. of “C” atoms	Melting point (^{o}C)	Density (kg/m^3)	Thermal conductivity (W/mK)	Latent heat (Jg^{-1})
n - Dodecane	12	-12	750	0.21	n.a
n - Tridecane	13	-6	756		n.a
n - Tetradecane	14	4.5-5.6	771		231
n - Pentadecane	15	10	768	0.17	207
n - Hexadecane	16	18.2	774	0.21	238
n - Heptadecane	17	22	778		215
n - Octadecane	18	28.2	775	0.149	245
n - Nonadecane	19	31.9	769	0.21	222
n - Eicosane	20	37			247
n - Heneicosane	21	41			215
n - Docosane	22	44			249
n - Tricosane	23	47			234
n - Tetracosane	24	51			255
n-Pentacosane	25	54			238
Paraffin wax	n.a.	32	749	0.224	251
n - Hexacosane	26	56	770	0.21	257
n - Heptacosane	27	59	773		236
n - Octacosane	28	61	765		255
n - Nonacosane	29	64			240
n - Triacontane	30	65			252
n - Hentriacontane	31	n.a	830		n.a
n - Dotricontane	32	70			n.a
n – Tritricontane	33	71			189

(Abhat, 1983; Lane, 1983; Sharma et al., 1999; Sharma & Sagara, 2005)

ii. Fatty acids

A fatty acid is characterized by the formula CH$_3$(CH$_2$)$_{2n}$COOH. In contrast to paraffin, one end of the molecule of fatty acids ends with a –COOH instead of a –CH$_3$ group (Mehling & Cabeza, 2008). There is a growing interest in utilizing fatty acid as PCMs as they possess desirable thermodynamic and kinetic characteristics for low-temperature

LHS. They exhibit a higher latent heat of fusion than paraffin, have reproducible melting and freezing behavior, with little or no subcooling. However, fatty acids are more expensive than technical grade paraffin, and are mildly corrosive (Sharma et al., 2009). The melting and freezing points, the heat of melting and the degree of crystallization would gradually increase as the number of carbon atoms in the fatty acids molecule increases. Carboxylic acids with an even number of carbon atoms in the structure possess higher values of thermal parameters than those with odd numbers of C-atoms and show a tendency for more regular alignment and a more dense crystalline lattice arising from hydrogen bonding between the carboxylic acid molecules (Pielichowski & Flejtuch, 2003b). The melting and boiling points of fatty acids are relatively high and saturated fatty acids exhibit low phase transition volume changes with very little or no subcooling when freezing (Pielichowski & Flejtuch, 2003a). Fatty acid-base PCMs are chemically and thermally stable, retains colour, heat and are nontoxic because of the protected carboxyl group. (Rozanna et al., 2005). Fatty acids are also stable upon cycling since the PCM consist of only one component and thus, phase separation would not be applicable (Mehling & Cabeza, 2008).

The difference of fatty acids to paraffin is in the compatibility of fatty acids to metals, as highlighted by Sari and Kaygusuz (Sari & Kaygusuz, 2001; Sari & Kaygusuz, 2002a, 2002b; Sarı & Kaygusuz, 2001, 2002). Unique PCMs with different melting temperatures can be developed by mixing a combination of fatty acids, and data on such mixtures has been reported in past studies (Kenisarin & Mahkamov, 2007; Nikolić et al., 2003; Tunçbilek et al., 2005).

Feldman et al. (1989) reported that the range of melting temperature of fatty acids (capric, lauric, palmitic and stearic acids) and their binary mixtures varied from 30 to 65 ^{o}C and their latent heat of fusion was in the range of 153 to 182 kJ/kg. Dimaano and D.

Escoto (1998) had also studied a mixture of capric acid (CA) and lactic acid (LA) as possible PCMs for low-temperature TES systems. In subsequent work the authors made an initial assessment of the thermal performance of CA–LA acid/pentadecane (PD) mixtures and found that a 50:50 CA-LA:PD mixture provided the highest change of enthalpy of all the combinations evaluated (Dimaano & Watanabe, 2002). The authors have also evaluated the thermophysical and heat transfer characteristics of the CA-LA blend with some organic additives using DSC and have concluded that the most effective additive was methyl salicylate, having the narrowest melting range and the highest heat of fusion of the additives investigated. (Roxas et al., 2002).

Buddhi and Sharma (1999) found that the transmissivity of the liquid phase of stearic acid (SA) is relatively high. Because of this high transmittance and low thermal conductivity it can be used as a transparent insulation and can be integrated for PCM solar windows or PCM window shutters. Sari and Kaygusuz (2001) studied the phase change stability of SA experimentally and have found that its melting stability is better in the radial direction than in the axial direction. The authors established that the PCM was more effective with steady phase change characteristics when the heat exchanger tube was horizontal rather than vertical. The same results were found for lactic acid (LA) (Sarı & Kaygusuz, 2002), MA (Sarı & Kaygusuz, 2001), and PA (Sari & Kaygusuz, 2002b).

The thermal characteristics of a eutectic mixture of LA and SA, during the melting and solidification processes in a vertical two concentric pipe-energy storage system, were also determined (Sari & Kaygusuz, 2002a). It was established that the LA–SA binary system had good thermal and heat transfer properties during the melting and solidification processes. Hence, the authors concluded that these fatty acids have good thermal properties and thermal reliability for use as PCMs.

2.4 Thermo-physical properties of PCMs

The proposed PCMs for use in the design of thermal energy storage (TES) application should have these desired thermo-physical, kinetic, and chemical properties (Cabeza et al., 2011; Dincer & Rosen, 2002; Mehling & Cabeza, 2008; Sharma et al., 2009; Tyagi & Buddhi, 2007):

- Thermal properties:
    - ✓ Melting temperature in the desired operating temperature range: to ensure storage and extraction of heat in an application within a fixed temperature range.
    - ✓ High latent heat of fusion per unit volume: to achieve high storage density compared to sensible storage.
    - ✓ High specific heat
    - ✓ High thermal conductivity of both solid and liquid phases to assist the charging and discharging energy of the storage system.
    - ✓ Small volume change on phase transformation and small vapor pressure at operating temperature to reduce containment requirements.
    - ✓ Congruent melting of the phase change material for a constant storage capacity of the material with each freezing/melting cycle.
    - ✓ Reproducible phase change: for long term usage of the material (also called cycling stability).
- Physical properties:
    - ✓ High nucleation rate to avoid super cooling of the liquid phase, and to ensure that melting and solidification occurs at the same temperature.
    - ✓ High rate of crystal growth, so that the system can meet the demand of heat recovery from the storage system.
- Chemical properties:

- ✓ Complete reversible freeze/melt cycle.
- ✓ No degradation after a large number of freeze/melt cycles.
- ✓ Non-corrosive to the construction materials.
- ✓ Non-toxic, non-flammable and non-explosive material for safety: for environmental and safety reasons.

- Economics properties:
  - ✓ Abundant.
  - ✓ Available.
  - ✓ Cost effective: to be competitive with other options for heat and cold storage.

2.4.1 Measurement technique of thermal properties PCMs

The measurements techniques presently used for evaluating latent heat of fusion and phase transition temperature (melting, solidifying) of PCMs are: (i) differential thermal analysis (DTA), and (ii) differential scanning calorimeter (DSC) (Buddhi et al., 1987; Sharma et al., 2009). In DSC and DTA techniques, sample and reference materials are heated at a constant rate. The temperature difference between them is proportional to the difference in heat flow between the two materials. The recommended reference material is alumina (Al_2O_3). Latent heat of fusion is calculated using the area under the peak of the DSC curve and the melting temperature is estimated by the tangent at the point of greatest slope on the face portion of the peak (Sharma et al., 2009).

2.4.2 Subcooling on phase change material

Subcooling (also called supercooling) is the effect that a temperature significantly below the melting temperatures has to be reached, until a material begins to solidify and release heat. As described in Fig. 2.2, if the subcooling temperature is not reached, the PCM will not solidify at all and thus only store sensible heat (Mehling & Cabeza, 2008).

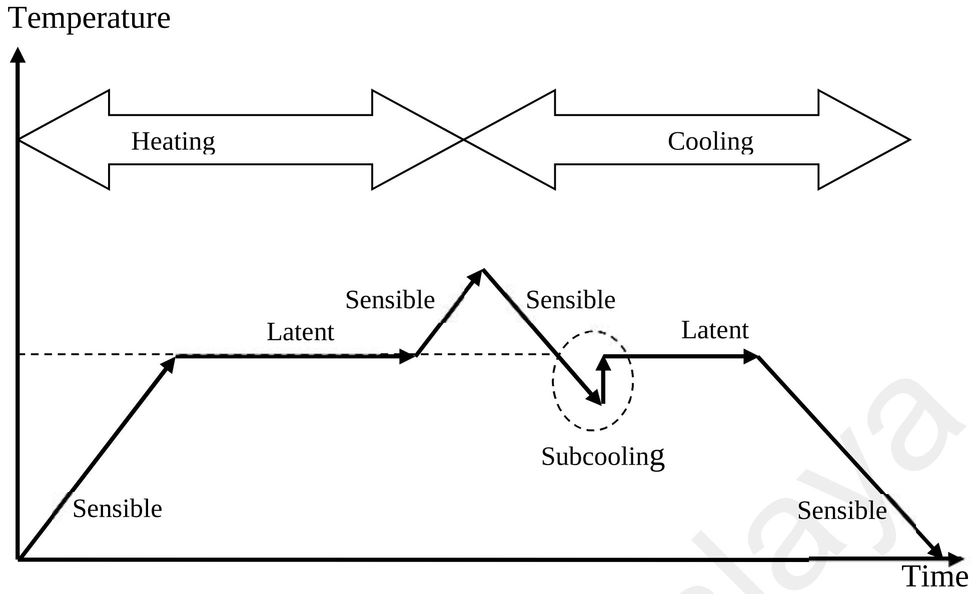


Figure 2.2. Schematic temperature change during heating (melting) and cooling (solidification) of a PCM with subcooling (Mehling & Cabeza, 2008).

Many PCM do not solidify immediately upon cooling below the melting temperature, but start crystallization only after a temperature well below the melting temperature is reached. For example, liquid water can be cooled to temperatures well below 0 ^{o}C, if it is highly pure and in small quantities, at temperatures even below -15 ^{o}C. Fig. 2.3 shows the effect of subcooling on heat storage.

During the supply of heat, there is no difference whether a PCM shows subcooling or not. However, during extraction of heat, subcooling prevents the release of the latent heat when the melting temperature is reached, thus requiring temperature well below the phase change temperature to start crystallization and to release the latent heat stored in the material. If nucleation does not happen, the latent heat is not released at all and the material only stores sensible heat (Mehling & Cabeza, 2008). Thus, in technical applications of PCM, subcooling can be a serious problem.

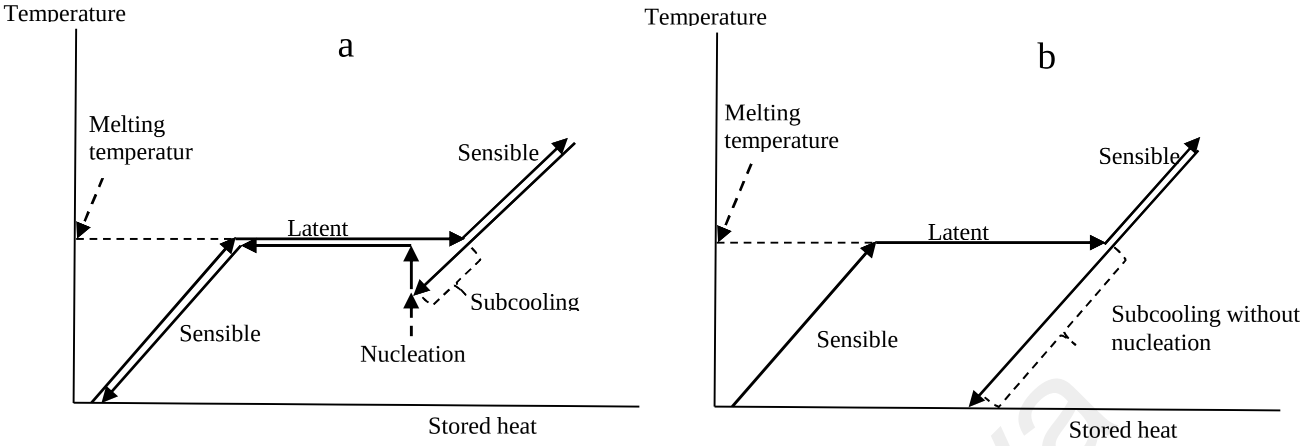


Figure 2.3. Effect of subcooling on heat storage. a) with little subcooling and nucleation, b) severe subcooling without nucleation (Harald Mehling & Cabeza, 2008).

As an example, when water is subcooled to -8 ^oC and crystallization starts, the latent heat of crystallization is released. At that temperature of -8 ^oC, 8 · 4 kJ/kg. = 32 kJ/kg of sensible heat are lost due to subcooling, much less than the latent heat value of 333 kJ/kg which is released during crystallization. If the heat released upon solidification is larger than the sensible heat lost due to subcooling, the temperature rises to the melting temperature and stays there until the phase change is complete, as shown in Fig. 2.3a. If the loss of sensible heat during subcooling is larger than the latent heat released upon crystallization, or if the rate of heat loss to the ambient is larger than the rate of heat release during crystallization, it is possible that the temperature will not rise to the melting temperature again, as shown in Fig. 2.3b. This indicates that subcooling may cause a surprising effect in dynamic experiments.

Fig. 2.4 shows the effect of subcooling on a cool down experiment with $NaOAc \cdot 3H_2O$. After the crystallization has started at a temperature of about 55 ^oC, the temperature rises sharply until melting at about 57 ^oC is reached. When the melting temperature is reached at a certain location, no more phase change enthalpy is released and the temperature rise stops. From the location where the first crystallization occurs, the phase front moves until the boundaries of the sample are reached and the phase change takes place throughout the sample. This usually leads to a longer or shorter plateau in the temperature at the melting temperature. The length of this plateau depends on the rate of heat loss at the boundaries of the sample to the environment. In Fig. 2.4, the plateau is about 1 hour long before the temperature decreases to the temperature of the environment, which is 40 ^{o}C (Mehling & Cabeza, 2008).

Solidification means that the amount of solid phase grows because the liquid phase at the interface with the solid phase solidifies. However, this has to start at some point, which can be a problem to initiate. The starting points, or the nucleus, can be in the form of small solid particles. For the nucleus to grow by solidifying liquid phase on its surface, the system has to release heat to get its energetic minimum. There is however a competition between the surface energy, which is proportional to the surface area and therefore to r^2 (r is the radius of the nucleus), and the heat released by changing the phase, which is proportional to the volume and therefore to r^3. At small radius, it is possible that the heat released by crystallization is smaller than the surface energy gained and the energy barrier is not exceeded. The solidification would start when a nucleus of sufficiently large radius is present. In some cases, temperatures significantly lower than the melting temperature are necessary (Mehling & Cabeza, 2008). Thus, nucleation is divided into two categories:

1. Homogeneous nucleation, which is solely started by the PCM itself. This occurs due to the temperature decrease low enough for nucleation to initiate or by the addition of solid particles of PCM to the subcooled PCM, in the process also known as secondary nucleation.
2. Heterogeneous nucleation which is not initiated by the PCM itself. Origins of heterogeneous nucleation can be additives intentionally added to the PCM, or by impurities, or cracks in the wall of the vessel that may contain solid PCM.

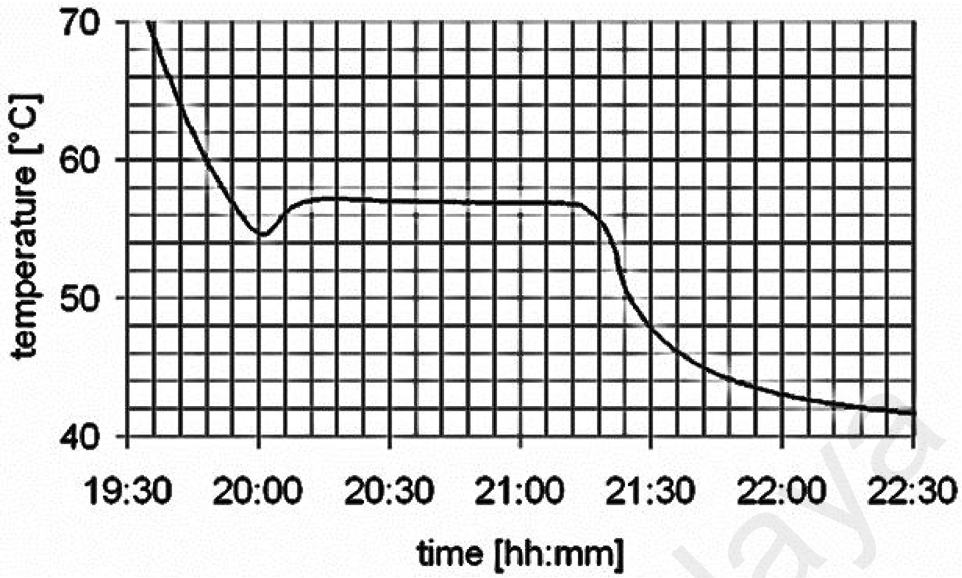


Figure 2.4. Cooling of NaOAc·$3H_2O$ at an ambient temperature of 40 °C with about 2K subcooling (Mehling & Cabeza, 2008).

The most common approach to eliminate subcooling in the PCM is to add special additives, also called nucleator, to the PCM to initiate heterogeneous nucleation. Nucleators have been developed for most types of PCM, and have reduced subcooling typically to a few Celcius. Most nucleators are materials with a similar crystal structure as the solid PCM to allow the solid phase of the PCM to grow on their surface, but have higher melting temperatures to avoid deactivation when the PCM is melted (Farid et al., 2004). The problem with this method is that materials with a similar crystal structure usually would have a similar melting temperature. Thus, many nucleators are only stable up to a temperature of 10 °C to 20 °C above the melting temperature of the PCM.

There are also nucleators where the mechanism is completely unknown. The fact that there is still no reliable theoretical approach makes the search for the new nucleators time consuming (Mehling & Cabeza, 2008). Examples of nucleators for some of the most important PCM are given in Farid et al. (2004) and in Lane (1983).

2.5 Thermal reliability of PCMs

Over the past two decades, several reviewers have elaborated on the importance of PCMs selection based on their long-term stability in term of thermo-physical properties (Abhat, 1983; Agyenim et al., 2010; Delgado et al., 2012; Farid et al., 2004; Gil et al., 2010; Hasnain, 1998; Kenisarin & Mahkamov, 2007; Rathod & Banerjee, 2013; Sharma et al., 2009; Sharma & Sagara, 2005; Zalba et al., 2003). Hasnain (1998) has emphasized that the selection of the PCM plays an important role in enhancing the heat transfer mechanisms for the development of a latent heat thermal energy storage system. It was highlighted that a large-scale use of PCMs would require a thorough study of their thermo-physical properties in solid and liquid states. Zalba et al. (2003) presented a critical review of a thermal energy storage system using PCMs from 237 sources. Over 150 materials were identified as PCMs along with their thermo-physical properties. It was noted that there was a large discrepancy in the available data for the melting temperatures and latent heat for some PCM. In addition, one of the conclusions made by researchers was that the widespread use of latent heat storage was limited due to the insufficient long-term stability of storage materials.

(Farid et al., 2004) presented a review pertaining to the development of new classes of phase change materials for applications in heating and cooling of buildings, thermal storage in satellites, protective clothing and new innovations in other areas. They highlighted the issues of separation, supercooling and stability of thermal properties of PCMs for long-term cycle processes. It was concluded that the melting point was the most important criterion for selecting a PCM for passive solar applications. (Sharma and Sagara, 2005) compiled a practical information of more than 250 PCMs and have also discussed the thermo-physical measurement techniques, thermal cycles and heat transfer enhancement techniques. They emphasized the need to study the effects of thermal cycling on melting point and latent heat of commercial grade PCMs. A list of 15 PCMs was presented which have been tested for thermal stabilities by several researchers (Rathod & Banerjee, 2013). Kenisarin and Mahkamov (2007) have analyzed the properties and applications of PCMs and suggested various methods of enhancing heat and mass transfer. They have indicated that information on temperature dependent heat capacity, thermal conductivity and density of materials in solid and liquid states were not widely available in the literature. It was suggested that, for use in commercial latent heat storage products, the thermal stability of PCMs should be tested for at least 1,000 thermal cycles. Although the preparation, leakage, thermal storage properties of PCMs have been extensively studied, the reports on the thermal reliability of PCMs are relatively inadequate (Rathod & Banerjee, 2013). Thus, the thermal reliability test of PCMs should be carried out before they are used in actual applications.

2.5.1 Thermal reliability test

To ensure the long-term performance of the storage unit, the changes in the thermo-physical properties of the PCMs should be observed after a repeated number of thermal cycles. A PCM is reliable if it is thermally, chemically and physically stable after extensive repeated thermal cycles. However, in reality PCMs may degrade over time, due to the inherent characteristics of these materials. Thus, although small degradations are expected, large degradations of the thermo-physical properties over time are not desirable for any PCMs (Rathod & Banerjee, 2013).

Commercial grade PCMs are preferred for latent heat storage systems, due to their wide-scale availability and low costs. However, it has been noted that the thermo-physical properties and behavior of commercial grade materials can vary from the values quoted in the literature. Therefore, the influence of the number of repeated thermal cycles on the melting temperature and latent heat of fusion in commercial grade PCMs must be evaluated before the selection of a PCM for a particular application (Rathod & Banerjee, 2013).

The most common application for PCM-based energy storage unit is in solar applications. A solar thermal system with latent heat storage undergoes at least one melt/freeze thermal cycle per day, considered as a normal cycle. Accelerated thermal cycle tests can be conducted under controlled conditions in the laboratory by a series of repeated, consistent thermal cycles using an oven or an electric hot plate with a temperature controller (Sharma et al., 1999).

2.6 Enhancement of thermal conductivity of PCM

Even though the regular PCMs offer high energy density, but they have a low heat transfer rate during heating or cooling that make these PCMs less potential in applications. Most of regular PCMs, whether organic and also inorganic-based, have small thermal conductivities which range by 0.1 to 0.6 W/m K. Table 2.11 lists the thermal conductivity values and the latent heat values of several PCMs which are widely investigated by view researchers (Farid et al., 2004; Sharma & Sagara, 2005; Zalba et al., 2003).

Table 2.11. Thermal conductivity and latent heat of selected PCMs

Name of the PCM	**Thermal conductivity ($W.m^{-1}K^{-1}$)**	**Latent heat of fusion ($J.g^{-1}$)**
Inorganics		
KNO_3	0.5	266
$NaNO_3$	0.5	172
$MgCl_2.6H_2O$	0.694	168.6
$CaCl_2.6H_2O$	1.088	190.8

Table 2.11, *continued*

Organics		
n-Octadecane	0.35	245
n-Docosane	0.22	194.6
Paraffin wax	0.514	251
Caprylic acid	0.149	149
Capric acid	0.153	153

(Farid et al., 2004; Jegadheeswaran & Pohekar, 2009; Sharma & Sagara, 2005; Zalba et al., 2003)

Integrating of high conductivity materials may improve the thermal conductivity of regular PCMs. Previous scientific study has offered the following solutions to further improve the thermal conductivity values of PCMs:

- Impregnation of high conductivity porous material to the PCM.
- Dispersion of high conductivity particles in the PCM.
- Inserting of the metal component into the PCM.
- Use of high conductivity, low-density materials.

2.6.1 Impregnation of high conductive material

A porous structure can either be matrices constructed from metals such as aluminum or copper, or even coming from naturally porous materials such as graphite. Fiedler et al. (2008) were reported that the copper matrices can enhance approximately 80% of thermal conductivity as compared to that of aluminum matrices. Further development on increasing thermal conductivity also possible by using diamond coated copper matrices. The effect of impregnating high conductive porous matrix to thermal conductivity and thermal properties of PCM in different porosities was investigated by Mesalhy et al. (2005). The numerical study accomplished to evaluate the melting process of these PCMs in a horizontal cylindrical annulus shows the indication that the performance enhancement was dependent on both porosity and thermal conductivity of the matrix. In pure PCM, the rate of melting was less at the lower part of the container as compared to that at the upper part as the melting process was dominated by convection. With the addition of high conductivity porous matrix, the melting rate at the lower portion could be increased. The enhancement as a result of the porous structure was found to be dependent on the porosity of matrix, where decreasing in porosity will decrease the enhancement during melting process. Hence, it was noted that the low porosity matrix dampens the motion of liquid PCM and subsequently reduces the natural convection within the liquid PCM. The results of the numerical study have shown that low porosity samples would follow conduction-like temperature profiles rather than a convection-like profiles (Mesalhy et al., 2005).

Krishnan et al. (2005) have done the numerical analysis and reported the same result of heat transfer rate on the melting process in a rectangular enclosure filled with metal foam impregnated with PCM. In the case of the composite PCM, the melt volume fraction at steady state was lower than that of pure PCM due to the restricted convective flow. However, a considerable decrease in a response time of the system was observed. Thus, it can be noted that the porous matrix should haves criteria which are high thermal conductivity and also high porosity in order to obtain the best performance enhancement.

Graphite is popular for its high thermal conductivity, high electrical conductivity and high absorbability. The thermal conductivity range of graphite from 24 to 470 $Wm^{-1}K^{-1}$ (Mehling et al., 2000). According to Haillot et al. (2008), the thermal conductivity of PCM (0.2–1 W/m K) can be increased depend on the density of graphite added into the PCM. Cabeza et al. (2006) have reported that the using of the PCM-graphite composite is the best solution in applications such as thermally stratified storage tank. The cheapest type of graphite is natural graphite flakes, which are composed of dense stacked graphite layers. However, expanded graphite (EG) can be a perfect choice as it is of greater absorbability than graphite flakes due to its high porosity. Generally, EG can be prepared from natural graphite through chemical oxidation in the presence of concentrated sulphuric/nitric acid/mixture of sulphuric and nitric acids, followed by a drying process in an oven and a final rapid heating in a furnace (Jegadheeswaran & Pohekar, 2009). When the EG is mixed with PCM, the melted PCM will be absorbed into the pores of the EG and become as a composite PCM. The thermal conductivity and thermal capacity of the composite PCM depend upon the relative composition of graphite with PCM.

Sarı and Karaipekli (2007) have investigated the thermal conductivity enhancement and thermal storage enhancement of paraffin-based by the addition of EG in an LHTES system. The paraffin/EG composites were prepared with a different mass ratio of EG. Besides analyzing the heat performance enhancement, the experimental study has also conducted to prepare a form-stable composite. The form-stable composite is a composite of PCM/EG without leakage of liquid PCM. It was obtained that a composite PCM with 10% EG mass fraction was the best composition of form-stable to held paraffin properly by the capillary and surface tension forces of the porous EG. As the density of paraffin/10% EG composite was less than that of pure paraffin, it had also lead in a lighter LHTES unit having the same volume. The thermal conductivity values obtained for composites with different mass fraction ratio of EG have shown that the thermal conductivity was increased by increasing the mass fraction of EG. On the other hand, the increasing of mass fraction EG in composites also lead to decreasing the latent heat value and resulted in a decrease in storage capacity. The optimum mass fraction ratio GE obtained was 10% in paraffin with thermal conductivity value is four times higher than that of pure paraffin with only a small decrease in latent heat value. The comparison of melting times pure PCM and composite PCMs were evaluated to prove the impact of improvement in the thermal conductivity. The results presented a significant reduction in melting time of form-stable composite PCM which is about 32%once used in the LHTES system (Jegadheeswaran & Pohekar, 2009; Sarı & Karaipekli, 2007).

In contrast to of Sarı and Karaipekli (2007) results, Yin et al. (2008) have reported that the thermal conductivity of paraffin/EG composites gradually increased by maximum mass fraction ratio of EG up to 6.25%. Above of this value, the thermal conductivity of composite PCM shows start to decreased. The reason why the thermal conductivity in these work reduced is due to the appearance of some gases and hollow space in the lax structure of composite PCM with high EG mass fraction. This means that composite with appropriate mass fraction EG should be prepared in such a method that the unfilled spaces and gases are not appearing in the pores. However, the composite PCM became form-stable at mass fraction EG 6.25%, which shows a significant improvement in heat transfer rate, during heat absorbing and heat releasing processes. The effect was found to be clearer during heat absorbing. The phase transition time through heating and cooling was noted reduced about 65.3% and 26.2% respectively compared to that pure paraffin.

Recently, Kim and Drzal (2009) proposed a new type of graphite as exfoliated graphite nanoplatelets (XGnP) to prepare a paraffin/graphite composite. These XGnP, was obtained in less than 10 mm thicknesses and 15 mm diameters average after pulverizing the EG by an ultrasonic processor. The results of these composite indicate a strong relationship between the mass percentage of XGnP and thermal conductivity improvement. The regular improvement of thermal conductivity was observed in a different mass fraction of XGnP in paraffin and the result shows that the highest is obtained at 7% mass fraction of XGnP. Moreover, the latent heat value of composite for each mass fractions composition of XGnP ware closely matched to those of pure paraffin. As mentioned previously that the increasing in the amount of expanded graphite in paraffin would carry out the reducing of the latent heat value of PCM. But, in the case of these XGnP composite, as the high surface area of XGnP allows good dispersion in the PCM, there was no decrease in the latent heat (Jegadheeswaran & Pohekar, 2009). Therefore, it can be specified that XGnP is more effective than EG as it enhances the thermal conductivity without reducing the storage capacity of pure PCM.

The use of graphite as a high conductive material to improve the thermal conductivity of PCM is not only limited to low melting point PCMs such as paraffin, but was also proposed for high melting point PCMs such as salts or eutectic mixtures (Pincemin et al., 2008; Pincemin et al., 2008). Generally, composite PCMs are prepared by blending the graphites with molten PCM. The same method also was applied by Pincemin et al. (2008) to prepare eutectic salt/graphite composite. The graphite particles could be well dispersed within the molten salts because of the high viscosity of salt and the similarity in densities between salt and graphite, resulting in an isotropic composite (Jegadheeswaran & Pohekar, 2009). However, this method has any disadvantage which is required more energy to melted the molten PCM because of their high melting point to inclusion the graphite, and the corrosion effects on equipment as well as the safety issues. Therefore, a cold compression method could be an alternative to using by mixing solid PCM with graphite powder and compressed at room temperature. The resulting monolithic composite can be easily shaped to fit the geometry of the storage system. The composite obtained from cold compression methods possessed anisotropic characteristics because of rearrangement of graphite layer orthogonally to the compression axis. The thermal conductivity measurement showed that radial thermal conductivity was much higher than that of the values in the axial direction. It was found that, the thermal conductivity of cold compressed composite PCM was twice the values of the composites PCM made by mixing graphite with molten PCM at the same amount of graphite. However, the cold compressed composited PCM cannot be form-stable as salt leakage was observed, which was probably due to the presence of impurities and mechanical stresses (Jegadheeswaran & Pohekar, 2009).

Pincemin et al., 2008 used graphite powders of different particle sizes in forming composites with eutectic salts. The thermal conductivity was found to be dependent on two parameters which are the graphite amount and also the particle sizes. For the composite with a high mass fraction of graphite was prefer to use large sizes particle of graphite as they bring out a better conductive network. Whereas, for the composite with low graphite quantities, a particle used should be of small sizes. In term of heat storage capacity, the smallest particle size may increase the heat storage capacity if the graphite quantity was more. While the small amount of graphite, effect of particle size was not significant on the heat storage capacity. The results have also shown a decrease in phase transition temperature variation of composites due to the addition of graphite, i.e. the composite PCM possessed almost a congruent melting point.

2.6.2 Dispersion of high conductive particles in PCM

The composite PCM was become more compact and efficient by the addition of graphite as well as was able to enhance the performance of LHTES systems. However, a composites PCM with graphite only can prepare by involving duration and energy consumption processes such as heat treatment, drying, mixing, and grinding/compression. Elgafy and Lafdi (2005) have reported that the porosity of graphite is very important in determining the effectiveness of the composites. If graphite of small mean pore sizes is used, there may be a decrease in latent heat value since small mean pore sizes hinder the molecular motion, making it very difficult to impregnate the porous media with the PCM. On the other hand, increasing pore size reduces the capillary force resulting in leakage of liquid PCM. These limitations are not applicable to metal particles, thus the dispersion of high conductivity metal particles into the PCM is a relatively simpler technique to enhance the thermal conductivity of PCM (Jegadheeswaran & Pohekar, 2009).

Mettawee and Assassa (2007) have conducted experiments to evaluate the effect of dispersion of micro aluminum particles within a PCM-based solar collector. The solar radiation was absorbed by the PCM stored in the container and the cold water was supplied through the pipes embedded in the PCM, during charging and discharging processes, respectively. Even though the heat transfer rate could be enhanced by adjusting the mass fraction of aluminum, it was identified that the improvement of heat transfer rate was insignificant above 0.5% mass fractions of aluminum. The inclusion of micro aluminum particles has enhanced the thermal conductivity, and was able to reduce the charging time up to 60% compared to pure PCM. The effect was bolder during the discharging process, as the conduction-dominated solidification process by showing more homogeneous. The average daily efficiency was measured to evaluate the overall advantages of using aluminum particles. The average daily efficiency is explained as the ratio of the heats transferred to fluid (water) during discharging and total absorbing solar radiation during charging. The results confirmed a significant increase in average daily efficiency. For all mass flow rates of fluid, the highest average daily efficiency obtained was 94% with composite PCM and 55% obtained with pure PCM. Although the improvement of heat transfer performance by using aluminum is reported, but the effect of adding these particles to the heat storage capacity was not discussed in detail.

In the other work, Khodadadi and Hosseinizadeh (2007) reported that the heat capacity of PCM showing a decrease as the mass fraction of added particles is increased. They have conducted the simulation during the solidification of nanofluid (water + nano copper particles) in a square storage prototype. The duration time of the solid/liquid interface during solidification was observed for pure PCM and for PCM with different mass fractions of nano copper particles. At the beginning there was not showed much increase in the duration time of the interface due to the inclusion of particles. After a few moment, the effect was seen more clearly as the interface was at advanced locations in case of higher mass fractions. This resulted in considerable reduction in overall solidification time.

Silver has also been proposed in the advancement of composite PCM. Zeng et al. (2007) prepared a composite of 1-tetradecanol with distributed silver nanoparticles and investigate the effect of different mass fraction silver particles on the thermal performance of PCM. In this study was found that the thermal conductivity of the composite PCM increased as increasing the loading of silver particles. In addition, the interaction between of organic PCM and silver particles was not occurred a chemical reaction, and the thermal stability obtained was almost similar to that of the based PCM. However, the phase transition temperature of the composite was found to be slightly lower than that of based PCM. Although it is reported that latent heat of composites decreases with increase in the mass fraction of particles (Khodadadi & Hosseinizadeh, 2007; Zeng et al., 2007), there is no extended work has been made in those studies to investigate the outcomes of different particles mass fraction (Jegadheeswaran & Pohekar, 2009).

The effect of high conductive particles in PCM has been extensively studied by Seeniraj et al. (2002) in their numerical work on shell and tube setup. The increase in the amount of particle mass fraction would lead to a decrease in heat stored capacity, even though the improvement of heat transfer rate could be achieved. Hence, it is crucial to determine the optimum mass fraction of particles, so that maximum heat transfer rate with a low decrease in latent heat storage capacity can be obtained. (Seeniraj et al., 2002) have calculated the ratio of cumulative energy stored with particles and without particles in order to determine the optimum particle mass fraction installed within PCM. The results described the presence of an optimum mass fraction of the particle at which the highest ratio of cumulative energy stored was observed. At any given conditions, there is a range of optimum particle fraction, thus it is suggested to choose the lower value in the band to ensure high mass of PCM for better energy storage capacity. The analysis result indicated that the optimum mass fraction for maximum energy stored would depend on the thermal conductivity of particle and maximum acceptable radius for interface location. For a particle with high thermal conductivity value, the optimum mass fraction was also correspondingly higher. Similarly, the increase in optimum mass fraction was observed with the increase in maximum allowable radius for the interface. The maximum allowable radius for the interface is determined by the dimensions of the LHTS unit. Hence, an appropriate combination of particle thermal conductivity and particle mass fraction is quite important in the process of conductivity particles dispersion the PCM to enhance the performance of the unit.

2.6.3 Placing of metal structures

Placements of metal structures into the PCM have been proposed as one of the thermal conductivity enhancement techniques by some researchers. Velraj et al. (1999) placed thin walled hollow cylindrical steel structures into paraffin stored in a cylindrical LHTS system. This structure, shown in Fig. 2.5a, is named as lesser rings. The results indicated a considerable reduction in solidification time due to the addition of lesser rings. The time for complete solidification with lesser rings was approximately 1/9th of that without lesser rings, whereas with longitudinal fins, the time for complete solidification was around 1/4th of that without fins. One may conclude from this observation that lesser rings are more effective than fins. However, the reduction in solidification time was achieved with the lesser rings occupying 20% of total volume as compared to metal fins occupying just 7% of the total volume. It is also reported that the enhancement due to lesser rings depended upon the diameter of the cylindrical module, whereas in the case of fins, it remains almost constant for a fixed number of fins irrespective of the diameter of the module. Thus, the lesser rings are more suitable for the large storage system.

The enhancement is observed for other types of metal structures (Ettouney et al., 2004). The placement of stainless steel balls combined with stainless steel screens placed inside the PCM in a double pipe arrangement, as shown in Fig. 2.5b, had increased the melting rate of the PCM. The enhancement of the metal ball arrangement was purely dependent on the diameter and number of balls. Increasing the diameter and number of balls resulted in an increase in enhancement by a factor of 3. The enhancement may be limited for smaller systems (Jegadheeswaran & Pohekar, 2009). Ettouney et al. (2006) investigated the effect of steel balls inserted into the PCM stored in small spherical modules, as shown in Fig. 2.5c. Both melting and solidification processes were analyzed and the results showed a 15% reduction in melting and solidification times due to the addition of balls.

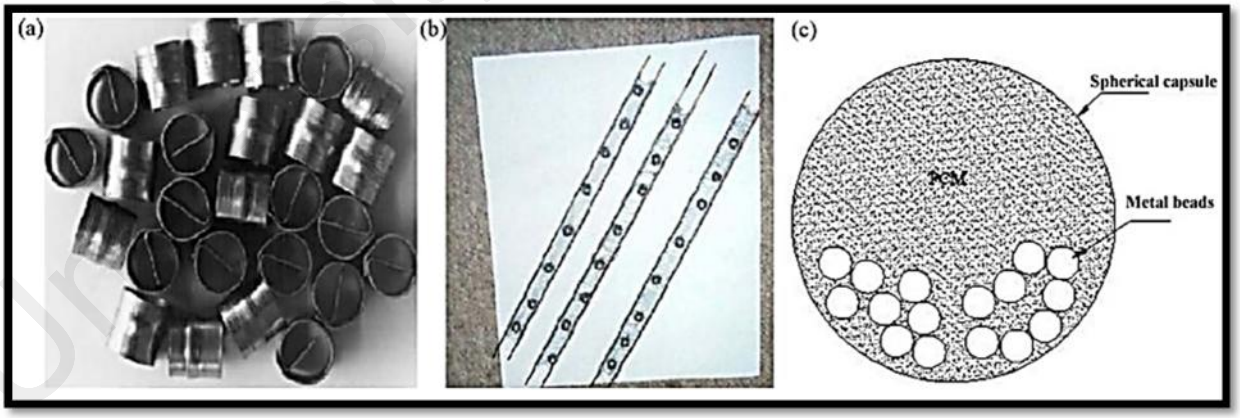


Figure 2.5. Type of metal structure: a) lesser rings (Velraj et al., 1999); b) metal balls combined with metal screens (Ettouney et al., 2004); c) metal beads (Ettouney et al., 2006).

2.6.4 Use of high conductivity and low density materials

Metal particles/metal structures incorporated in PCM may settle on the bottom of the container due to their relatively high density, and may add considerable weight to the system. Fukai et al. (2000) advised that some metal particles are not compatible with all

PCMs. For example, aluminum is compatible with paraffin, whereas copper and nickel are not compatible. Similarly, aluminum and copper are not compatible with some salt hydrates.

Several researchers have proposed the incorporation of carbon fibers in PCMs. Carbon fibers have lower densities than metals and thermal conductivities are almost equal to that of aluminum and copper. In addition, they possess a high corrosive resistance and hence compatible with most of the PCMs. Elgafy and Lafdi (2005) have developed a composite PCM by adding carbon nanofibers of 100 nm average diameter and 20 mm average length into paraffin wax using shear mixing and melting. The thermal conductivity of the composite was found to increase almost linearly with increase in mass fraction of nanofiber and high solidification rate was observed. A reduction in solidification time by 23% is reported for only 1% mass fraction addition of carbon fiber. There was also no reduction in the storage capacity due to the additives as the output power was found to increase linearly with increase in fiber mass fraction. The study was then extended to investigate the effect of surface characteristics of fibers on solidification rate and it was found that higher transfer rate was obtained for surface treated fibers than that of fibers with an untreated surface. The importance of the uniform distribution of fibers in the PCM to increase the performance was also highlighted.

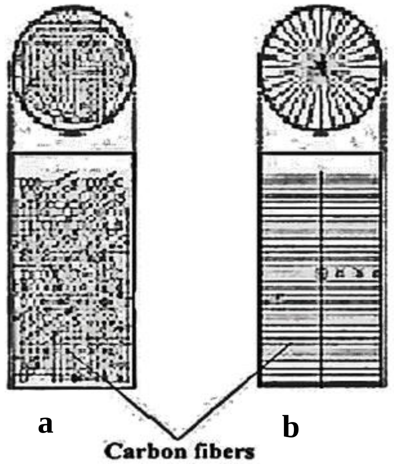


Figure 2.6. Distribution of carbon fibers in the cylindrical capsule (Fukai, Kanou, Kodama, & Miyatake, 2000): (a) random distribution; (b) brush type.

The importance of the uniform distribution of carbon fibers was reported by Fukai et al. (2000). In a cylindrical capsule, carbon fibers were added in the PCM in two ways, either randomly or orderly using brush-type fibers, as illustrated in Fig 2.6. The effective thermal conductivity with the brush-type arrangement was found to be three times higher than the sample with randomly arranged specimens. In the brush type arrangement, the fibers were distributed uniformly in a radial direction, which was in the heat flow direction. For a lower mass fraction of fibers, the randomly distributed arrangement had a lower melting rate than that of pure paraffin, even though the effective thermal conductivity was greater. This is probably due to the loss in natural convection. However, the loss in natural convection did not affect the higher melting rate for the brush type arrangement. Thus, it was recommended that fibers should be arranged to be oriented in the direction of heat flow.

The superiority of brush-type arrangement in the shell tube is also proven by Fukai et al. (2003). A 30% higher solidification rate and 20% melting rate were obtained with an addition of 1% mass fraction carbon brush type fibers as compared to pure PCM. Hamada et al. (2003) have also compared the performance of fiber brush with fiber chips. The experiments were conducted for melting processes and the results have shown that fiber chips resulted in higher thermal resistance near the heat transfer tube and thus the overall heat transfer rate was lower than that of fiber brush type. According to Fukai et al. (2002) there is a critical diameter for the brush for use in heat transfer tube. It was observed that the thermal response of the system increased with the increase in brush diameter. If the diameter of the brush was increased beyond a critical value at which the brushes cross the heat transfer tubes, there was no further improvement in thermal response. It is thought that beyond this critical diameter, the thermal resistance between fibers and the tube surface would be high. Hamada et al. (2005) have also stated that if the brush diameter is too large, then the fibers leaving the heat transfer surface to form a region where the density of fibers is low, and prevent further improvements in heat transfer rate.

From an economical point of view, (Hamada & Fukai, 2005) have reported that carbon fiber brushes could effectively reduce the overall cost and space. Evaluations on the utilization of carbon fiber brushes inserted in LHTES unit used for the air conditioning system have shown a 25% reduction in cost for the same thermal output as compared to the normal LHTES units. Furthermore, for the same thermal output, the space required for LHTES units with carbon fiber brushes is significantly less than normal LHTES units.

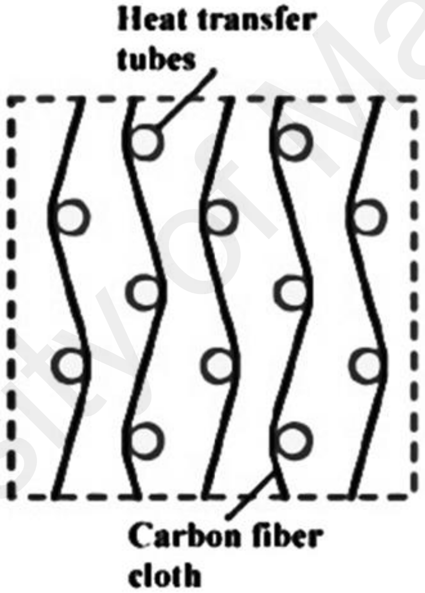


Figure 2.7. Carbon fiber cloths stretched over heat transfer tube

The thermal contact resistance between carbon fiber brush and heat transfer surface may affect the heat transfer enhancement especially when the volume fraction of fiber is small. Nakaso et al. (2008) have proposed a new technique of using carbon fibers cloth instead of brushes. The cloths made of carbon fibers were highly stretched over the heat transfer surface from one end of the tube to the other, as shown in Fig. 2.7. It is reported that these cloths with high surface density can act as fins. The results showed that fiber cloths of 0.42% volume fraction gave the same thermal performance of fiber brushes at 0.75% volume fraction.

Table 2.12. Studies on PCM thermal conductivity enhancement by additives.

Type of additive	**PCMs**	**Phase change process**
Natural graphite, expanded graphite and ground expanded graphite	NaNO3 + KNO3	Both melting and solidification
Aluminum/copper metal matrix	Paraffin	Not investigated
Expanded graphite	Paraffin, stearic acid, sodium acetate hydrate and barium hydroxide octa hydrate	Both melting and solidification
Graphite	Sodium acetate hydrate	Both melting and solidification
Expanded graphite	Paraffin	Both melting and solidification
Exfoliated graphite	Paraffin	Both melting and solidification
Aluminum particles	Paraffin	Both melting and solidification
Copper nano-particles	Water	Solidification only
Silver nano-particles	1-Tetradecanol	Both melting and solidification
Lesser rings	Paraffin	Solidification only
Metal screens and beads	Paraffin	Melting only
Metal beads	Paraffin	Both melting and solidification
Carbon fiber	Paraffin	Both melting and solidification
Carbon fiber	n-Octadecane	Melting only
Carbon fiber cloths	Paraffin	Solidification only

(Jegadheeswaran & Pohekar, 2009)

The review on thermal conductivity enhancement methods has shown that the phase change rates (melting/solidification) can be increased considerably by the addition of high conductivity substances. However, these additives may lead to loss of storage capacity of pure PCM. The loss in storage capacity limits the mass/volume fraction of additives. Thus it is important to estimate the optimum mass/volume fraction of additives. Table 2.12 presents a list of past studies on the effect of the addition of various high conductivity additives on the thermal responses of PCMs.

2.7 Compatibility PCMs with construction materials

Insufficient long-term stability of the storage materials and containers has limited the widespread use of latent heat storage systems. This poor stability is due to two factors: poor stability of the materials properties due to thermal cycling, and/or corrosion between the PCM and the container (Dincer & Rosen, 2002; Farid et al., 2004; Mehling & Cabeza, 2008; Mehling et al., 2007; Zalba et al., 2003). A relevant criteria is the useful life of these systems, and the number of cycles they can withstand without any degrading of their properties. Hadjieva et al. (1992) have evaluated the cyclic effect on three paraffin mixtures and have verified the stability of the PCMs. Other authors, such as Gibbs and Hasnain (1995), also confirmed that neither the cycles nor contact with metals degrade the thermal behavior of paraffin, indicating excellent thermal stability of the PCM.

2.7.1 Corrosion of construction materials

The compatibility of PCM with other materials is important with respect to a lifetime of the encapsulating material (or vessel) that contains the PCM, and the potential damage to the surrounding environment in case of leakage of the encapsulation (Mehling & Cabeza, 2007). Common problems in materials compatibility with PCM includes corrosion of metals in contact with inorganic PCM, stability loss of plastics in contact with organic PCM, and migration of liquid or gas through plastics that affect the performance of a contained organic or inorganic PCM and the outside environment (Mehling & Cabeza, 2007).

Most references to corrosion tests using salt hydrates were performed with diluted salt hydrates, as typically used in the chemical industry. Normally only a few results are presented, usually based on observations from experimental set-ups (Heine, 1981; Pettit). Porisini (1988) tested the corrosion of four commercially available salt hydrates used as PCMs. In addition, Cabeza et al. (Cabeza et al., 2001; Cabeza et al., 2002) studied corrosion resistance of five common metals (aluminium, brass, copper, steel and stainless steel) in contact with molten salt hydrates (zinc nitrate hexahydrate, sodium hydrogen phosphate dodecahydrate, calcium chloride hexahydrate, sodium carbonate, potassium hydrogen carbonate, potassium chloride, water, sodium acetate trihydrate, and sodium thiosulphate pentahydrate) in an immersion corrosion test.

Uncategorized References

Abhat, A. (1983). Low temperature latent heat thermal energy storage: Heat storage materials. *Solar Energy, 30*(4), 313-332. doi:10.1016/0038-092x(83)90186-x

Agyenim, F., Hewitt, N., Eames, P., & Smyth, M. (2010). A review of materials, heat transfer and phase change problem formulation for latent heat thermal energy storage systems (LHTESS). *Renewable and Sustainable Energy Reviews, 14*(2), 615-628. doi:http://dx.doi.org/10.1016/j.rser.2009.10.015

Birchenall, C. E., & Riechman, A. (1980). Heat storage in eutectic alloys. *Metallurgical Transactions A, 11*(8), 1415-1420. doi:10.1007/BF02653497

Biswas, D. P. (1977). Thermal energy storage using sodium sulfate decahydrate and water. *Solar Energy, 19*, 99.

Buddhi, D., Sawhney, R. L., Sehgal, P. N., & Bansal, N. K. (1987). A simplification of the differential thermal analysis method to determine the latent heat of fusion of phase change materials. *Journal of Physics D: Applied Physics, 20*(12), 1601.

Buddhi, D., & Sharma, S. D. (1999). Measurements of transmittance of solar radiation through stearic acid: a latent heat storage material. *Energy Conversion and Management, 40*(18), 1979-1984. doi:http://dx.doi.org/10.1016/S0196-8904(99)00077-1

Bugaje, I. M. (1997). Enhancing the thermal response of latent heat storage systems. *International Journal of Energy Research, 21*(9), 759-766. doi:10.1002/(SICI)1099-114X(199707)21:9<759::AID-ER254>3.0.CO;2-7

Cabeza, L. F., Castell, A., Barreneche, C., de Gracia, A., & Fernández, A. I. (2011). Materials used as PCM in thermal energy storage in buildings: A review. *Renewable and Sustainable Energy Reviews, 15*(3), 1675-1695. doi:http://dx.doi.org/10.1016/j.rser.2010.11.018

Cabeza, L. F., Illa, J., Roca, J., Badia, F., Mehling, H., Hiebler, S., & Ziegler, F. (2001). Immersion corrosion tests on metal-salt hydrate pairs used for latent heat storage in the 32 to 36°C temperature range. *Materials and Corrosion, 52*(2), 140-146. doi:10.1002/1521-4176(200102)52:2<140::AID-MACO140>3.0.CO;2-R

Cabeza, L. F., Roca, J., Nogués, M., Mehling, H., & Hiebler, S. (2002). Immersion corrosion tests on metal-salt hydrate pairs used for latent heat storage in the 48 to 58°C temperature range. *Materials and Corrosion, 53*(12), 902-907. doi:10.1002/maco.200290004

Cabeza, L. F., Svensson, G., Hiebler, S., & Mehling, H. (2003). Thermal performance of sodium acetate trihydrate thickened with different materials as phase change energy storage material. *Applied Thermal Engineering, 23*(13), 1697-1704. doi:http://dx.doi.org/10.1016/S1359-4311(03)00107-8

Chandra, D., Chellappa, R., & Chien, W.-M. (2005). Thermodynamic assessment of binary solid-state thermal storage materials. *Journal of Physics and Chemistry of Solids, 66*(2–4), 235-240. doi:http://dx.doi.org/10.1016/j.jpcs.2004.08.047

Delgado, M., Lázaro, A., Mazo, J., & Zalba, B. (2012). Review on phase change material emulsions and microencapsulated phase change material slurries: Materials, heat transfer studies and applications. *Renewable and Sustainable Energy Reviews, 16*(1), 253-273. doi:http://dx.doi.org/10.1016/j.rser.2011.07.152

Dimaano, M. N. R., & D. Escoto, A. (1998). Preliminary assessment of a mixture of capric and lauric acids for low-temperature thermal energy storage. *Energy, 23*(5), 421-427. doi:http://dx.doi.org/10.1016/S0360-5442(97)00108-4

Dimaano, M. N. R., & Watanabe, T. (2002). The capric–lauric acid and pentadecane combination as phase change material for cooling applications. *Applied Thermal*

Engineering, 22(4), 365-377. doi:http://dx.doi.org/10.1016/S1359-4311(01)00095-3

Dincer, I., & Rosen, M. (2002). *Thermal energy storage: systems and applications*: John Wiley & Sons.

Elgafy, A., & Lafdi, K. (2005). Effect of carbon nanofiber additives on thermal behavior of phase change materials. *Carbon, 43*(15), 3067-3074. doi:http://dx.doi.org/10.1016/j.carbon.2005.06.042

Ettouney, H., Alatiqi, I., Al-Sahali, M., & Al-Hajirie, K. (2006). Heat transfer enhancement in energy storage in spherical capsules filled with paraffin wax and metal beads. *Energy Conversion and Management, 47*(2), 211-228. doi:http://dx.doi.org/10.1016/j.enconman.2005.04.003

Ettouney, H. M., Alatiqi, I., Al-Sahali, M., & Ahmad Al-Ali, S. (2004). Heat transfer enhancement by metal screens and metal spheres in phase change energy storage systems. *Renewable Energy, 29*(6), 841-860. doi:http://dx.doi.org/10.1016/j.renene.2003.11.003

Farid, M. M., & Husian, R. M. (1990). An electrical storage heater using the phase-change method of heat storage. *Energy Conversion and Management, 30*(3), 219-230. doi:http://dx.doi.org/10.1016/0196-8904(90)90003-H

Farid, M. M., & Kanzawa, A. (1989). Thermal performance of a heat storage module using PCM's with different melting temperatures. *Journal Name: J. Sol. Energy Eng.; (United States); Journal Volume: 111:2*, Medium: X; Size: Pages: 152-157.

Farid, M. M., Khudhair, A. M., Razack, S. A. K., & Al-Hallaj, S. (2004). A review on phase change energy storage: materials and applications. *Energy Conversion and Management, 45*(9–10), 1597-1615. doi:10.1016/j.enconman.2003.09.015

Farid, M. M., & Mohamed, A. K. (1987). Effect Of Natural Convection On The Process Of Melting and Solidification of Paraffin Wax. *Chemical Engineering Communications, 57*(1-6), 297-316. doi:10.1080/00986448708960492

Farrell, A. J., Norton, B., & Kennedy, D. M. (2006). Corrosive effects of salt hydrate phase change materials used with aluminium and copper. *Journal of Materials Processing Technology, 175*(1–3), 198-205. doi:http://dx.doi.org/10.1016/j.jmatprotec.2005.04.058

Feldman, D., Shapiro, M. M., Banu, D., & Fuks, C. J. (1989). Fatty acids and their mixtures as phase-change materials for thermal energy storage. *Solar Energy Materials, 18*(3–4), 201-216. doi:http://dx.doi.org/10.1016/0165-1633(89)90054-3

Fukai, J., Kanou, M., Kodama, Y., & Miyatake, O. (2000). Thermal conductivity enhancement of energy storage media using carbon fibers. *Energy Conversion and Management, 41*(14), 1543-1556. doi:http://dx.doi.org/10.1016/S0196-8904(99)00166-1

Gibbs, B. M., & Hasnain, S. M. (1995). *DSC study of technical grade phase change heat storage materials for solar heating applications*.

Gil, A., Medrano, M., Martorell, I., Lázaro, A., Dolado, P., Zalba, B., & Cabeza, L. F. (2010). State of the art on high temperature thermal energy storage for power generation. Part 1—Concepts, materials and modellization. *Renewable and Sustainable Energy Reviews, 14*(1), 31-55. doi:http://dx.doi.org/10.1016/j.rser.2009.07.035

Gong, Z.-X., & Mujumdar, A. S. (1996). Enhancement of energy charge-discharge rates in composite slabs of different phase change materials. *International Journal of Heat and Mass Transfer, 39*(4), 725-733. doi:http://dx.doi.org/10.1016/0017-9310(95)00179-4

Hamada, Y., & Fukai, J. (2005). Latent heat thermal energy storage tanks for space heating of buildings: Comparison between calculations and experiments. *Energy Conversion and Management, 46*(20), 3221-3235. doi:http://dx.doi.org/10.1016/j.enconman.2005.03.009

Hasnain, S. M. (1998). Review on sustainable thermal energy storage technologies, Part I: heat storage materials and techniques. *Energy Conversion and Management, 39*(11), 1127-1138. doi:http://dx.doi.org/10.1016/S0196-8904(98)00025-9

Heine, D. (1981). *The chemical compatibility of construction materials with latent heat storage materials.* Paper presented at the Proceedings of the International Conference on Energy Storage, Brighton, UK.

Himran, S., Suwono, A., & Mansoori, G. A. (1994). Characterization of Alkanes and Paraffin Waxes for Application as Phase Change Energy Storage Medium. *Energy Sources, 16*(1), 117-128. doi:10.1080/00908319408909065

Jegadheeswaran, S., & Pohekar, S. D. (2009). Performance enhancement in latent heat thermal storage system: A review. *Renewable and Sustainable Energy Reviews, 13*(9), 2225-2244. doi:http://dx.doi.org/10.1016/j.rser.2009.06.024

Kaygusuz, K., & Sari, A. (2007). High Density Polyethylene/Paraffin Composites as Form-stable Phase Change Material for Thermal Energy Storage. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 29*(3), 261-270. doi:10.1080/009083190957568

Kenisarin, M., & Mahkamov, K. (2007). Solar energy storage using phase change materials. *Renewable and Sustainable Energy Reviews, 11*(9), 1913-1965. doi:http://dx.doi.org/10.1016/j.rser.2006.05.005

Khodadadi, J. M., & Hosseinizadeh, S. F. (2007). Nanoparticle-enhanced phase change materials (NEPCM) with great potential for improved thermal energy storage. *International Communications in Heat and Mass Transfer, 34*(5), 534-543. doi:http://dx.doi.org/10.1016/j.icheatmasstransfer.2007.02.005

Kim, S., & Drzal, L. T. (2009). High latent heat storage and high thermal conductive phase change materials using exfoliated graphite nanoplatelets. *Solar Energy Materials and Solar Cells, 93*(1), 136-142. doi:http://dx.doi.org/10.1016/j.solmat.2008.09.010

Lane, G. A. (1980). Low temperature heat storage with phase change materials. *International Journal of Ambient Energy, 1*(3), 155-168. doi:10.1080/01430750.1980.9675731

Lane, G. A. (1983). *Solar heat storage: Latent heat materials*.

Liu, M., Saman, W., & Bruno, F. (2012). Review on storage materials and thermal performance enhancement techniques for high temperature phase change thermal storage systems. *Renewable and Sustainable Energy Reviews, 16*(4), 2118-2132. doi:http://dx.doi.org/10.1016/j.rser.2012.01.020

Mehling, H., & Cabeza, L. (2008). Basic thermodynamics of thermal energy storage *Heat and cold storage with PCM* (pp. 1-10): Springer Berlin Heidelberg.

Mehling, H., & Cabeza, L. F. (2007). Phase change materials and their basic properties *Thermal energy storage for sustainable energy consumption* (pp. 257-277): Springer.

Mehling, H., Cabeza, L. F., & Yamaha, M. (2007). Phase change materials: application fundamentals *Thermal Energy Storage for Sustainable Energy Consumption* (pp. 279-313): Springer.

Mehling, H., Hiebler, S., & Ziegler, F. (2000). Latent heat storage using a PCM-graphite composite material.

Mesalhy, O., Lafdi, K., Elgafy, A., & Bowman, K. (2005). Numerical study for enhancing the thermal conductivity of phase change material (PCM) storage using high thermal conductivity porous matrix. *Energy Conversion and Management, 46*(6), 847-867. doi:http://dx.doi.org/10.1016/j.enconman.2004.06.010

Mettawee, E.-B. S., & Assassa, G. M. R. (2007). Thermal conductivity enhancement in a latent heat storage system. *Solar Energy, 81*(7), 839-845. doi:http://dx.doi.org/10.1016/j.solener.2006.11.009

Nakaso, K., Teshima, H., Yoshimura, A., Nogami, S., Hamada, Y., & Fukai, J. (2008). Extension of heat transfer area using carbon fiber cloths in latent heat thermal energy storage tanks. *Chemical Engineering and Processing: Process Intensification, 47*(5), 879-885. doi:http://dx.doi.org/10.1016/j.cep.2007.02.001

Nikolić, R., Marinović-Cincović, M., Gadžurić, S., & Zsigrai, I. J. (2003). New materials for solar thermal storage—solid/liquid transitions in fatty acid esters. *Solar Energy Materials and Solar Cells, 79*(3), 285-292. doi:http://dx.doi.org/10.1016/S0927-0248(02)00412-9

Pettit, F. Molten salts. *Corrosion Test Standards, ASTM, 380*.

Pielichowska, K., & Pielichowski, K. (2014). Phase change materials for thermal energy storage. *Progress in Materials Science, 65*(0), 67-123. doi:10.1016/j.pmatsci.2014.03.005

Pielichowski, K., & Flejtuch, K. (2003a). Binary blends of polyethers with fatty acids: A thermal characterization of the phase transitions. *Journal of Applied Polymer Science, 90*(3), 861-870. doi:10.1002/app.12775

Pielichowski, K., & Flejtuch, K. (2003b). Differential Scanning Calorimetry Study of Blends of Poly(ethylene glycol) with Selected Fatty Acids. *Macromolecular Materials and Engineering, 288*(3), 259-264. doi:10.1002/mame.200390022

Pillai, K. K., & Brinkworth, B. J. (1976). The storage of low grade thermal energy using phase change materials. *Applied Energy, 2*(3), 205-216. doi:http://dx.doi.org/10.1016/0306-2619(76)90025-8

Pincemin, S., Olives, R., Py, X., & Christ, M. (2008). Highly conductive composites made of phase change materials and graphite for thermal storage. *Solar Energy Materials and Solar Cells, 92*(6), 603-613. doi:http://dx.doi.org/10.1016/j.solmat.2007.11.010

Pincemin, S., Py, X., Olives, R., Christ, M., & Oettinger, O. (2008). Elaboration of conductive thermal storage composites made of phase change materials and graphite for solar plant. *Journal of solar energy engineering, 130*(1), 011005.

Porisini, F. C. (1988). Salt hydrates used for latent heat storage: Corrosion of metals and reliability of thermal performance. *Solar Energy, 41*(2), 193-197. doi:http://dx.doi.org/10.1016/0038-092X(88)90136-3

Rathod, M. K., & Banerjee, J. (2013). Thermal stability of phase change materials used in latent heat energy storage systems: A review. *Renewable and Sustainable Energy Reviews, 18*(0), 246-258. doi:http://dx.doi.org/10.1016/j.rser.2012.10.022

Roxas-Dimaano, M. N., & Watanabe, T. (2002). The capric and lauric acid mixture with chemical additives as latent heat storage materials for cooling application. *Energy, 27*(9), 869-888. doi:http://dx.doi.org/10.1016/S0360-5442(02)00024-5

Rozanna, D., Chuah, T. G., Salmiah, A., Choong, T. S. Y., & Sa'ari, M. (2005). Fatty Acids as Phase Change Materials (PCMs) for Thermal Energy Storage: A Review. *International Journal of Green Energy, 1*(4), 495-513. doi:10.1081/ge-200038722

Sarı, A., & Karaipekli, A. (2007). Thermal conductivity and latent heat thermal energy storage characteristics of paraffin/expanded graphite composite as phase change material. *Applied Thermal Engineering, 27*(8–9), 1271-1277. doi:http://dx.doi.org/10.1016/j.applthermaleng.2006.11.004

Sari, A., & Kaygusuz, K. (2001). Thermal energy storage system using stearic acid as a phase change material. *Solar Energy, 71*(6), 365-376. doi:http://dx.doi.org/10.1016/S0038-092X(01)00075-5

Sari, A., & Kaygusuz, K. (2002a). Thermal performance of a eutectic mixture of lauric and stearic acids as PCM encapsulated in the annulus of two concentric pipes. *Solar Energy, 72*(6), 493-504. doi:http://dx.doi.org/10.1016/S0038-092X(02)00026-9

Sari, A., & Kaygusuz, K. (2002b). Thermal performance of palmitic acid as a phase change energy storage material. *Energy Conversion and Management, 43*(6), 863-876. doi:http://dx.doi.org/10.1016/S0196-8904(01)00071-1

Sarı, A., & Kaygusuz, K. (2001). Thermal performance of myristic acid as a phase change material for energy storage application. *Renewable Energy, 24*(2), 303-317. doi:http://dx.doi.org/10.1016/S0960-1481(00)00167-1

Sarı, A., & Kaygusuz, K. (2002). Thermal and heat transfer characteristics in a latent heat storage system using lauric acid. *Energy Conversion and Management, 43*(18), 2493-2507. doi:http://dx.doi.org/10.1016/S0196-8904(01)00187-X

Sarier, N., & Onder, E. (2012). Organic phase change materials and their textile applications: An overview. *Thermochimica Acta, 540*(0), 7-60. doi:http://dx.doi.org/10.1016/j.tca.2012.04.013

Seeniraj, R., Velraj, R., & Narasimhan, N. L. (2002). Heat transfer enhancement study of a LHTS unit containing dispersed high conductivity particles. *Journal of solar energy engineering, 124*(3), 243-249.

Sharma, A., Sharma, S. D., & Buddhi, D. (2002). Accelerated thermal cycle test of acetamide, stearic acid and paraffin wax for solar thermal latent heat storage applications. *Energy Conversion and Management, 43*(14), 1923-1930. doi:10.1016/s0196-8904(01)00131-5

Sharma, A., Tyagi, V. V., Chen, C. R., & Buddhi, D. (2009). Review on thermal energy storage with phase change materials and applications. *Renewable and Sustainable Energy Reviews, 13*(2), 318-345. doi:http://dx.doi.org/10.1016/j.rser.2007.10.005

Sharma, S. D., Buddhi, D., & Sawhney, R. L. (1999). Accelerated thermal cycle test of latent heat-storage materials. *Solar Energy, 66*(6), 483-490. doi:http://dx.doi.org/10.1016/S0038-092X(99)00045-6

Sharma, S. D., & Sagara, K. (2005). Latent Heat Storage Materials and Systems: A Review. *International Journal of Green Energy, 2*(1), 1-56. doi:10.1081/ge-200051299

Sun, J., & Zhang, R. (2005). Review of thermal energy storage with metal phase change materials. *Mater Rev, 19*, 99-101.

Telkes, M. (1952). Nucleation of Supersaturated Inorganic Salt Solutions. *Industrial & Engineering Chemistry, 44*(6), 1308-1310. doi:10.1021/ie50510a036

Tunçbilek, K., Sari, A., Tarhan, S., Ergüneş, G., & Kaygusuz, K. (2005). Lauric and palmitic acids eutectic mixture as latent heat storage material for low temperature heating applications. *Energy, 30*(5), 677-692. doi:http://dx.doi.org/10.1016/j.energy.2004.05.017

Tyagi, V. V., & Buddhi, D. (2007). PCM thermal storage in buildings: A state of art. *Renewable and Sustainable Energy Reviews, 11*(6), 1146-1166. doi:http://dx.doi.org/10.1016/j.rser.2005.10.002

Velraj, R., Seeniraj, R. V., Hafner, B., Faber, C., & Schwarzer, K. (1999). Heat Transfer Enhancement In a Latent Heat Storage System. *Solar Energy, 65*(3), 171-180. doi:http://dx.doi.org/10.1016/S0038-092X(98)00128-5

Zalba, B., Marı́n, J. M., Cabeza, L. F., & Mehling, H. (2003). Review on thermal energy storage with phase change: materials, heat transfer analysis and applications.

Applied Thermal Engineering, 23(3), 251-283. doi:10.1016/s1359-4311(02)00192-8

Zeng, J., Sun, L., Xu, F., Tan, Z., Zhang, Z., Zhang, J., & Zhang, T. (2007). Study of a PCM based energy storage system containing Ag nanoparticles. *Journal of Thermal Analysis and Calorimetry, 87*(2), 371-375. doi:10.1007/s10973-006-7783-z

CHAPTER 3

MATERIAL AND METHODS

This chapter describes the methods used in preparing the phase change materials (PCMs), the related analysis and characterizations, as well as the quality assurance procedures taken for the phase change materials (PCMs) prior to their application in the latent heat thermal energy storage (LHTES) system. In the experiment stage, as shown in Fig. 3.1, we have outlined four objectives to achieve high quality thermal energy storage (TES) materials or phase change materials (PCMs), namely, 1. Enhancing the thermal properties of phase change materials (PCMs); 2. Evaluation of the thermal reliability of phase change materials (PCMs); Improvement of the thermal conductivity of phase change material (PCMs); 4. Evaluation of the compatibility of the developed phase change materials (PCMs) with container materials.

Fatty acids were selected as the base for the phase change material (PCM) due to their wide range of phase transition temperatures and the ability for combining different types of fatty acids together to develop customised PCMs suitable for domestic water heating application in tropical countries. The experimental setup were designed, fabricated and validated as a suitable performance tools to measure the characteristics of the combination of fatty acids as phase change material (PCM).

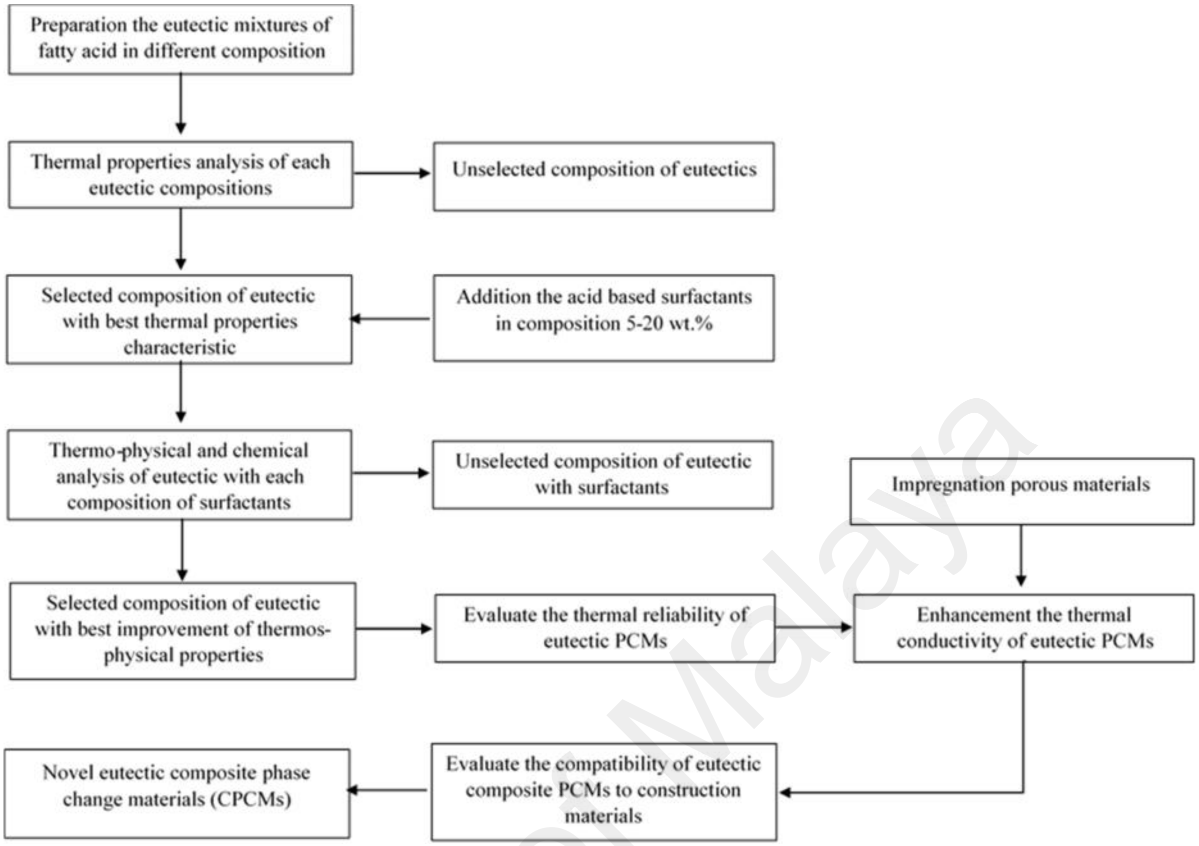


Figure 3.1. Research chart diagram

3.1 Materials

3.1.1 Eutectic phase change material (PCM)

In this study, myristic acid (MA) with 99% purity and palmitic acid (PA) with 98% purity having melting temperatures (T_m) of 54.7 ^oC and 63.08 ^oC, respectively, were chosen as the single component phase change materials (PCM). Four types of acid based surfactants chosen were sodium myristate (SM) (pure, 99%), sodium palmitate (SP) (pure, 98.5%), sodium stearate (SS) (pure, 99%), and sodium laurate (SL) (pure, 98%). The fatty acids and surfactants were both used, as received, without further purifications.

3.1.2 Porous material

The prepared binary mixture phase change materials (PCMs), Myristic acid/palmitic acid/ 5 % sodium myristate (MA/PA/5%SM), Myristic acid/palmitic acid/ 5% sodium palmitate (MA/PA/5%SP), Myristic acid/palmitic acid/ 5% sodium stearate (MA/PA/5%SS), and Myristic acid/palmitic acid/ 10% sodium laurate (MA/PA/10%SL) were selected as the base PCMs for use to prepare the eutectic composite phase change materials (CPCMs) by a impregnation of a high conductive/porous material.

A natural *damar gum,* scientufically known as s*horea javanica,* was selected as the porous material. *Shorea javanica* are obtained from *damar* trees, a tropical tree growth from the Indonesian forest. The porous material is first treated with organic solvents to remove impurities. The unpurified and purified *shorea javanica* is shown in Fig. 3.2, with the purified sample exhibiting a brighter outlook after the removal of impurities.

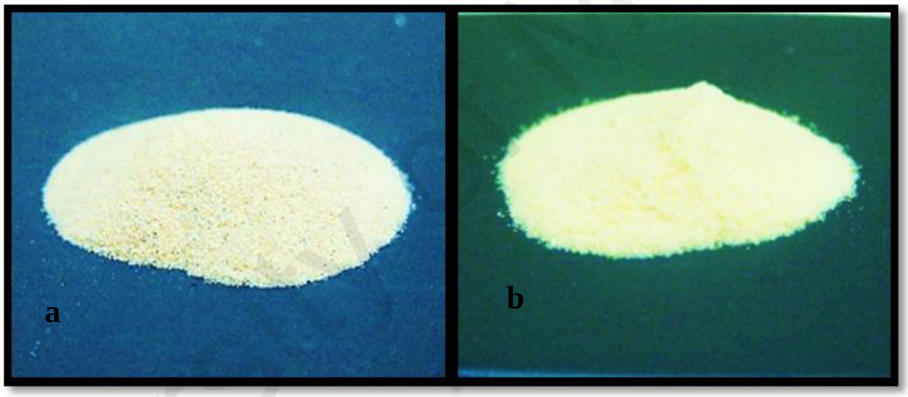


Figure 3.2. Porous materials; a). *shorea javanica* sources; b). *shorea javanica* purified.

The purification process of shorea javanica (SJ) is schematically shown in Fig. 3.3. Toluene (MW: 92.14) is used as a solvent to dissolve the *shorea javanica* (SJ) in a composition ratio of 8:1 wt.%. The solution of toluene/*sorea javanica* was stirred at 2000 rpm for 20 minutes under ambient temperature until a homogenous solution was obtained. 1% of activated charcoal (AC) was then added and stirred with the solution for 15 minutes at a temperature 45 °C.

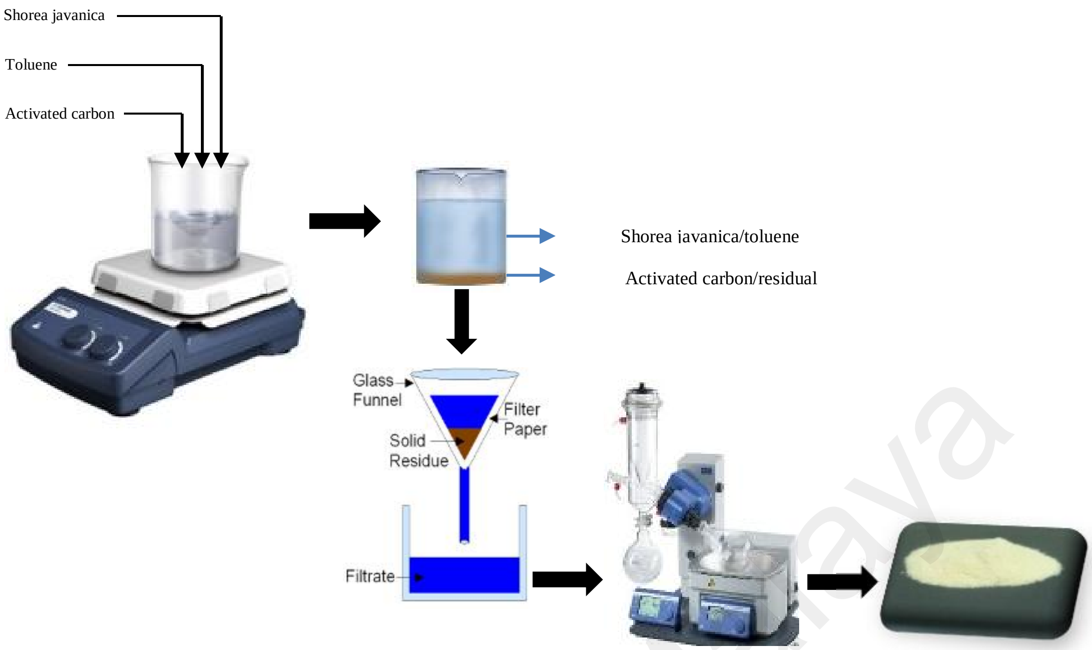


Figure 3.3. Flow of purification process of *shorea javanica*

The addition of activated charcoal (AC) was to decolorize and absorb impurities present in the as-received *sorea javanica* (SJ). The solutions was then precipitated for 2 hours to separate residual impurities from *shorea javanica* solution and filtered to remove small particle impurities from the solutions. Subsequently, the binary solution of toluene/*shorea javanica* (SJ) was placed in a rotary evaporator and maintained at 80 °C and under vacuum pressure to vaporize the toluene and obtained a purified *shorea javanica* (SJ) as the final product (Setianingsih, 1992). The purified *shorea javanica* (SJ) was then dried in an oven at 80 °C for 8 hours. To obtain a uniform particulate size, the *shore javanica* (SJ) powder was ground in a rotary ball mill and sieved using a sieved shaker separator, as shown in Appendix A.3, to obtain *shorea javanica* (SJ) powders in particle sizes of 100 µm.

Table 3.1. Construction materials and composition

Metal samples	**Composition, wt.%**
Stainless steel 304 L	Fe: 69.588, Cr: 18.7, Ni: 9.2, C: 0.03, Si: 0.65, Mn: 1.80, P: 0.032
Carbon steel C 20	Fe: 98.69, C: 0.20, Si: 0.27, Mn: 0.80, S: 0.03, P:0.01

3.1.3 Construction materials

Four prepared composite phase change materials; MA/PA/SS/SJ, MA/PA/SL/SJ, MA/PA/SM/SJ, and MA/PA/SP/SJ eutectic mixtures were chosen for the evaluation on the compatibility with construction materials. Two types of construction materials were chosen, their compositions listed in Table 3.1, based on their typical usage as container materials in solar water heating applications.

Polished metal samples having dimensions of 15 mm length, 10 mm width, and 5 mm thickness were prepared as specimens for the compatibility tests.

3.2 Methods and experimental setup

3.2.1 Preparation and thermal properties Eutectic PCMs

The eutectic mixtures of myristic acid/palmitic acid (MA/PA) was formulated by blending its single components in mass fraction composition ratio of 0 to 100 wt.% in intervals of 10%. 10 grams of individual components of MA and PA were blended in a jacketed flask reactor in contact with heat transfer fluid (HTF) at a temperature of 80 °C, as shown in Fig 3.4. This preparation method was used by Karaipekli et al. (2009) using a hot plate for heating. A modification to the set-up was made by spreading the heat fluid evenly across the surface of the reactor for homogeneous distribution of the heat to the eutectic PCM. The mixture was stirred for 30 minutes and subsequently cooled to room temperature.

The addition of acid-based surfactants in increasing percentages of 5 wt.%, 10 wt.%, 15 wt.% and 20 wt.% is expected to improve the thermal characteristics of the myristic acid/palmitic acid (MA/PA) eutectic mixture. The composition was prepared using a similar set-up as previously used to prepare the binary mixture of myristic acid/palmitic acid (MA/PA), with the stirring time increased from 30 minutes to 1 hour (Matsui et al., 2007).

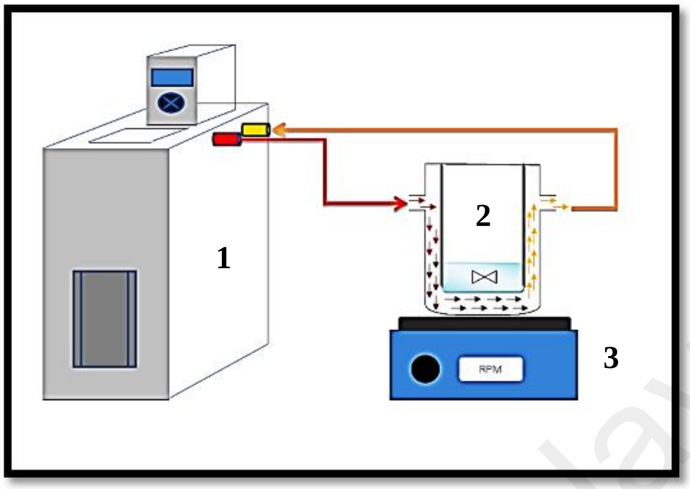


Figure 3.4. Preparation process of eutectic mixtures myristic acid/palmitic acid (MA/PA); 1). Circulated bath, 2). Glass reactor, 3). Stirrer

3.2.1.1 Thermal properties analysis

A Differential Scanning Calorimetric (DSC) thermal analyser (Metler Toledo, DSC1 Star^{e} system), as shown in Appendix A.4, was used to determine the phase transition temperatures, T_f, T_s, and latent heat capacities, ΔH_f, of the binary mixtures of myristic acid/palmitic acid (MA/PA) and also the compositions of myristic acid/palmitic acid mixtures with the additions of surfactants. The measurements were performed under heating and cooling rates of 5 °C/min and Nitrogen (N_2) gas flow. Three repeated measurements were taken to ensure accuracy of the results. The standard deviation of the liquid/solid phase change temperature and latent heat of MA/PA eutectic mixture obtained were 0.064 °C and 2.7 Jg^{-1}, respectively.

3.2.1.2 Thermal conductivity analysis

A hot wire method using a KD2Pro thermal conductivity analyzer (Decagon, USA) was used to determine the thermal conductivities of the pure mixtures of MA/PA and MA/PA with surfactants. A single needle (TR-1) sensor, as shown in Appendix A.5.a and A.5.b, with a 2.4 mm diameter and 100 mm length was used as the contacting probe with the materials.

3.2.2 Thermal reliability of eutectic phase change materials (PCMs)

The thermal reliability cycling test set-up was designed to evaluate the thermal properties, chemical and physical characteristic stabilities of prepared binary phase change materials (PCMs) after the PCM has undergone a large numbers of thermal cyclic process.

3.2.2.1 Thermal cycling system design

a. System setup

Fig. 3.5 shows the system setup for the continuous heating/cooling cycles. An integrated controller and data acquisition system (DAQ) was assembled, consisting of a thermocouple input module (NI 9211) and an 8 channel digital output module (NI 9472) installed in a USB CompactDAQ 9174 (cDAQ) chassis. The thermocouple module would record the temperature data from the 3 thermocouples installed at various locations, as described in Table 3.2. The digital output module would trigger the 6 units of 24V solenoid valves to control the water flow. To ensure minimal loss of heat, the length of the piping assembly was kept below 10 meters and 1/2" diameter heat resistant pipes were used. The overall assembly consisted of Boiling tank (Hot water Supply), Cooling tank (Cold Water Supply), Glass Vessel and Fluids Chamber connected together with the valves and piping network, as shown in Fig. 3.6.

Table 3.2. Thermocouples position

Thermocouples	**Location**
Thermocouple 1	Glass vessel A
Thermocouple 2	Glass vessel B
Thermocouple 3	Fluid chamber

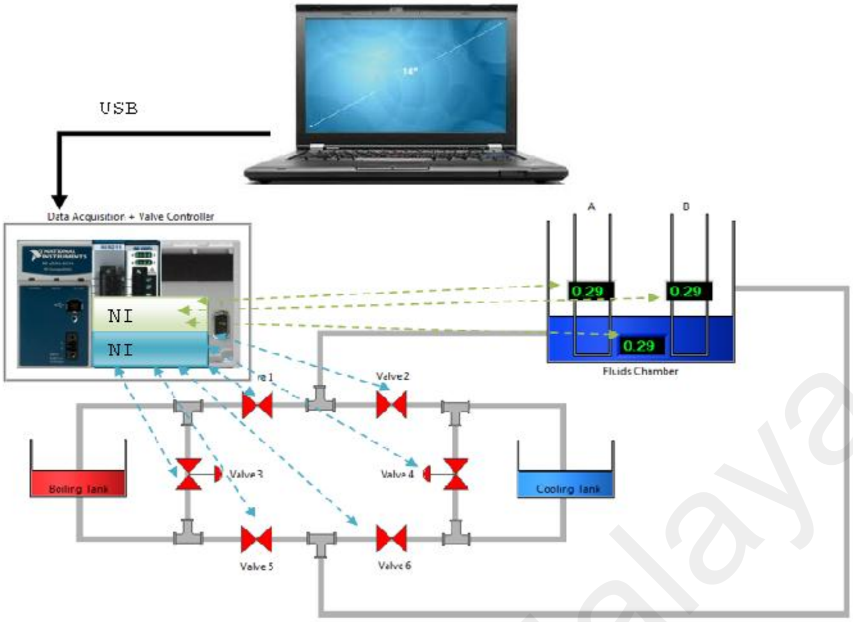


Figure 3.5. compactDAQ setup for continuous heating/cooling cycles processes

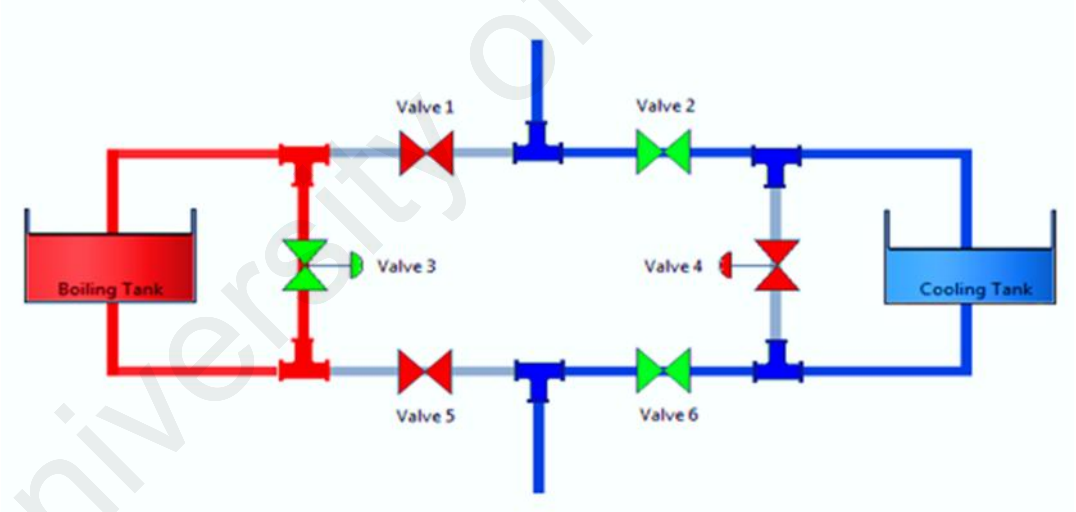


Figure 3.6. Solenoid valve type and configuration

b. Hardware

The hardware used in setting up the thermal cycling test is listed in Table 3.3.

Table 3.3. Hardware list for thermal cycling test setup

No.	Items	Unit
1.	Personal computer (PC)	1
2.	CompactDAQ Controller	1
3.	Thermocouple Input Module	1
4.	Sourcing Digital Output Module	1
5.	Thermocouple J-Type with Cable	3

Continue, Table 3.3

6.	½” 10 meter with T-junction pipe	1
7.	Pilot-Operated Steam Solenoid Valve	6
8.	Fluid circulation bath	2
9.	Fluid chamber	1
10.	Glass sample tubes	2

3.2.2.2 Thermal cycling test set-up

Previous studies have evaluated thermal stabilities of PCMs by cycling tests on a set-up consisting of an electronic hot plate with a temperature controller, where the samples of PCM were placed in a closed stainless steel container (Sharma et al., 2002; Shilei et al., 2006; Silakhori et al., 2013). Several methods have been used in conducting the thermal cycling test of PCMs that have utilised a thermostatic chamber with temperature controllers (Dimaano & D. Escoto, 1998; Karaipekli et al., 2008; Sari, 2003; Sari, 2006; Sari et al., 2008; Sharma et al., 2001). Improvements to the thermal cycling test methods were made by connecting the thermocouples to a data logger or data acquisition system to observe real-time changes of the PCM temperatures throughout the cycle (Matsui et al., 2007; Shukla et al., 2008). For the current work, a significant modification on the thermal cycling test set-up was made by integrating a valve control system, as shown in Fig. 3.7, to ensure the continuity for large numbers of heating/cooling cycles.

The thermal cycling test set-up consisted of a hot water supply and cool cold water supply which circulate the heat transfer fluid (HTF) to the thermostatic chamber for contact with the sample capsules. The binary mixture of phase change materials (PCMs) were placed in two cylindrical capsules, made of Pyrex glass with a lid. These sample capsules were then placed in the thermostatic chamber and thermocouples (J-type) were connected for temperature readings of the eutectics PCM in the capsules.

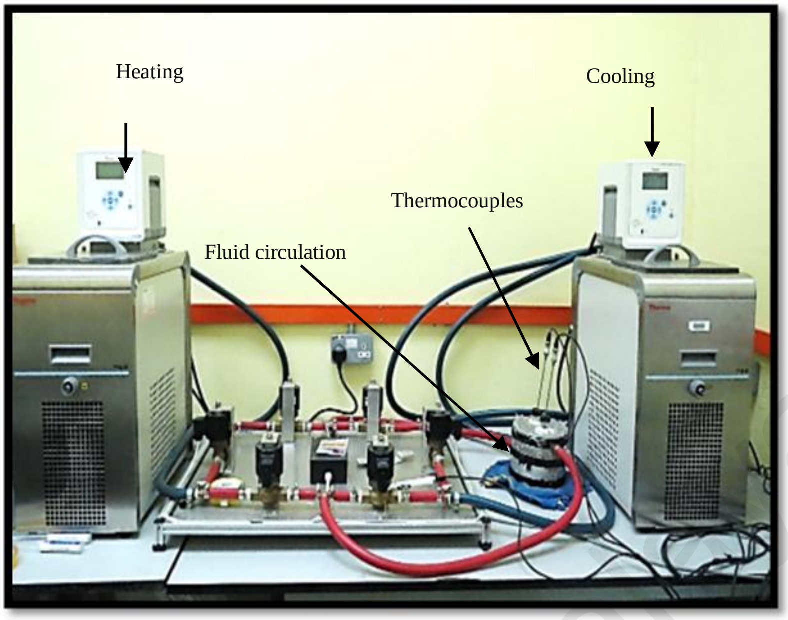


Figure 3.7. Thermal cycling test setup

A compactDAQ 9174 (cDAQ) (National Instrument) unit, shown in Fig. 3.5, was used as the data acquisition system to record the temperature data and also as the auto valve control during the thermal cycling tests. 3 J-type thermocouples were connected to a 9211 module (National Instrument) for temperature recording while 6 units of 24V solenoid valves connected to a 9472 module (National Instrument) with 8 channels digital output were used to control the water flow. The recorded data are displayed and recorded in a personal computer connected to the system.

The heating/cooling cycle process involves the absorption and release of heat by the eutectic phase change materials (PCMs) from the heat and cool heat transfer fluid (HTF). The temperature of the HTF in heat absorbing process was set at approximately 70 °C, which is above of melting temperature of eutectic phase change materials PCMs, and in the releasing heat process, the HTF temperature was set at 30 °C, which is below the solidifying temperature of the eutectic PCMs.

The thermal cycling test were performed for a total of 1500 cycles for the myristic acid/palmitic acid (MA/PA) and myristic acid/palmitic acid/sodium stearate

(MA/PA/SS) mixtures, 1000 cycles for myristic acid/palmitic acid/sodium laurate (MA/PA/SL), and 3600 cycles for myristic acid/palmitic acid/sodium myristate (MA/PA/SM) and palmitic acid/myristic acid/sodium palmitate (MA/PA/SP) eutectic mixtures. Every thermal cycles approximately required 35 minute to complete the thermal charging and discharging processes.

3.2.2.3 Stability of thermal properties analysis

The thermal properties of MA/PA and MA/PA/SS eutectic mixtures at 200, 500, 1000 and 1500 thermal cycles, and MA/PA/SL eutectic mixture at 300, 700, and 1000 thermal cycles were evaluated using a Differential Scanning Calorimetric (DSC, Mettler Toledo, DSC1 Star^e system). 6-8 mg from each eutectic PCM were placed in a sealed aluminum crucible pan and analyzed under heating and cooling at 5 °C/min. The melting temperature, T_m, was obtained from the onset during heating while the solidification temperature, T_f, was obtained from the onset during cooling and the latent heat of fusion, ΔH_f was calculated accordingly based on the area under the peak of DSC curve (Dodd et al., 1987).

The mixtures tested at large number of thermal cycles were evaluated using a Differential Scanning Calorimetric (DSC, Perkin Elmer DSC 8000), shown in Appendix A.6, by placing the specimens in a sealed aluminum crucible pan and analyzed under heating and cooling rate at 5 °C/min with a flow of Nitrogen (N_2) gas and the temperature range of 0-70 °C. The apparatus was used to evaluate the melting temperatures, T_m, and latent heat of fusions, ΔH_f, for MA/PA/SM and MA/PA/SP binary mixtures subjected to 1000, 2000, 3000 and 3600 thermal cycles.

The changes of thermal properties of those fatty acid binary mixtures subjected to each thermal cycles were further validated by Fourier Transform Infrared (FT-IR) methods.

3.2.2.4 Chemical degradation analysis

A Fourier transform infrared spectroscopy apparatus (FT-IR, Bruker IFS 66/S), shown in Appendix A.7, was used to evaluate the degradation of chemical structure of MA/PA and MA/PA/SS eutectic mixtures prior to and after 1500 thermal cycles, and MA/PA/SL prior to and after 1000 thermal cycles. The eutectic PCMs were analyzed on a KBr disk with spectra in the frequency range of 4000 - 400 cm^{-1}.

The changes of chemical structure of MA/PA/SM and MA/PA/SP eutectic mixtures prior to and after 3600 thermal cycles were evaluated using another Fourier transform infrared spectroscopy apparatus (FT-IR, Bruker Tensor 27), as shown in Appendix A.8. These fatty acids binary mixture were analyzed on an ATR sample compartment with MIR spectra in the wavenumber range of 4000 – 400 cm^{-1}.

3.2.2.5 Volume change analysis

The volume changes of MA/PA, MA/PA/SS, MA/PA/SL, MA/PA/SM, and MA/PA/SP eutectic mixtures prior to and after undergoing the prolonged thermal cycles were evaluated using the phase transition method in which the eutectic PCMs are placed into similar sized tubes that are used for thermal cycling. The PCMs were heated to a constant temperature of 70 °C which is above their melting temperatures. The height of the PCMs in the tube was measured once the PCMs melted to form a homogenous liquid and also when it solidified. The volume change was obtained from the difference in the heights of PCMs between liquid and solid state (Matsui et al., 2007)

3.2.3 Eutectic composite phase change material (CPCM)

3.2.3.1 Preparation of composite phase change materials (CPCMs)

Nomura et al. (2009) and Kim and Drza (2009) have prepared composite phase change materials (CPCM) by vacuum impregnation and simple stirring method, respectively. Thus for this study, the two methods are combined to obtain an improved distribution of porous material in CPCM mixture. The preparation set-up of CPCM consisted of flask reactor, vacuum pump, stirrer bar and water bath, as shown in Fig. 3.8.

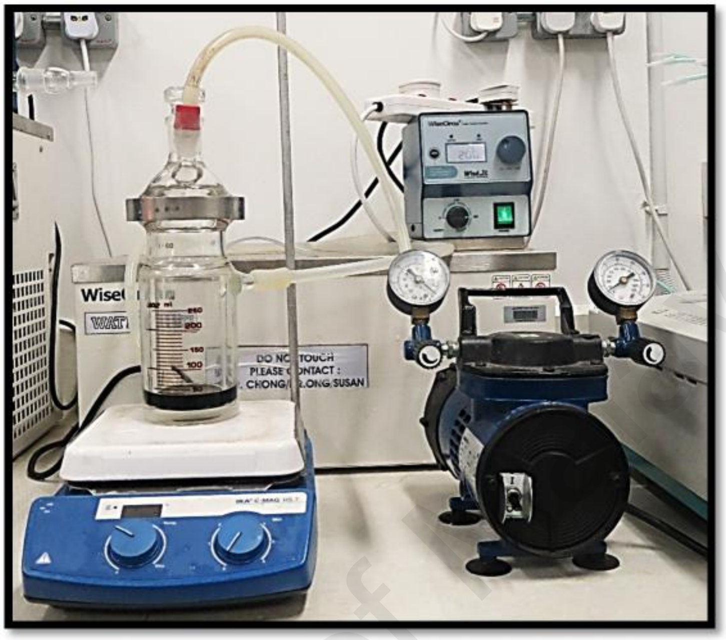


Figure 3.8. Impregnation setup of composite phase change material (CPCM)

The preparation of eutectic composite phase change materials (CPCMs), MA/PA/SM/SJ; MA/PA/SP/SJ; MA/PA/SS/SJ; and MA/PA/SL/SJ were conducted separately in a jacketed flask reactor for 2 hours with the heat source from isothermal heat transfer fluid (HTF) at a temperature of 70 ^{o}C, circulated by the water chiller and stirred by a plate stirrer. A vacuum pump was used to remove air from the mixture, which may be present in the pores of the porous materials. The mass compositions of porous s*horea savanica* (SJ) impregnated into MA/PA/SM, MA/PA/SP, MA/PA/SS, and MA/PA/SL binary mixture were 1, 2, 3, 4, and 5 wt.%, respectively.

3.2.3.2 Thermal properties and thermal conductivity analysis

The thermal properties analysis of prepared eutectic composite phase change materials (CPCMs) were conducted using Differential Scanning Calorimetric (DSC) thermal analysis (Metler Toledo, DSC1 Star^{e} system), to evaluate the melting temperature (T_m) and latent heat of fusion (ΔH_f) of CPCMs.

The thermal conductivities of these eutectic composite phase change materials (CPCMs) were measured by a thermal conductivity analyzer (Hot Disc, TPS 2500 S), shown in Appendix A.9. The measurements were performed at room temperature and using a sensor design of 5465 with radius of 3.189 mm. The samples preparation was in sandwich pellet configuration with minimum sizes diameter of 12 mm and height 3 mm, respectively.

3.2.3.3 Thermal energy storage/release performance analysis

The thermal storage/release performance analysis was conducted using the same set-up shown in Fig. 3.7 to evaluate heat transfer characteristic of prepared eutectic CPCMs during heat storage and heat extraction processes. For each prepared eutectic CPCMs, MA/PA/SS/SJ, MA/PA/SL/SJ, MA/PA/SM/SJ, and MA/PA/SP/SJ were weighed in 6 g quantities and placed in two separate glass tubes of the same diameters and thicknesses. The tubes were then placed in the circulated fluid chamber, allowing the heat transfer fluid (HTF) to be in contact with the sample tubes. The thermocouples (J-type, Omega) were placed in the center of each sample tubes to detect the temperature of heat storage and heat extraction of samples throughout the test duration. The heat transfer fluid (HTF) used was distilled water.

Cool water with a constant temperature of 25 °C was first circulated into the chamber until the temperature of the eutectic CPCMs in the sample tubes was equal to the water temperature. The circulation of the cooling water was then switched off and replaced by a circulation of hot water at 65 °C until the temperatures of the samples reach 55 °C. Once the temperature is reached, the hot water circulation was closed and the flow of cool water resumed automatically. The eutectic PCMs and eutectic CPCMs will release heat during the circulation of cool water and drops the temperature to 30 °C. The thermal performances of these eutectic PCMs and eutectic CPCMs are shown as functions of time (t) and temperature (T) during the heat storage/release between the melting and solidification points.

3.2.3.4 Chemical reaction analysis

The Fourier transform infrared spectroscopy (FT-IR, Bruker Tensor 27), was used to identify the chemical reactions which had taken place between the base PCMs and the porous materials. The analysis was performed using ATR sample compartment with MIR spectra in the wavenumber range of 4000 – 400 cm^{-1}.

3.2.3.5 Thermal stability analysis

The thermal stability of prepared eutectic CPCMs, MA/PA/SM/SJ, MA/PA/SP/SJ, MA/PA/SS/SJ, and MA/PA/SL/SJ were measured using a simultaneous thermal analyzer (STA 6000, Perkin Elmer), shown in Appendix A.10, in a temperature range of 30 ^{o}C to 300 ^{o}C with a heating rate 10 ^{o}C/sec under inert gas flow conditions. The samples was placed in a standard aluminum pan with lid.

3.2.4 Compatibility of composite phase change materials (CPCMs) with construction materials

3.2.4.1 Compatibility test setup

10 g amounts of prepared eutectic CPCMs of MA/PA/SS/SJ, MA/PA/SL/SJ, MA/PA/SM/SJ, and MA/PA/SP/SJ were placed in four cylindrical glass tubes separately. Stainless steel and carbon steel specimens were weighed to record their initial weights before testing, and are then placed inside each eutectic CPCMs tubes. The tubes are then placed in the fluid chamber, as shown Fig. 3.9.

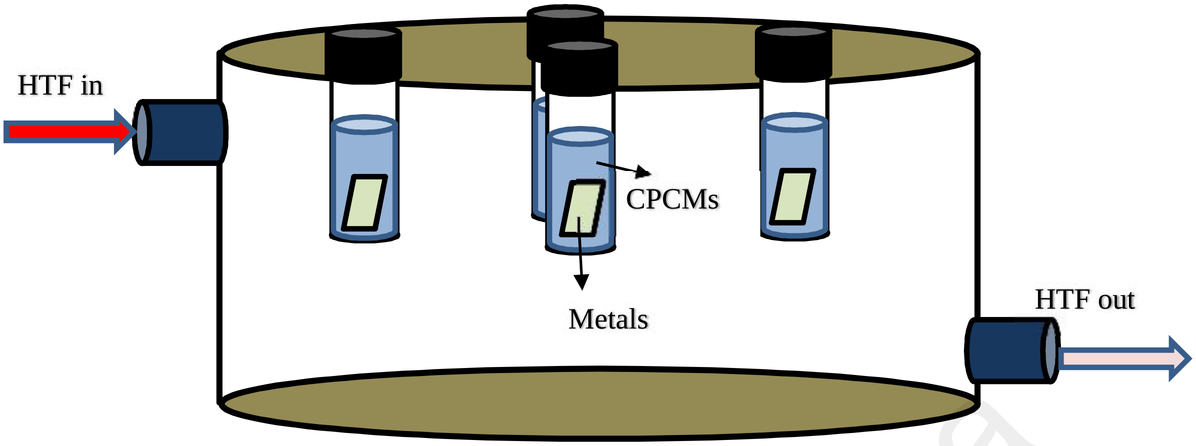


Figure 3.9. CPCMs and metals in cylindrical glass tubes for compatibility test

Two circulation water baths (hot and cool) were used for the heating and cooling cycle of the CPCMs for the compatibility tests. The heating and cooling cycles are conducted as Section 3.2.1, heating the CPCMs to 65 °C and cooling at 30 °C for a duration of 1800 thermal cycles, which is equivalent to 5 years utilization.

3.2.4.2 Corrosion behavior analysis

Once the compatibility tests of the eutectic CPCMs with metals materials were completed, the weights of the metal specimens were measured. A gravimetric analysis method (Sari & Kaygusuz, 2003) was used to evaluate the corrosion of metal samples in terms of mass loss, mg/cm^2, corrosion rate, mg/day (assumed the eutectic CPCMs have only one thermal cycles a day) at 300, 700, 1200, and 1800 thermal cycles. The weight losses and corrosion rates of metal samples were calculated using following equations:

$$\text{Weight loss, } \Delta W = \frac{(W_{int} - W_{fin})}{A} \qquad (3.2)$$

$$\text{Corrosion rate, } K_{corr} = \frac{(K \times \Delta W)}{A \times T \times D} \qquad (3.3)$$

Where, W_{int} = initial weight before contact with eutectic CPCMs, W_{fin} = final weight after thermal cycles, K = unit conversion constant, T = time of exposures, A = area in (cm^2), ΔW = weight loss (g), and D = density of metal (g/cm^3).

Reference

Dimaano, M. N. R., & D. Escoto, A. (1998). Preliminary assessment of a mixture of capric and lauric acids for low-temperature thermal energy storage. *Energy, 23*(5), 421-427. doi: http://dx.doi.org/10.1016/S0360-5442(97)00108-4

Dodd, J. W., Tonge, K. H., & Currell, B. R. (1987). *Thermal methods*.

Karaipekli, A., Sari, A., & Kaygusuz, K. (2008). Thermal Properties and Long-term Reliability of Capric Acid/Lauric Acid and Capric Acid/Myristic Acid Mixtures for Thermal Energy Storage. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 30*(13), 1248-1258. doi: 10.1080/15567030701258295

Kim, S., & Drza, L. T. (2009). High latent heat storage and high thermal conductive phase change materials using exfoliated graphite nanoplatelets. *Solar Energy Materials and Solar Cells, 93*(1), 136-142. doi: DOI 10.1016/j.solmat.2008.09.010

Matsui, T., Yoshida, M., Yamasaki, H., & Hatate, Y. (2007). Thermal Properties of Multicomponent Fatty Acids as Solid-Liquid Phase Change Materials for Cooling Applications. *Chemical Engineering Communications, 194*(1), 129-139. doi: 10.1080/00986440600715920

Sarı, A. (2003). Thermal reliability test of some fatty acids as PCMs used for solar thermal latent heat storage applications. *Energy Conversion and Management, 44*(14), 2277-2287. doi: 10.1016/s0196-8904(02)00251-0

Sarı, A. (2006). Eutectic mixtures of some fatty acids for latent heat storage: Thermal properties and thermal reliability with respect to thermal cycling. *Energy Conversion and Management, 47*(9–10), 1207-1221. doi: http://dx.doi.org/10.1016/j.enconman.2005.07.005

Sari, A., Karaipekli, A., & Kaygusuz, K. (2008). Capric Acid and Myristic Acid for Latent Heat Thermal Energy Storage. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 30*(16), 1498-1507. doi: 10.1080/15567030701436362

Sarı, A., & Kaygusuz, K. (2003). Some fatty acids used for latent heat storage: thermal stability and corrosion of metals with respect to thermal cycling. *Renewable Energy, 28*(6), 939-948. doi: http://dx.doi.org/10.1016/S0960-1481(02)00110-6

Setianingsih, N. (1992). Pemurinian Damar Shorea javanica dengan Menggunakan pelarut Organik dan Bahan Pemucat.

Sharma, A., Sharma, S. D., & Buddhi, D. (2002). Accelerated thermal cycle test of acetamide, stearic acid and paraffin wax for solar thermal latent heat storage applications. *Energy Conversion and Management, 43*(14), 1923-1930. doi: 10.1016/s0196-8904(01)00131-5

Sharma, A., Sharma, S. D., Buddhi, D., & Sawhney, R. L. (2001). Thermal cycle test of urea for latent heat storage applications. *International Journal of Energy Research, 25*(5), 465-468. doi: 10.1002/er.692

Shilei, L., Neng, Z., & Guohui, F. (2006). Eutectic mixtures of capric acid and lauric acid applied in building wallboards for heat energy storage. *Energy and Buildings, 38*(6), 708-711. doi: http://dx.doi.org/10.1016/j.enbuild.2005.10.006

Shukla, A., Buddhi, D., & Sawhney, R. L. (2008). Thermal cycling test of few selected inorganic and organic phase change materials. *Renewable Energy, 33*(12), 2606-2614. doi: http://dx.doi.org/10.1016/j.renene.2008.02.026

Silakhori, M., Naghavi, M. S., Metselaar, H. S. C., Mahlia, T. M. I., Fauzi, H., & Mehrali, M. (2013). Accelerated Thermal Cycling Test of Microencapsulated Paraffin Wax/Polyaniline Made by Simple Preparation Method for Solar Thermal Energy Storage. *Materials, 6*(5), 1608-1620.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter is divided into four sections. In the first section, the preparation of meristic acid/palmitic acid (MA/PA) eutectic mixtures as a phase change material (PCM) and the effect of adding acid-based surfactants on thermal properties of PCM is discussed. In the second section, the thermal reliability of the prepared PCMs binary mixture is subjected to a number of thermal cycling tests. Eutectic composite phase change materials (CPCMs) were subsequently developed by inclusion of a high conductive material in the composition. The thermal characteristics and performances of these eutectic CPCMs are discussed in the third section. The final section discusses the compatibility of the eutectic composite phase change materials (CPCMs) with metallic construction materials.

4.1 Enhancement the thermal properties of fatty acid binary mixture

A major objective of current research and development on thermal energy storage (TES) is to obtain a heat storage system with high heat capacity and good heat transfer mechanism. Selection of the appropriate material to store heat is one of the key consideration in the development of heat storage systems, particularly the investigation of solid-liquid PCMs which takes into account the most suitable temperature range, involves high latent heat PCMs, and narrow phase transition temperatures (Sari, 2003b; Abhat, 1983). Proper selection of heat storage material would optimize the thermal efficiency, be economically feasible, and ensure durability of latent heat thermal energy storage (LHTES) systems (Farid et al., 2004). In general, the disadvantages of phase change materials in LHTES are the low thermal conductivity, changes of thermal properties after extended usage, and undercooling (Farid et al., 2004).

Phase change materials developed for LHTES can be from organic and inorganic origins. Past studies have evaluated the thermal properties and stabilities of inorganic PCMs eutectic mixtures such as $Mg(NO_3)_2.NH_4NO_3 + 6H_2O$ (61.5/38.5, wt.%), $Mg(NO_3)_2.6H_2O + MgCl_2.6H_2O$ (58.7/41.3, wt.%), $Mg (NO_3)_2.6H_2O + Al(NO_3)_2.9H_2O$ (53/47, wt.%), urea + acetamite (37.5/63.5, wt.%), naphthalene + benzoic acid (67.1/32.9, wt.%), showing that these eutectics are potentially viable as PCM for LHTES (Abhat, 1983; Lane, 1980; Zalba et al., 2003; Zhou et al., 2012). Zalba et al. (2003) reported that inorganic PCMs are affected by problems of subcooling, phase separation, phase segregation, lack of thermal stability and corrosion in utilizations. Organic PCMs perform better than inorganic PCM due to no or low-levels of subcooling, good chemical and thermal stabilities as well as non-corrosivity in interactions with others materials.

Organic PCMs based on paraffin waxes, fatty acids and their derivatives have been extensively studied in the past. Sharma and Sagara (2005) and Hasnain (1998) have reported that paraffin has low thermal conductivity and high volume change during phase change transition. Sari and Kaygusuz (2003) have reported that the compatibility of paraffin to metal is lower as compared to fatty acids. In addition, fatty acids can be mixed to develop PCM with different melting temperatures.

In previous studies, Sari (2003a, 2003b) and Sari and Onal (2004) have prepared a myristic acid/palmitic acid (MA/PA) eutectic mixture having a melting temperature and latent heat of fusion of 42.6 ^{o}C (58/42, wt.%) and 169,7 $J.g^{-1}$, respectively. Matsui et al. (2007) improved the phase transition temperature and latent heat of fusion of Capric acid/Lauric acid (70/30, wt.%) eutectic mixture by adding acid based surfactant as additives in quantities of 5, 10, 15, and 20%, respectively.

In this study, fatty acid binary PCM mixture is prepared by blending myristic acid (MA) and palmitic acid (MA). Four kinds of acid based surfactants; sodium myristate (SM), sodium palmitate (SP), sodium stearate (SS) and sodium laurate (SL) were used as additives to enhance the thermal properties of the fatty acid eutectic mixture.

4.1.1 Thermal properties of MA/PA eutectic mixture

Fig. 4.1 shows the DSC curves of the single component myristic acid (MA), palmitic acid (PA), and myristic acid/ palmitic acid (MA/ PA) eutectic mixture. The results show that the melting temperatures (T_m) and the latent heat of fusions (ΔH_f) of single components fatty acids, MA and PA, were 54.7 ^oC, 63.08 ^oC, and 161.37 $J.g^{-1}$ and 173.69 $J.g^{-1}$, respectively. The thermal properties of the MA/PA eutectic mixtures with combinational mass ratio from 0 to 100 wt.% is tabulated in Table 4.1. It was seen that a 70:30 wt.% MA/PA eutectic mixture gave the lowest phase transition temperature, indicating the composition is the most suitable to use as a PCM candidate for LHTES application.

Table 4.1. Thermal properties of MA/PA eutectic mixture measured by DSC analysis

MA/PA (wt.%)	T_m (^oC)	T_s (^oC)	$T_m - T_s$ (^oC)	ΔH_m ($J.g^{-1}$)	ΔH_s ($J.g^{-1}$)
0.0-100.0	63.08	61.90	1.18	173.69	172.92
10.0-90.0	59.89	58.33	1.56	172.09	170.35
20.0-80.0	56.43	54.61	1.82	181.00	176.80
30.0-70.0	49.32	47.88	1.44	159.21	153.70
40.0-60.0	47.95	45.26	2.69	154.29	153.57
50.0-50.0	47.91	46.44	1.47	153.12	152.32
60.0-40.0	47.08	50.73	3.65	151.72	151.15
70.0-30.0	46.73	44.76	1.97	155.43	152.64
80.0-20.0	49.81	45.67	4.14	154.57	150.32
90.0-10.0	51.16	48.83	2.33	127.94	128.47
100.0-0.0	54.70	52.58	2.12	161.37	161.14

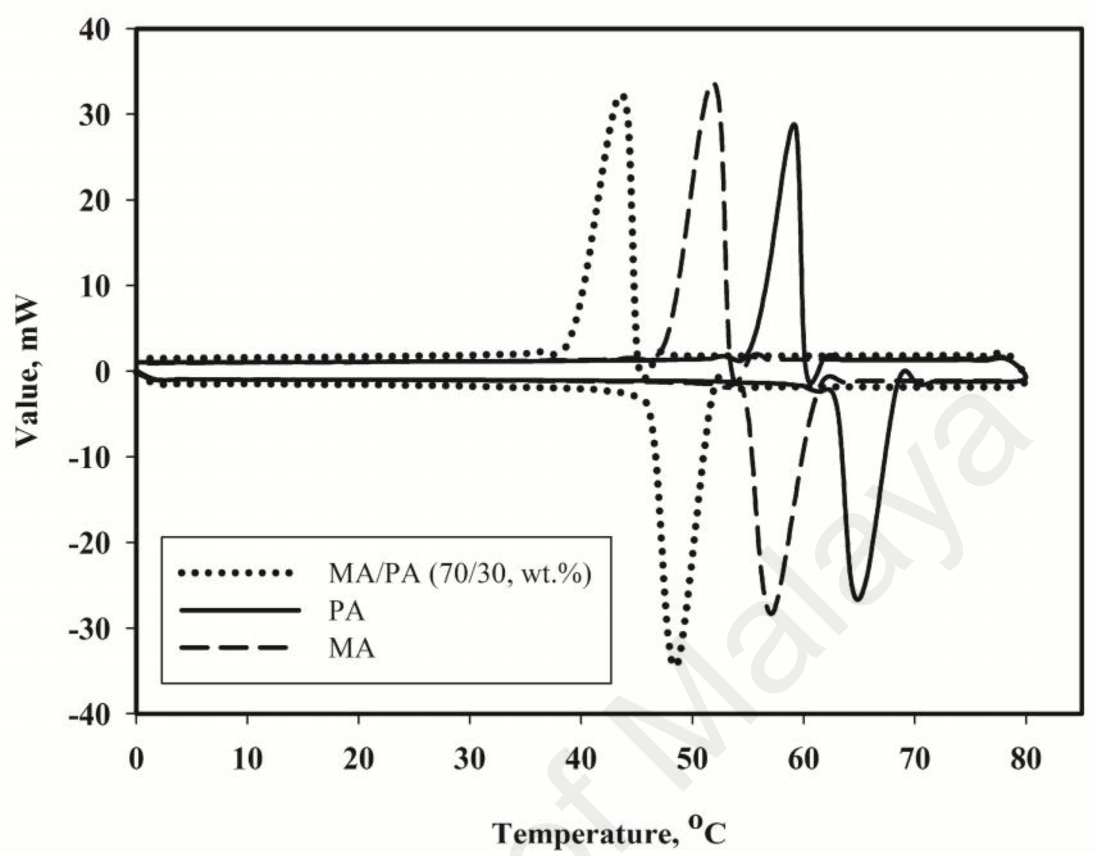


Figure 4.1. DSC Curve thermal properties of MA, PA components, and MA/PA eutectic mixture

The DSC curve shows in Fig. 4.1 clear indicated that thermal properties of MA/PA (70/30 wt.%) eutectic mixture has a lowest phase transition temperature than initial single fatty acid MA and PA. Karaipekli et al. (2008, 2009) measured the melting temperature of CA/SA eutectic mixture (83:17, wt.%), CA/LA (64:36, wt.%), and CA/MA (73:27, wt.%) and observed that the phase transition temperatures of the eutectic PCMs were lower than the melting temperatures of single component fatty acids.

Detailed evaluation has indicated that there may be occurrence of subcooling in the MA/PA eutectic mixture (70:30, wt.%). Fig 4.2 shows a gap difference between the melting temperature (44.76 ^oC) and the solidifying temperature (46.73 ^oC), indicative of the effect of subcooling. The range of phase transition temperature of the eutectic PCM was expected to be in the range of 40-45 ^oC. Surfactant additives can be added into the

MA/PA eutectic mixture to control the subcooling, depress the melting temperature and increase the latent heat amount of the MA/PA eutectic mixture.

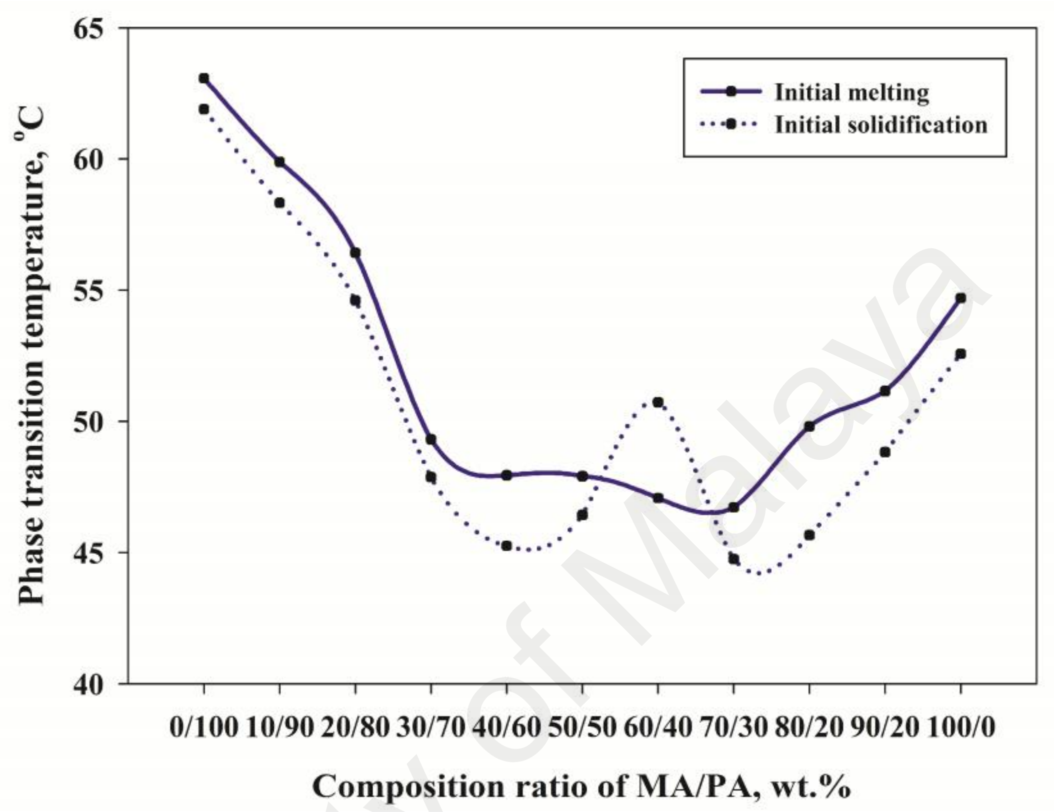


Figure 4.2. Curve of melting and solidifying temperature of MA/PA (70:30, wt.%) eutectic mixture

4.1.2 Effect of surfactant additives

Acid based surfactants such as sodium myristate (SM), sodium palmitate (SP), sodium stearate (SS) and sodium laurate (SL) were added to the MA/PA (70:30, wt. %) eutectic mixture as a control agent to minimize subcooling and depress the phase transition temperature (Matsui et al., 2007). The thermal properties of MA/PA eutectic mixtures with addition of surfactants, SM, SP, SS, and SL in mass compositions of 5, 10, 15, and 20 wt. % are listed in Table 4.2 to 4.5. The results shows that significant improvements of thermal properties of MA/PA were obtained by the additions of 5% SM, 5% SP, 5% SS and 10% SL, indicated by lowered subcooling, lowest phase transition temperature and good latent heat capacities as compared to other compositions. The phase transition temperatures of MA/PA eutectic mixtures with the additions of 5% SM, 5% SP, 5% SS and 10% SL have decreased to 41.36 ^{o}C, 41.58 ^{o}C, 41.81 ^{o}C and 42 ^{o}C, and the latent heat capacities increased to 179.12 J.g^{-1}, 184.14 J.g^{-1}, 191.85 J.g^{-1}, and 174.47 J.g^{-1}, respectively. The effects of these surfactants in improving the thermal properties of MA/PA can be seen on the DSC curve, shown in Fig. 4.3, Fig. 4.4, Fig. 4.5, and Fig. 4.6.

The eutectic PCMs compositions of MA/PA+5%SM, MA/PA+5%SP, MA/PA+5%SS, and MA/PA+10%SL were found to have the desired phase transition temperatures with high latent heat of fusions, comparable to other eutectic fatty acid mixtures, such as capric/stearic acid (Karaipekli et al., 2009), lauric/myristic acid, lauric/palmitic acid, myristic/stearic acid (Sari, 2005), myristic/palmitic acid, and palmitic/stearic acid (Sari et al., 2004).

Table 4.2. Thermal properties of MA/PA with SM

Phase change materials (PCMs)	**T_m (^{o}C)**	**ΔH_m (J.g^{-1})**	**T_s (^{o}C)**	**ΔH_s (J.g^{-1})**	**ΔT (^{o}C)**
MA/PA (7:3)+ SM0%	46.73	155.43	44.76	152.64	1.97
MA/PA (7:3)+ SM5%	41.36	179.12	41.70	176.26	0.34
MA/PA (7:3)+ SM10%	46.05	188.98	42.13	187.04	3.92
MA/PA (7:3)+ SM15%	46.54	174.55	42.49	166.10	4.05
MA/PA (7:3)+ SM20%	51.82	182.44	46.32	176.02	5.5

Table 4.3. Thermal properties of MA/PA with SP

Phase change materials (PCMs), (wt. %)	**T_m (^{o}C)**	**ΔH_m (J.g^{-1})**	**T_s (^{o}C)**	**ΔH_s (J.g^{-1})**	**ΔT (^{o}C)**
MA/PA (7:3)+ SP0%	46.73	155.43	44.76	152.64	1.97
MA/PA (7:3)+SP5%	41.58	184.14	41.98	184.06	0.4
MA/PA (7:3)+SP10%	43.51	181.28	42.88	179.57	0.63
MA/PA (7:3)+SP15%	43.61	180.08	42.12	160.67	1.49
MA/PA (7:3)+SP20%	50.36	175.92	42.21	174.23	9.36

In addition, the melting temperatures of MA/PA+5%SM, MA/PA+5%SP, MA/PA+5%SS, and MA/PA+10%SL have decreased by 5.37 ^{o}C, 5.15 ^{o}C, 4.92 ^{o}C and 4.73 ^{o}C, and the latent heat of fusions (ΔH_f) have increased by 23.69 J.g^{-1}, 28.71 J.g^{-1}, 36.42 J.g^{-1} and 19.04 J.g^{-1}, respectively. Therefore it can be concluded that the addition of surfactant additives are very effective in improving the thermal properties of MA/PA eutectic mixture.

Table 4.4. Thermal properties of MA/PA with SS

Phase change materials (PCMs), (wt. %)	**T_m (°C)**	**$\Delta H_{f,m}$ (J.g^{-1})**	**T_s (°C)**	**$\Delta H_{f,s}$ (J.g^{-1})**	**ΔT (°C)**
MA/PA (7:3)+SS0%	46.73	155.43	44.76	152.64	1.97
MA/PA (7:3)+SS5%	41.81	191.85	41.00	188.06	0.81
MA/PA (7:3)+SS10%	42.18	192.70	40.53	188.51	1.65
MA/PA (7:3)+SS15%	43.42	191.65	40.16	190.66	3.26
MA/PA (7:3)+SS20%	43.36	197.96	39.89	190.64	3.47

Table 4.5. Thermal properties of MA/PA with SS

Phase change materials (PCMs), (wt. %)	**T_m (°C)**	**ΔH_m (J.g^{-1})**	**T_s (°C)**	**ΔH_s (J.g^{-1})**	**ΔT (°C)**
MA/PA, 70/30	46.73	155.43	44.76	152.64	1.97
MA/PA, 70/30+SL5%	42.67	170.57	40.66	165.43	2.01
MA/PA, 70/30+SL10%	42.00	174.47	41.57	169.89	0.43
MA/PA, 70/30+SL15%	29.62	174.73	42.12	168.94	12.5
MA/PA, 70/30+SL20%	50.58	173.25	43.22	166.44	7.36

As mentioned by Mehling and Cabiza (2008), subcooling is the effect that a temperature significantly below the melting temperature has to be reached before the material begins to solidify and releases heat (Fig. 2.2). If this temperature is not reached, the PCM will not solidify at all and only releases sensible heat (Mehling & Cabeza, 2008).

The gap difference between the melting and solidification temperatures is due to the variations in characteristics and composition of the components in the binary mixture (Matsui et al., 2007). It was shown that the addition of 5% SM, 5% SP, 5% SS and 10% SL additives were able to decrease the temperature differences between the melting and solidification points in binary mixture to 0.34, 0.4, 0.82 and 0.43 °C, as shown in Table 4.2 to Table 4.5. This indicates that SM, SP, SS, and SL can be very effective in decreasing the subcooling of MA/PA binary mixture.

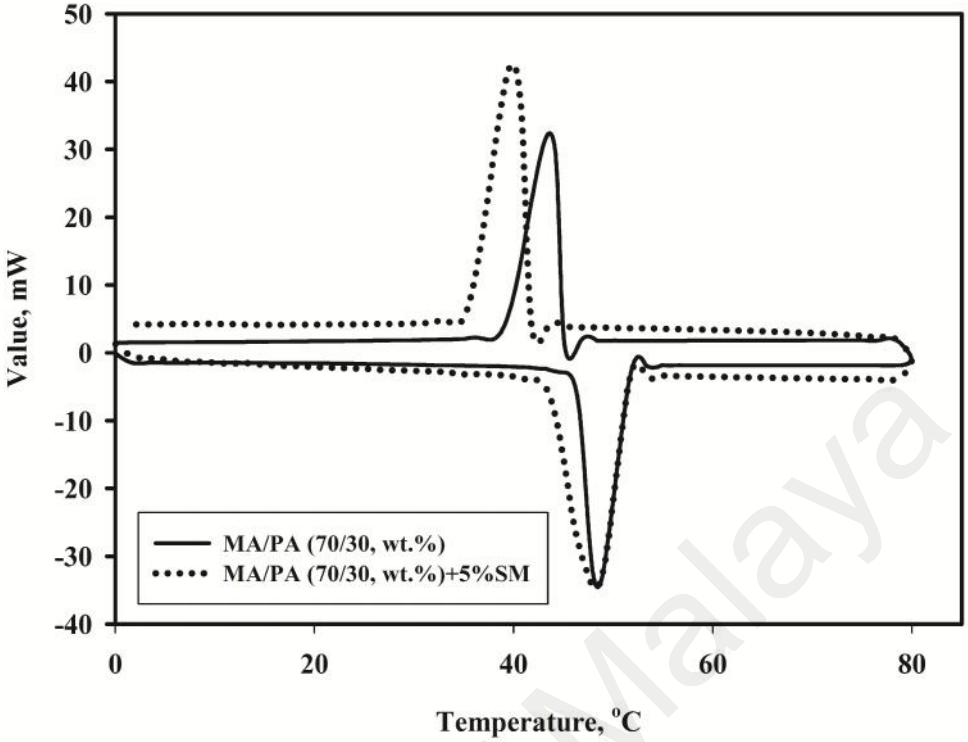


Figure 4.3. DSC curve thermal properties of MA/PA (70/30, wt.%) and MA/PA (70/30, wt.%) + 5%SM

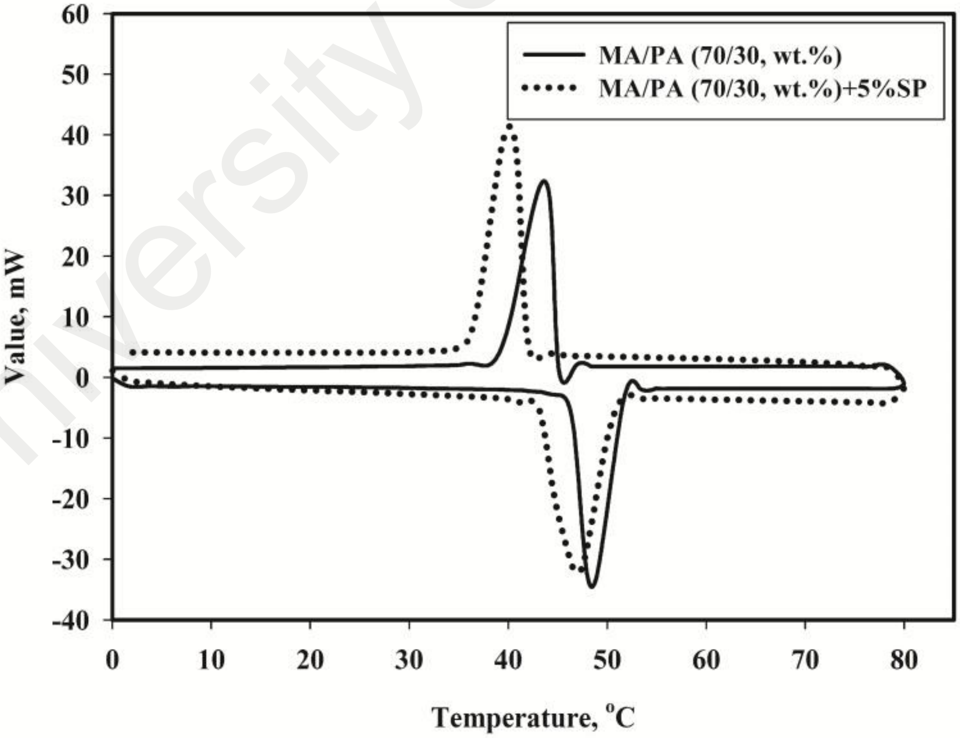


Figure 4.4. DSC curve thermal properties of MA/PA (70/30, wt.%) and MA/PA (70/30, wt.%) + 5%SP

The thermal properties of eutectic mixture of MA/PA have been studied by past researchers. Kauranen et al. (1991) obtained values of T_m=39.8 °C and ΔH_f =174.0 J.g^{-1}

for eutectic MA/PA with a composition ratio of 59.0:41.0 (wt,%). Similarly, Sari (2003) obtained values of T_m=42.6 °C and ΔH_f=169.7 J.g^{-1} for the same eutectic composition having a MA/PA ratio of 58.0:42.0 (w,%). The difference in composition ratio of MA/PA eutectics component may be caused by two factors, namely, the presence of impurities in the composition of eutectic mixture and the rate of heat flow in the DSC measurement (Bo et al., 1999).

This study has shown that the addition of 5% SM, 5% SP, 5% SS and 10% SL has improved the thermal properties of MA/PA eutectic mixture, making it suitable for the intended use as a latent heat storage material in solar space heating applications, such as building and domestic water heating.

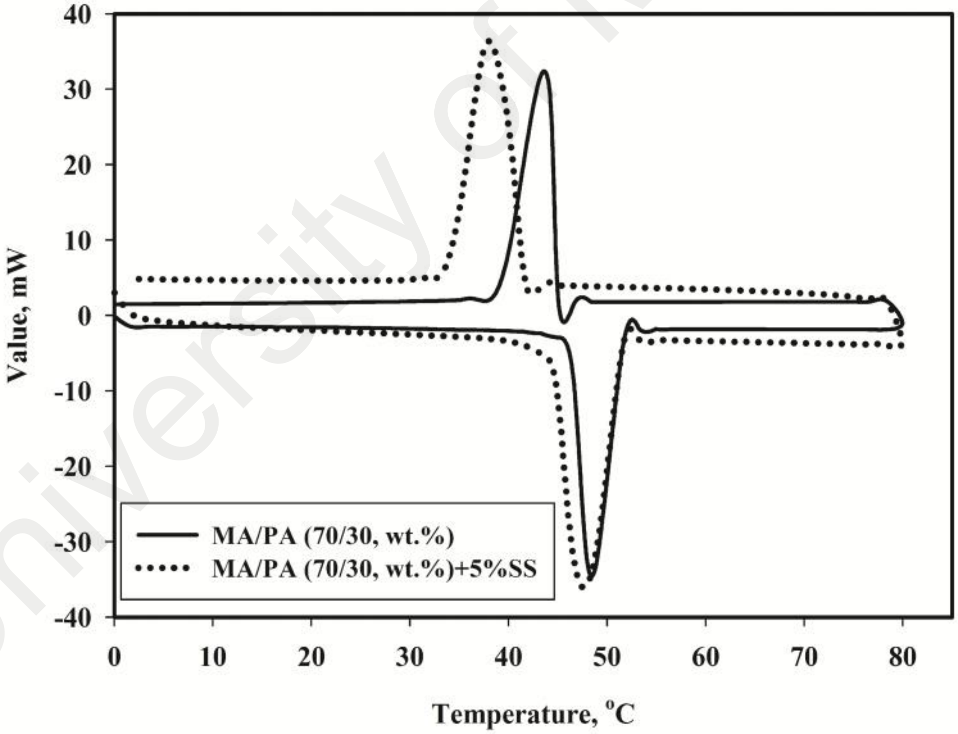


Figure 4.5. DSC curve thermal properties of MA/PA (70/30, wt.%) and MA/PA (70/30, wt.%) + 5%SS

Table 4.6 shows that the addition of 5% SM, 5% SP, 5% SS and 10% SL in MA/PA (70/30, wt.%) eutectic mixture has improved the thermal conductivity of eutectic mixture. These results were better than those found for paraffin, which has a thermal conductivity of 0.21 W.m.K^{-1} (Abhat, 1983; Sari & Karaipekli, 2007; Zhou & Zhao, 2011), and that of Naphthalene 67.1% + 32.9% benzoic acid, which has a thermal conductivity of 0.136 W·m.K^{-1} (Lane, 1980).

Table 4.6. Effect of additives in thermal conductivity of MA/PA eutectic mixture

Phase change materials (PCMs)	**Thermal conductivity (W/m.K)**	**Temperature (°C)**
MA/PA (7:3)	0.225	30.19 (solid)
MA/PA (7:3) + 5%SM	0.242	29.35 (solid)
MA/PA (7:3) + 5% SP	0.236	29.85 (solid)
MA/PA (7:3) + 5% SS	0.230	29.60 (solid)
MA/PA (7:3) + 10% SL	0.235	29.19 (solid)

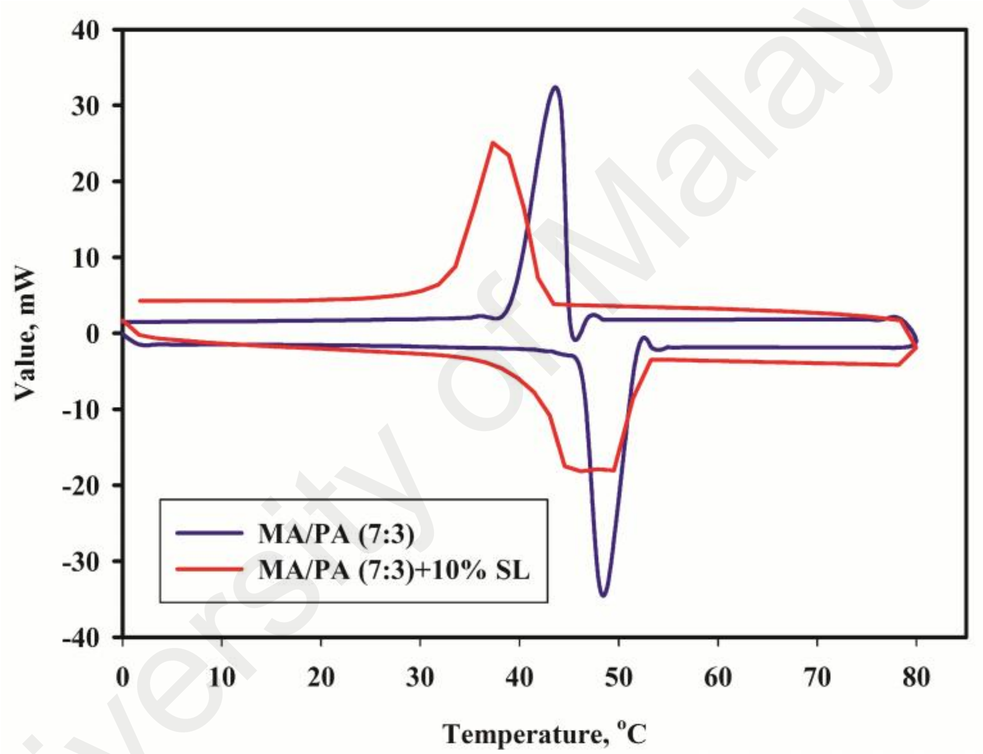


Figure 4.6. DSC curve thermal properties of MA/PA (70/30, wt.%) and MA/PA (70/30, wt.%) + 10%SL

4.2 Thermal reliability of eutectic PCMs

The ideal phase change material (PCM) for thermal energy storage (TES) application should have the following features: appropriate phase transition temperature, high latent heat capacity, low cost, ready availability, non-toxicity, non-flammability, and uniform phase change characteristics, such as no undercooling or phase separation. In addition, it should have a long life with regard to its thermal reliability over a large number of thermal cycles (Sari, 2003). The PCM in a LHTES system should possess desirable economic and thermo-physical properties to guarantee long term utilization of the system (Sari, 2005). The thermal properties reliability of a PCM should be verified using a thermal cycling test to assure long term stability before it is used in a LHTES system (Sari, 2005; Sari et al., 2004). The economic feasibility of a thermal energy storage system is depends on the life of the phase change material (PCM). There should not be major changes in the phase transition point and latent heat of fusion over time due to the melting/solidification cycles of the storage material (Sari, 2003; Sharma et al., 2002).

Sari (2003) determined the thermal reliabilities of stearic acid (SA), palmitic acid (PA), myristic acid (MA) and lauric acid (LA) subjected to 120, 560, 850 and 1200 thermal cycles and has found that the melting temperatures of the PCMs were almost constant after 120 thermal cycles, and would tend to decrease after 560 and 1200 thermal cycles. A decrease in latent heat of fusion have also occurred with the increase number of thermal cycles, although the decrease was irregular. Sharma et al. (1999) reported that the melting temperature and latent heat of SA showed no regular degradation after 20, 50, 70, 100, 150, 200, 250 and 300 thermal cycles (Sharma et al., 1999). In another work, Sari and Kaygusuz (2003) reported the reduction of the latent heat of fusion of SA, PA, MA and LA after 40 thermal cycles, 410 thermal cycles, and 910 thermal cycles. It was found that the latent heat of fusion of these PCMs decreased irregularly with increasing number of thermal cycles.

In this study, the thermo-physical stability of pure MA/PA (70/30,wt.%) and MA/PA with surfactants, MA/PA/SS, MA/PA/SL, MA/PA/SM, and MA/PA/SP eutectic mixtures were evaluated. The stability of thermal properties, degradation of chemical structure, and physical changes of each samples after a numbers of thermal cycles were also determined. In subsequent discussions, MA/PA (70/30,wt.%) will be referred to as as MA/PA, and MA/PA(70/30,wt.%)+ 5 wt.% SS, MA/PA(70/30,wt.%)+ 10 wt.% SL, MA/PA(70/30,wt.%)+ 5 wt.% SM, MA/PA(70/30,wt.%)+ 5 wt.% SP will be referred to as MA/PA/SS, MA/PA/SL, MA/PA/SM, MA/PA/SP, respectively

4.2.1 Stability of thermal properties

4.2.1.1 MA/PA and MA/PA/SS eutectic mixtures

Table 4.7 shows the phase transition temperatures (T_m, T_s) and latent heat of fusion ($\Delta H_{f,m}$, $\Delta H_{f,s}$) of MA/PA and MA/PA/SS eutectic mixtures at 0, 200, 500, 1000 and 1500 thermal cycles. It can be seen that MA/PA/SS has a lower melting temperature and greater latent heat of fusion (ΔH_f) than MA/PA.

Table 4.7. Thermal properties of MA/PA and MA/PA/SS eutectic mixtures with respect to thermal cycling number.

PCMs	**Thermal cycling numbers**	**Thermal properties**			
		T_m (^oC)	**$\Delta H_{f,m}$ (J g^{-1})**	**T_s (^oC)**	**$\Delta H_{f,s}$ (J g^{-1})**
MA/PA	0	46.73	155.43	44.76	152.64
	200	45.98	180.21	45.17	188.01
	500	47.20	160.91	46.38	165.99
	1000	46.19	191.32	45.92	199.11
	1500	45.30	164.50	45.18	161.40
MA/PA/SS	0	41.81	191.85	41.00	188.06
	200	42.06	192.53	41.88	193.54
	500	44.72	184.52	44.01	184.26
	1000	44.30	180.80	43.80	184.74
	1500	43.17	172.46	42.56	169.20

The DSC curves of MA/PA and MA/PA/SS eutectic mixtures subjected to 200, 500, 1000, and 1500 thermal cycles are shown in Fig. 4.7, Fig. 4.8, Fig. 4.9, and Fig. 4.10. It can be seen that as the number of thermal cycle increases, there are changes to the thermal properties of the eutectic PCMs. The decrease in the phase transition temperature of MA/PA eutectic mixture was irregular while the phase transition temperature of MA/PA/SS increases with the increasing number of thermal cycles.

However, the increase in the melting temperature of MA/PA/SS was still within the suitable range of 40-45 ^{o}C required for thermal energy storage application systems.

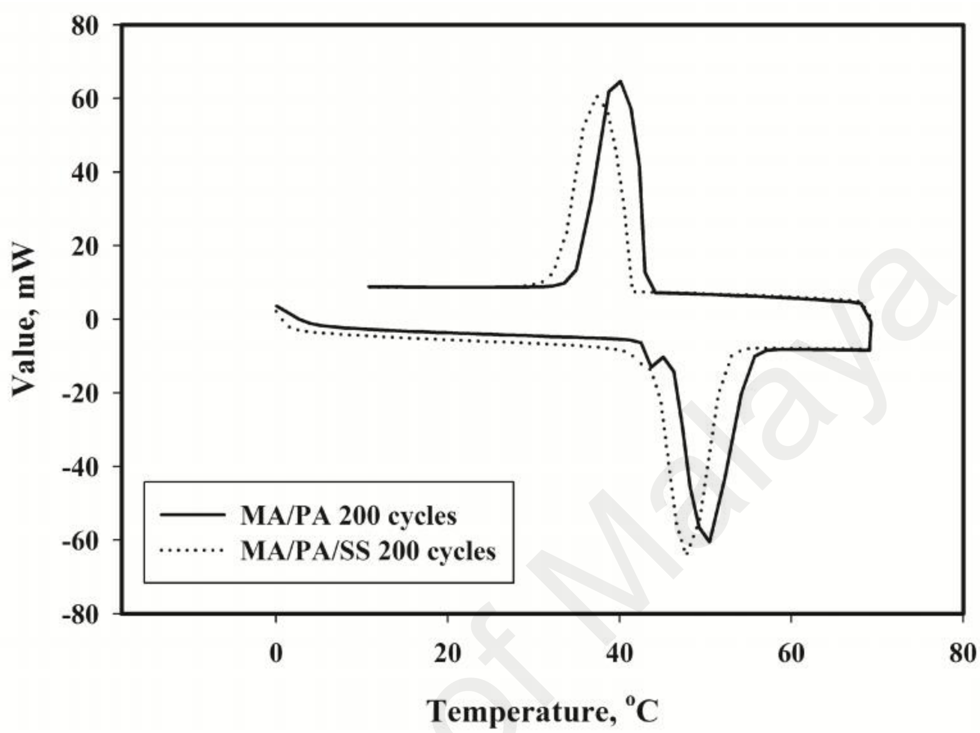


Figure 4.7. DSC curve MA/PA and MA/PA/SS eutectic mixtures at 200 thermal cycles.

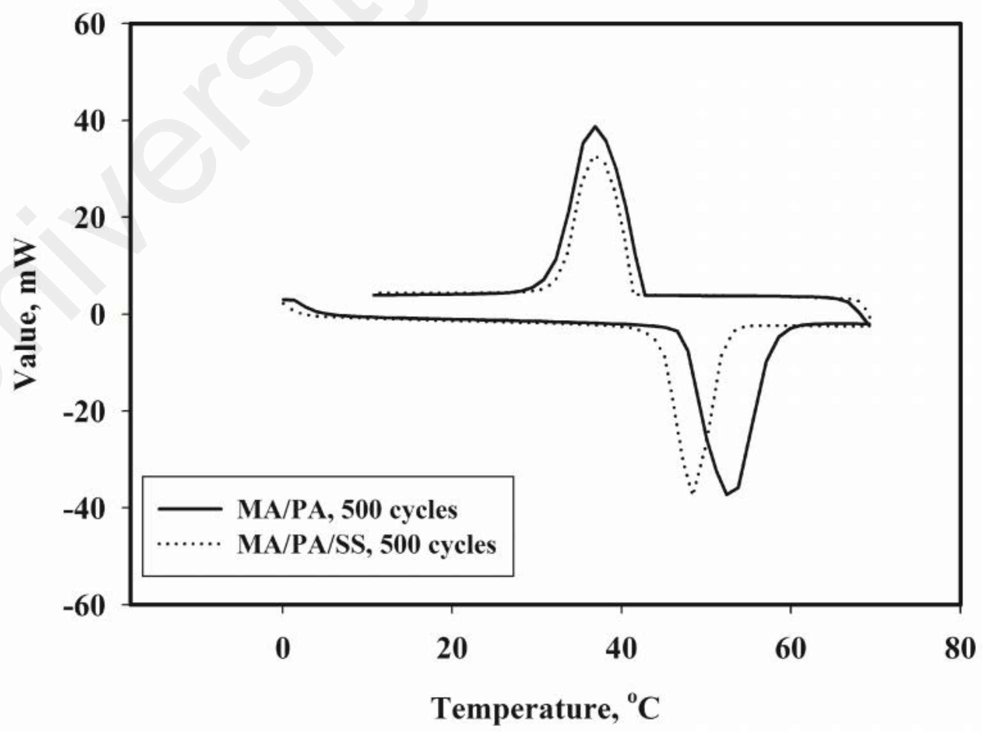


Figure 4.8. DSC curve MA/PA and MA/PA/SS eutectic mixtures at 500 thermal cycles.

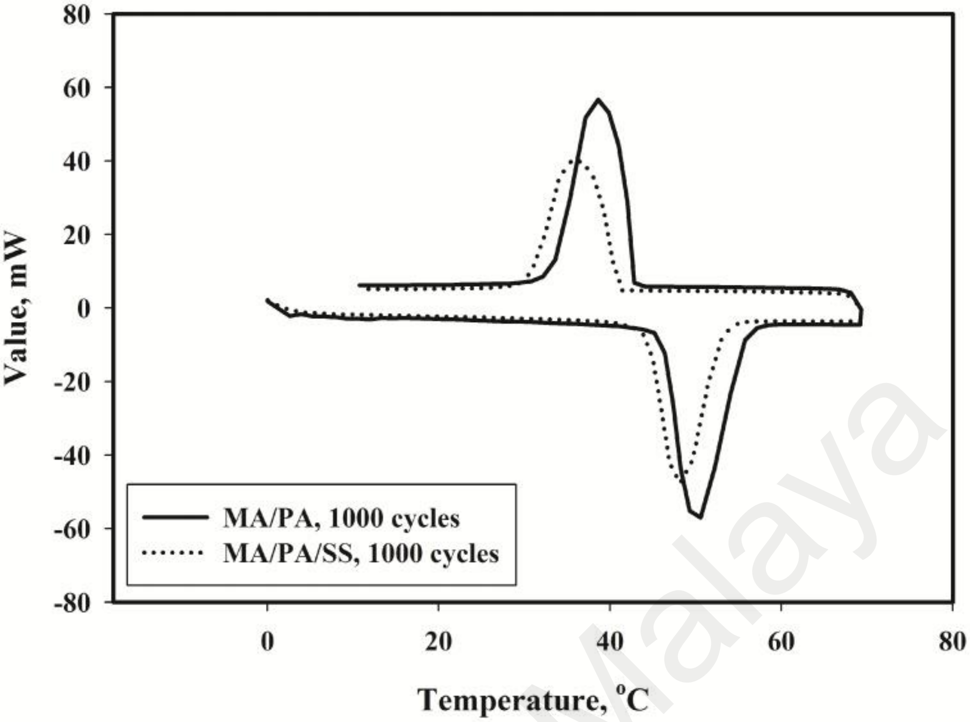


Figure 4.9. DSC curve MA/PA and MA/PA/SS eutectic mixtures at 1000 thermal cycles.

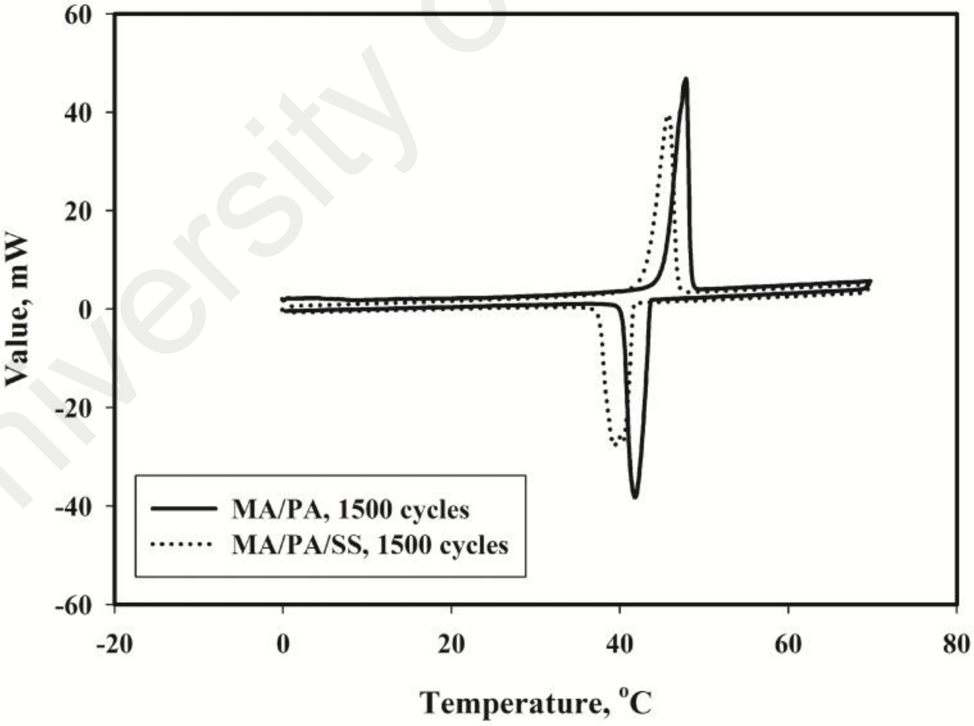


Figure 4.10. DSC curve MA/PA and MA/PA/SS eutectic mixtures at 1500 thermal cycles.

Fig. 4.11 shows the changes in the melting temperatures of MA/PA and MA/PA/SS whereas Fig. 4.12 shows the changes in latent heat of fusion of MA/PA and MA/PA/SS eutectic mixtures. Those figures are reflects the data in Table 4.7, indicating that the latent heat of fusion (ΔH_f) of MA/PA eutectic mixture was irregular after 200, 500, 1000, and 1500 cycles, whereas the ΔH_f of MA/PA/SS shows a decreasing trend.

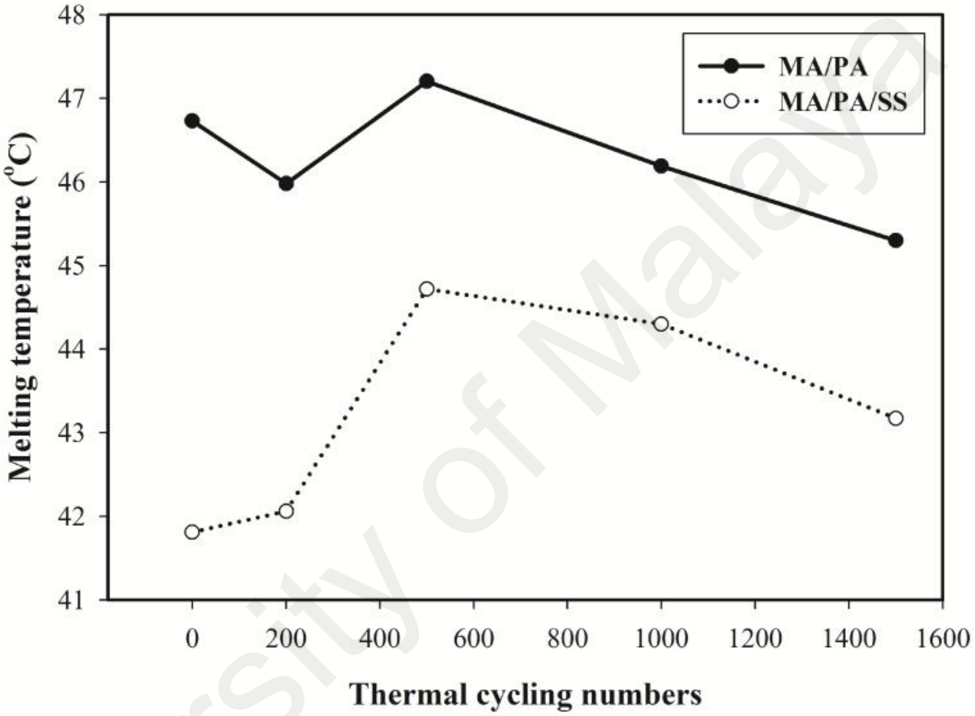


Figure 4.11. Changes on phase transition temperature of MA/PA and MA/PA/SS subjected to numbers of thermal cycles.

In other studies on thermal reliability of eutectic fatty acids as PCM, Zhang et al. (2001) reported that the thermal properties of lauric acid/palmitic acid (LA/PA) eutectic mixture were stable up to 100 cycles. Sari, et al. (2004) evaluated the thermal reliability of several fatty acid eutectic mixtures such as lauric acid/stearic acid (LA/SA), myristic acid/palmitic acid (MA/PA), and palmitic acid/stearic acid (PA/SA). Sari (2006) had also evaluated the thermal stabilities of LA/MA, LA/PA and MA/SA eutectic mixtures after 720, 1080 and 1460 thermal cycles. It was found that the thermal properties of T_m and ΔH_f for both PCM eutectic mixtures had tend to decrease with an increasing number of thermal cycles, although the amounts of decrease were irregular and minor.

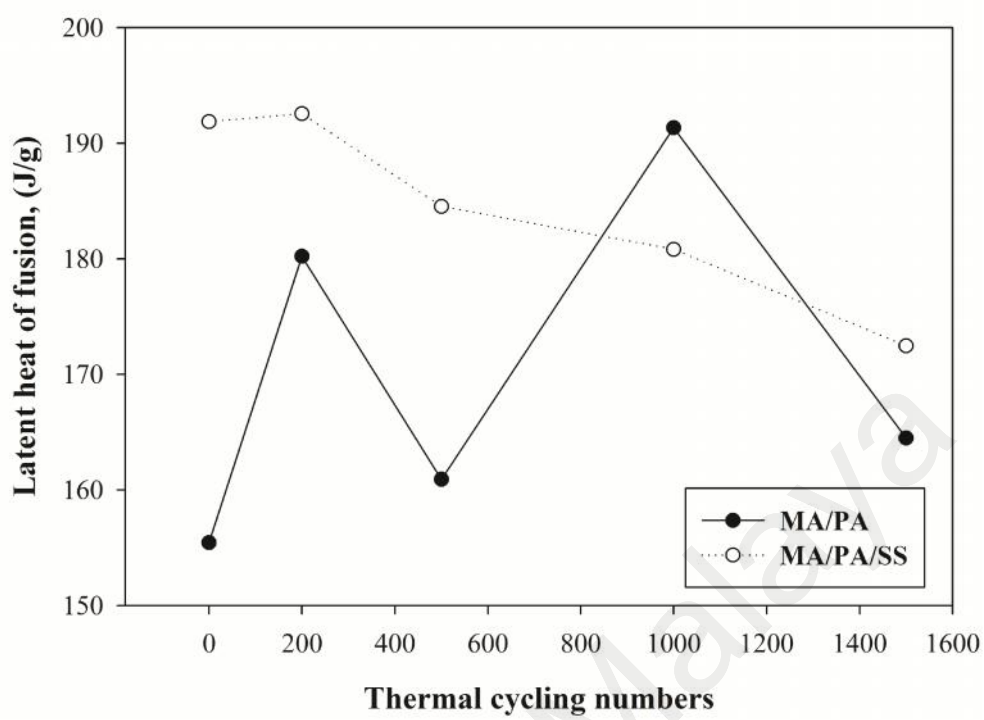


Figure 4.12. Changes on latent heat of fusion of MA/PA and MA/PA/SS subjected to numbers of thermal cycles.

Karaipekli et al. (2009) had observed the thermal stability of capric acid/stearic acid (CA/SA) subjected to 1000, 2000, 3000, 4000 and 5000 thermal cycles, and found that the melting temperature (T_m) and the latent heat of fusion (ΔH_f) of CA/SA changed irregularly during the thermal cycling test. However they concluded that the results are acceptable for PCM in LHTES applications.

Thus, the changes of thermal properties such as melting temperature (T_m) and latent heat of fusion (ΔH_f) of MA/PA and MA/PA/SS eutectic mixtures of this study are in agreement with the findings in the literature. The MA/PA and MA/PA/SS eutectic mixtures are therefore deemed acceptable for use in a thermal energy storage (TES) application system for up to at least 1500 thermal cycles, corresponding to 4 years utilization period.

4.2.1.2 MA/PA/SL eutectic mixture

The DSC curve of MA/PA/SL mixture subjected to 0, 300, 700, and 1000 thermal cycles are shown in Fig. 4.13. The melting temperature (T_m) and the latent heat of fusion are obtained from the onset point and numerical integration of under peak area each curve (Dodd, 1987).

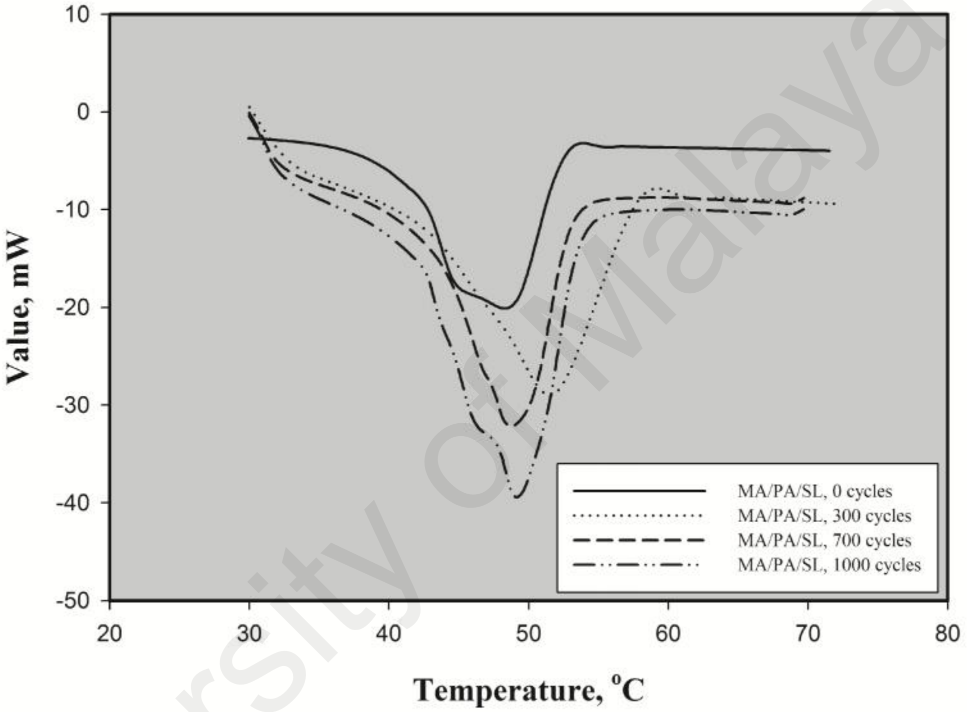


Figure 4.13. DSC curve of MA/PA/SL subjected to a different number of thermal cycles

The thermal properties of MA/PA/SL, shown in Table 4.8, indicate that the melting temperature and latent heat of fusion of MA/PA/SL changes irregularly with an increasing number of thermal cycles.

Table 4.8. Thermal properties of MA/PA/SL eutectic mixtures subjected to thermal cycling number

Eutectic PCM	Number of thermal	Melting temperature, T_m	Latent heat of fusion, ΔH_f (J. g-1)
MA/PA+ 10% SL	0	42.00	174.47
	300	46.79	176.79
	700	41.83	180.91
	1000	40.78	175.34

The melting temperature of MA/PA/SL increased from the initial value of 42.00 ^{o}C to 46.79 ^{o}C after 300 thermal cycles, then decreased to below the melting temperature of un-cycled MA/PA/SL after 700 and 1000 thermal cycles. The latent heat of fusion of MA/PA/SL showed and increasing trend after 300 and 700 thermal cycles to values of 176.79 J.g^{-1} and 180.91 J.g^{-1}, respectively. However, after 1000 thermal cycles, the latent heat of fusion of MA/PA/SL dropped to 175.34 J.g^{-1}, although it is above of latent heat of fusion of un-cycled MA/PA/SL. The changes of thermal properties of fatty acid eutectic mixtures as PCM after a large number of heating/cooling cycles could be caused by changes in the chemical structures of PCM or the increasing amount of impurities (2-3, wt.%) in the fatty acids used in preparation of the eutectic PCM.

By comparison with past studies, (Hasan & Sayigh, 1994; Sari, 2003; Sari & Kaygusuz, 2003; Sari et al., 2004; Sharma et al., 2002; Zhang et al., 2001), it can be noted that the changes in melting temperature (T_m) and latent heat of fusion (ΔH_f) of MA/PA/SL after 1000 thermal cycles are within the acceptable limits for use as PCM for LHTES applications such as solar space and solar water heating.

4.2.1.3 MA/PA/SM and MA/PA/SP eutectic mixtures

The thermal characteristic of MA/PA/SM and MA/PA/SP were also evaluated for 3600 thermal cycles, corresponding to 10 years utilization period. Table 4.9 shows the phase transition temperature (T_m, T_s) and latent heat of fusion of MA/PA/SM and MA/PA/SP binary mixtures subjected to 1000, 2000, 3000, and 3600 thermal cycles. The phase transition temperature and latent heat of fusion obtained from DSC curves are shown in Fig. 4.14 and Fig. 4.15, respectively.

Table 4.9. Thermal properties of fatty acid binary mixtures

No. of cycles	MA/PA/SM				MA/PA/SP			
	T_m (°C)	$\Delta H_{f,m}$ (J/g)	T_s (°C)	$\Delta H_{f,s}$ (J/g)	T_m (°C)	$\Delta H_{f,m}$ (J/g)	T_s (°C)	$\Delta H_{f,s}$ (J/g)
0	41.36	179.12	41.70	176.26	41.58	184.14	41.98	184.06
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	176.32

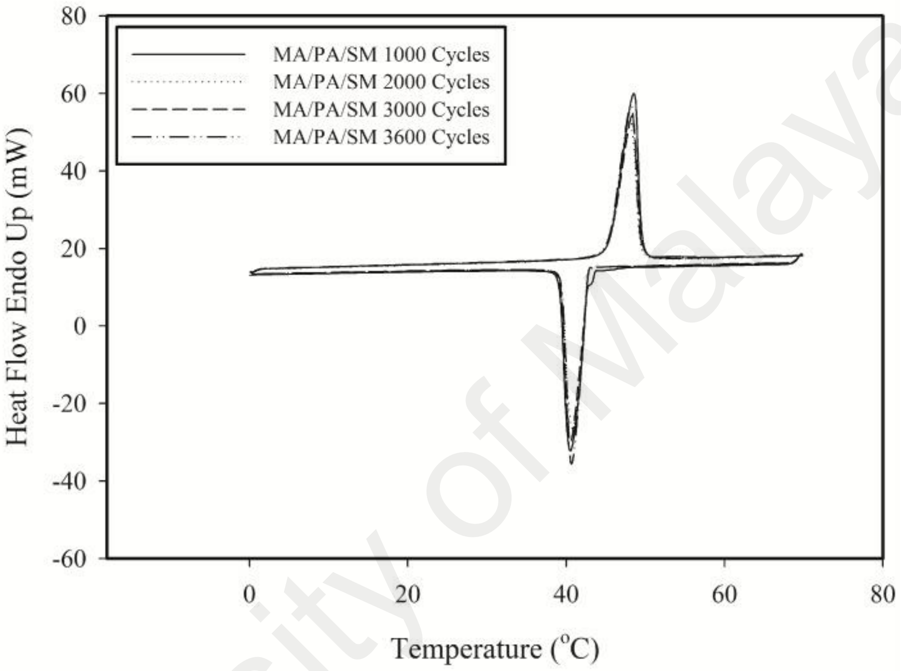


Figure 4.14. DSC curve subjected to 1000, 2000, 3000, 3600 thermal cycles of MA/PA/SM

As shown in Table 4.9, the melting temperature of MA/PA/SM and MA/PA/SP after 1000 thermal cycles had increased by 1.54 °C and 1.39 °C, while their solidification temperatures decreased after 1000 thermal cycles by -0.64 °C and -0.70 °C. Furthermore, the T_m of MA/PA/SM and MA/PA/SP were shown to be more stable after 2000, 3000, and 3600 thermal cycles, with only very small fluctuations 1.61 °C, 1.54 °C, 1.46 °C and 1.31 °C, 1.29 °C, 1.42 °C, respectively. Similar trends were observed for T_s of the binary PCMs, which decreased by -0.78 °C, -0.64 °C, -0.69 °C and -0.82 °C, -0.77 °C, -0.73 °C after 2000, 3000, and 3600 thermal cycles. The results in Table 4.9 also show that the latent heat of fusion (ΔH_f) of MA/PA/SM decreased by 5.27% and 5.29%

after 1000 and 2000 thermal cycles. However as the cycle increases, after 3000 and 3600 thermal cycles, the percentage reduction in ΔH_f was 2.86% and 2.84% respectively. In contrast, for MA/PA/SP binary mixture, there was a consistent decreasing trend in ΔH_f by 5.71%, 6.57%, 5.98%, and 6.70% for 1000, 2000, 3000, and 3600 cycles, respectively.

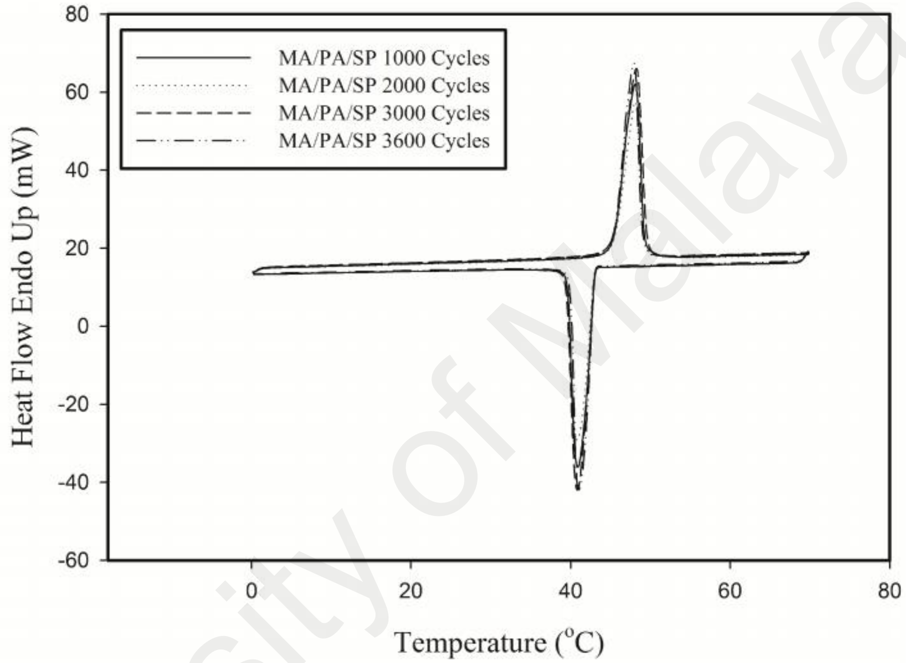


Figure 4.15. DSC curve subjected to 1000, 2000, 3000, 3600 thermal cycles of MA/PA/SP

Sari et al (Ahmet Sarı, 2003) in their work on 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 after 120 thermal cycles. However the T_m of SA, PA, MA and LA decreased by 5.04 °C, 2.52 °C, 2.21 °C, and 0.26 after 560 thermal cycles, and 7.87 °C, 5.84 °C, 6.78 °C, and 1.38 °C after 1200 thermal cycles, respectively. Furthermore, the changes of ΔH_f of SA, PA, MA, and LA were between -4.8% to 3.9%, -17.3% to 27.7%, and -12.9% to 11.3% after 120, 560 and 1200 thermal cycles, respectively. Sari (2005) had 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 these binary mixtures were decreasing irregularly as the number of thermal cycles increases. In addition, Karaipekli et al. (2008; 2009) had 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 recorded that the T_m values of CA/SA, CA/LA, and CA/MA were irregular, lying between 0.27 ^oC to 0.48 ^oC, 0.58 ^oC to 1.50 ^oC and 0.50 ^oC to 1.36 ^oC after 1000 to 5000 thermal cycles, respectively. The changes in ΔH_f were -10% to 6.4% for CA/SA, 6.5 to 20.3% for CA/LA, and 3.3 to 14.4% for CA/MA binary mixtures after 1000 to 5000 thermal cycles.

Due to the similarity with past studies, it can be concluded that the thermal properties of the proposed binary mixtures of fatty acids are deemed reliable for use as PCMs for thermal energy storage system.

4.2.2 Degradation of chemical structure analysis

4.2.2.1 MA/PA and MA/PA/SS eutectic mixtures

The FT-IR curve in Fig. 4.16 shows the spectra of the as-prepared MA/PA and MA/PA/SS. Since the peaks were found at the same frequency, it can be concluded that the addition of 5 wt.% sodium stearate (SS) in MA/PA (70/30, wt.%) did not result in any chemical reaction that may have changed the structure of MA/PA.

The spectra of as-prepared MA/PA and MA/PA after 1500 thermal cycles are shown in Fig. 4.17. It can be seen that after 1500 thermal cycles a new peak appears at 3832.57 cm^{-1}, indicating the formation of hydrogen bonds. Hydrogen bonds were also observed in the as-prepared and in cycled MA/PA/SS eutectic mixture at wavenumber 3805.20 cm^{-1}, as shown in Fig. 4.18. A wider different frequency band at MA/PA/SS as compared to MA/PA after 1500 thermal cycles is probably caused by the presence of sodium (Na) bonding of the sodium stearate (SS) in the mixture.

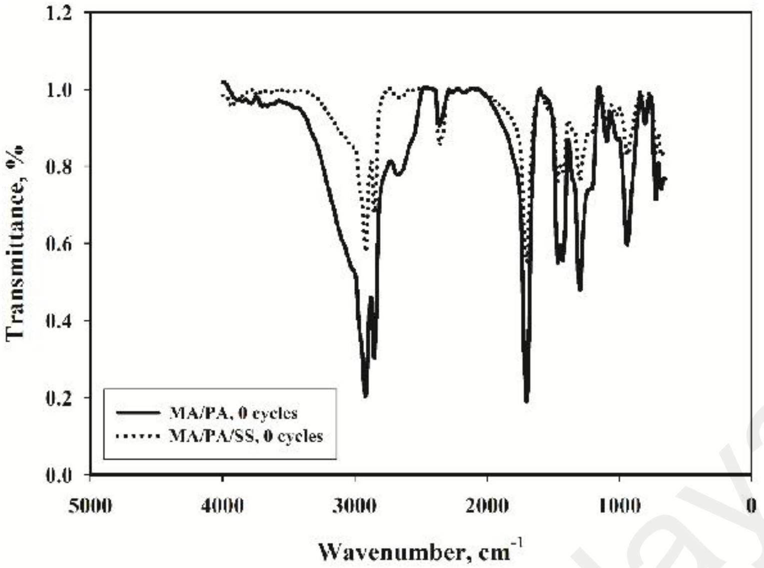


Figure 4.16. FT-IR curves of un-cycled MA/PA and MA/PA/SS.

Thus, it can be concluded that the thermal properties of MA/PA and MA/PA/SS eutectic mixture changes irregularly when subjected to 200, 500, 1000 and 1500 thermal cycles, which may have been caused by changes in the functional group of chemical structures.

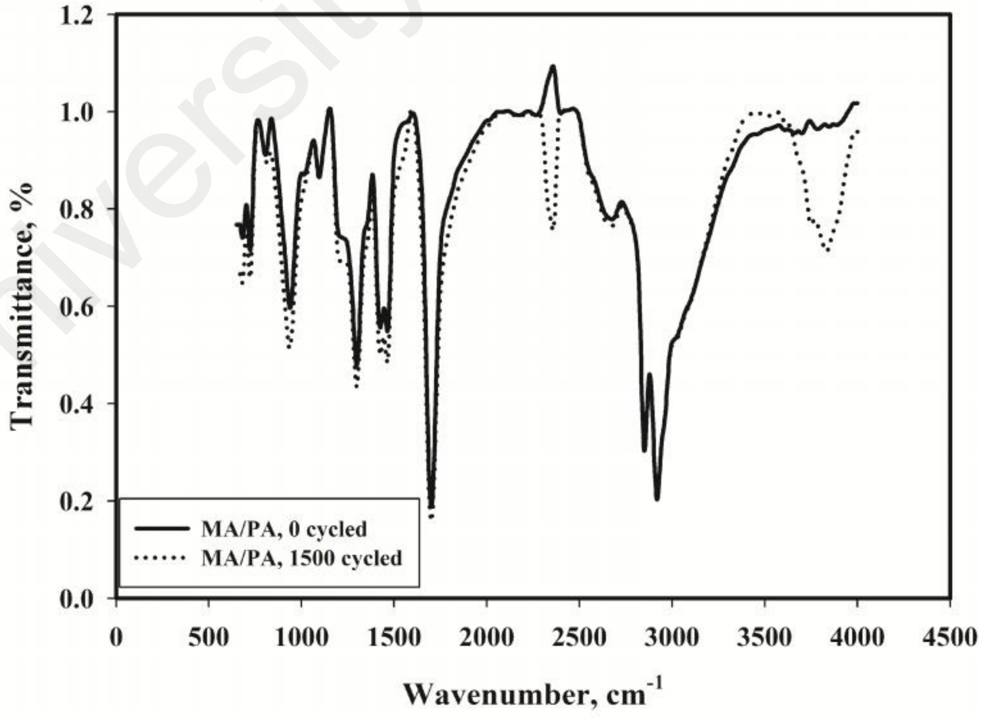


Figure 4.17. FT-IR curve of un-cycled MA/PA and MA/PA after 1500 thermal cycles.

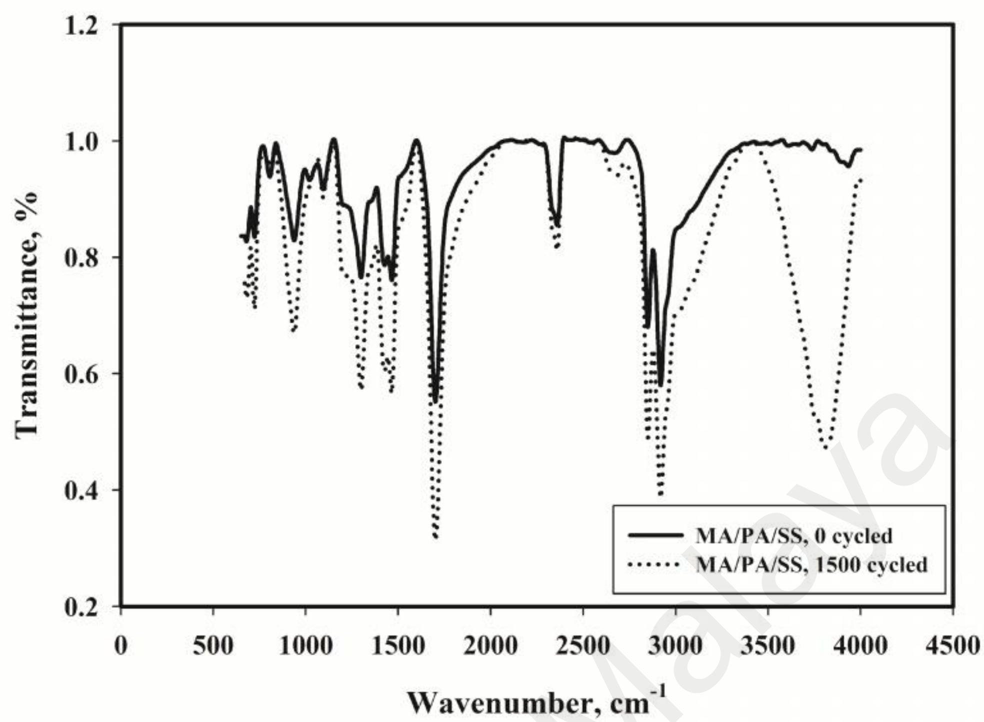


Figure 4.18. FT-IR curve un-cycled MA/PA/SS and MA/PA/SS after 1500 thermal cycles.

4.2.2.2 MA/PA/SL eutectic mixture

Fig. 4.19 shows the FT-IR curve of un-cycled MA/PA/SL and MA/PA/SL after 1000 thermal cycles. It can be seen that both spectra have all the peaks at the same frequencies, which is mean that the chemical structure of MA/PA/SL eutectic mixture did not degrade after 1000 melting/cooling cycles.

The chemical structure stability of MA/PA/SL eutectic mixture has confirmed that the changes in thermal properties of MA/PA/SL eutectic mixture after repeated thermal cycles were not caused by degradation of chemical functional group of these eutectic PCM.

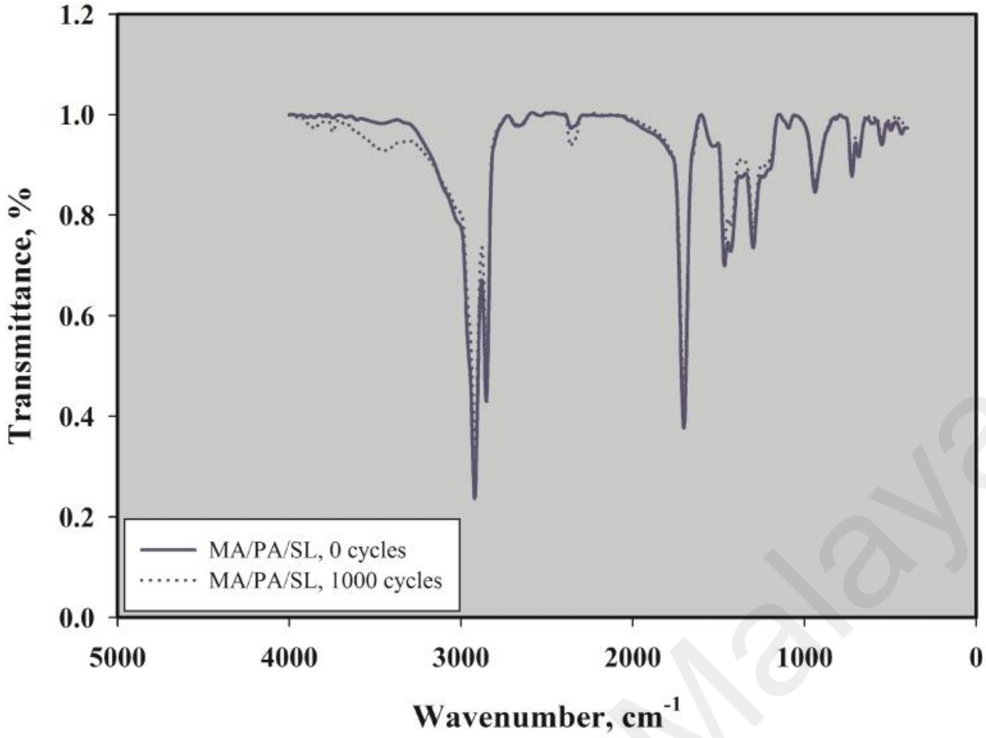


Figure 4.19. FT-IR curve of un-cycled MA/PA/SL and MA/PA/SL after 1000 thermal cycles

4.2.2.3 MA/PA/SM and MA/PA/SP eutectic mixtures

The FT-IR spectra of MA/PA/SM and MA/PA/SP eutectic mixtures before and after 3600 thermal cycles are shown in Fig. 4.20 and 4.21, indicating that all peak positions of MA/PA/SM and MA/PA/SP remained at the same frequency band throughout 3600 cycles. The same characteristic were observed for lauric acid/myristic acid (LA/MA), lauric acid/palmitic acid (LA/PA) and cupric acid/lauric acid (CA/LA), cupric acid/myristic acid (CA/MA) eutectic mixtures as reported by Sari (2006) and Himran et al. (1994).

These results showed that the chemical structures of both eutectic mixtures did not degrade during thermal cycles, thus indicating the changes in thermal properties of MA/PA/SM and MA/PA/SP during thermal cycling are not caused by chemical structure degradations.

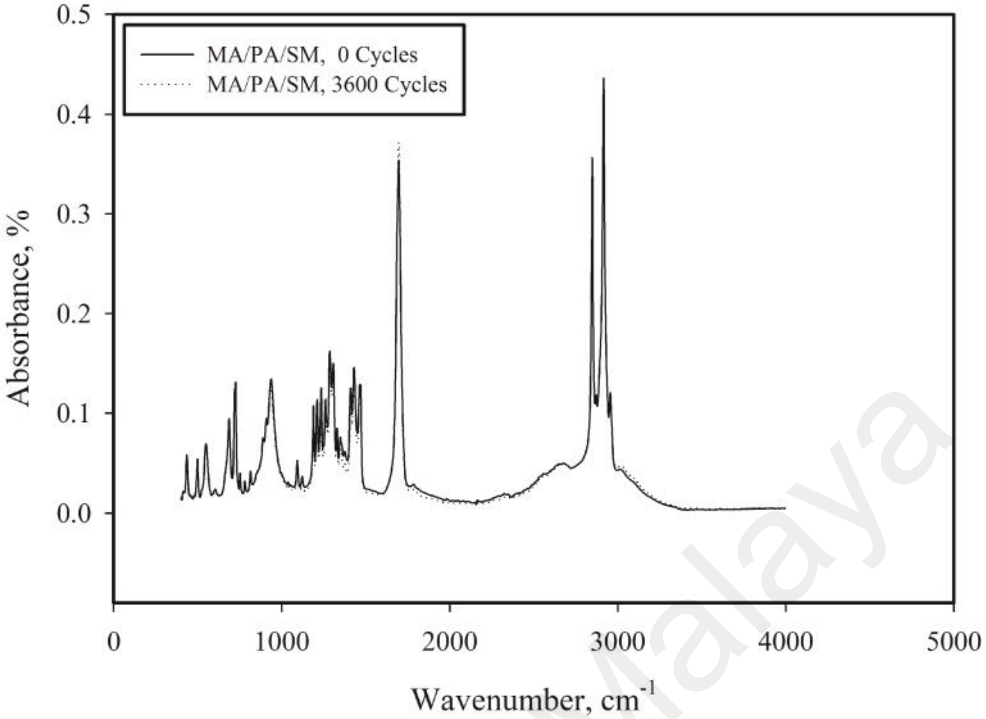


Figure 4.20. FT-IR curve of un-cycled and after 3600 thermal cycles MA/PA/SM

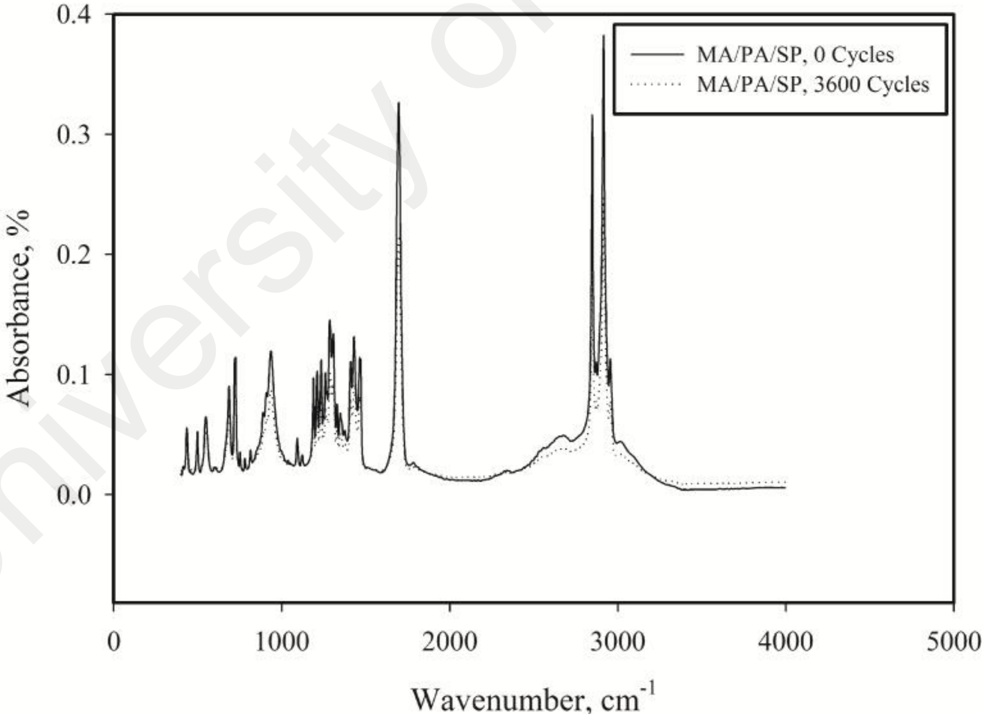


Figure 4.21. FT-IR curve of un-cycled and after 3600 thermal cycles MA/PA/SP

4.2.3 Physical change analysis

The physical changes of MA/PA, MA/PA/SS, MA/PA/SL, MA/PA/SM, and MA/PA/SP eutectic mixtures upon solidification and melting were measured using the phase transition method. Table 4.10 shows the comparison percentage of volume changes between solid and liquid phase of un-cycled eutectic PCMs and eutectic PCMs after large numbers of thermal cycles. The volumes of as-prepared MA/PA, MA/PA/SS, MA/PA/SL, MA/PA/SM, and MA/PA/SP eutectic mixtures in the liquid phase were 22.81 ml while in the solid phase these eutectic PCMs have volumes of 22.551 ml, 22.627 ml, 22.613 ml, 22.620 ml and 22.632 ml, respectively. After thermal cyclic of these eutectic PCMs, it was found that the volumes of The MA/PA and MA/PA/SS after 1500 thermal cycles were 22.91 ml and 22.89 ml in the liquid phase and 22.54 ml and 22.615 ml in the solid phase, respectively. Similarly, the volumes of MA/PA/SL after 1000 thermal cycles were 22.85 ml in the liquid phase and 22.571 ml in the solid phase. The volumes of MA/PA/SM and MA/PA/SP after 3600 thermal cycles were 22.86 ml and 22.84 ml in the liquid phase and 22.565 ml and 22.556 ml in the solid phase, respectively. The volume changes for as-prepared MA/PA, MA/PA/SS, MA/PA/SL, MA/PA/SM, and MA/PA/SP eutectic mixtures between solid and liquid phase were 1.10%, 0.80%, 0.86%, 0.83%, and 0.83%, respectively. After the thermal cycle tests, the volume changes of MA/PA and MA/PA/SS after 1500 thermal cycles, MA/PA/SL after 1000 thermal cycles, and MA/PA/SM and MA/PA/SP after 3600 thermal cycles were 1.60% and 1.20%, 1.22%, 1.31% and 1.24%, respectively.

Table 4.10. Volume change with phase transition of MA/PA and MA/PA/SS after 1500th thermal cycling test.

Eutectic PCMs	**Number of thermal cycles**	**Volume change (%)**
MA/PA	0 1500	1.10 1.60
MA/PA/SS	0 1500	0.80 1.20
MA/PA/SL	0 1000	0.86 1.22
MA/PA/SM	0 3600	0.83 1.31
MA/PA/SP	0 3600	0.78 1.24

The reduction volume of PCMs in solid phase compared to liquid phase happened due to the molecules or particles inside the PCMs became more stable and the intermolecular force became stronger after releasing heat. While in liquid phase, the PCM absorbed the heat which is make it’s inside molecule easy to move and make it’s intermolecular force became weak. Therefore, the volume of PCM in liquid phase a little bit more higher than solid phase.

In a previous study, Matsui, et al. (2007) have investigated the volume changes of pure water (H_2O), capric acid/lauric acid (CA/LA) and capric acid/lauric acid with 20 wt.% sodium oleate (CA/LA/SO). They reported that pure water has a volume expansion of 1.5% upon solidification, whereas CA/LA/SO and CA/LA had a volume contraction of -0.7% and -1.1% upon solidification, respectively. Mehling and Cabeza (2008) mentioned that the volume changes of typical PCMs are usually less than 10%. Therefore, in application of LHTES systems, the container is designed to fit the phase of the larger volume, and the pressure is not changed significantly. In this study, it is confirmed that the volume expansion properties of the developed PCMs are minimal and thus are acceptable for use in latent thermal heat application system.

4.3 Enhancement of the thermal conductivity of eutectic PCMs

Organic phase change materials (PCMs) such as paraffin and fatty acids have been used in a wide application of thermal energy storage due to their high thermal storage capacity, wide range of phase transition temperature, low subcooling, and good reliability (Fauzi, Metselaar, Mahlia, & Silakhori, 2014). However, a common problem of these organic PCMs is their low heat transfer rates due to low thermal conductivity, resulting in large temperature gradients. Thus, the enhancement of thermal conductivity of organic phase change materials (PCMs) is a significant issue for most thermal energy storage (TES) applications (Zhou et al., 2014).

Several methods have been proposed to enhance the thermal conductivity of PCMs. Encapsulation is a traditional method, usually utilising a plastic module, which is chemically neutral with respect to both the phase change material and the heat transfer fluid. The modules typically have a diameter of some centimeters. However this method can be affected by problems of the leakage and increased cost in production (Zhou et al., 2014). Another method to improve the thermal conductivity of PCM is by adding high conductive porous material using simple mixing method, solution casting method or impregnation method (Alkan & Sari, 2008; Kim & Drzal, 2009; Nomura et al., 2008; Zhang & Fang, 2006).

In this work, the composite phase change material (CPCM) was prepared by adding *shorea javanica* as a porous material to improve the thermal conductivity of prepared fatty acid eutectic mixtures using a combination technique of simple mixing and impregnation. The fatty acid mixtures chosen were myristic acid/palmitic acid/sodium stearate (MA/PA/SS), myristic acid/palmitic acid/sodium laurate (MA/PA/SL), myristic acid/palmitic acid/sodium myristate (MA/PA/SM), and myristic acid/palmitic acid/sodium palmitate (MA/PA/SP).

4.3.1 Thermal characteristic of CPCMs binary system

Previously, the thermal properties of myristic acid/palmitic acid (MA/PA) eutectic mixture were improved by adding 5 wt.% sidium stearate (SS), 10 wt.% sodium laurate (SL), 5 wt.% sodium myristate (SM), and 5 wt.% sodium palmitate (SP). It was reported that the addition of sodium myristate (SM) has reduced the subcooling on the phase transition temperature ($T_{m,s}$) and improved the latent heat of fusion (ΔH_f) of MA/PA eutectic mixture. However, the addition of these acid based surfactants did not show a significant improvement on thermal conductivity. Therefore, this extended study is designed to improve the thermal conductivity of the prepared eutectic PCMs.

The DSC curve, shown in Fig. 4.22 to Fig. 4.25, illustrates the thermal properties of CPCMs with various percentages of SJ. The melting temperature (T_m) and solidification temperature (T_s) of MA/PA/SS/SJ, MA/PA/SL/SJ, MA/PA/SM/SJ, and MA/PA/SP/SJ were interpreted as the onset point. The latent heat of fusion during melting (ΔH_{fm}) and solidification phase (ΔH_{fs}) were obtained from interpolating of charts peak area. The thermal properties of the eutectic CPCMs, shown in Table 4.11, Table 4.12, Table 4.13, and Table 4.14, generally indicate that the phase transition temperatures of MA/PA/SS/SJ, MA/PA/SL/SJ, MA/PA/SM/SJ, and MA/PA/SP/SJ eutectic composites increase as the percentage composition of SJ increases. However, their latent heats of fusion tend to decrease with increasing SJ composition.

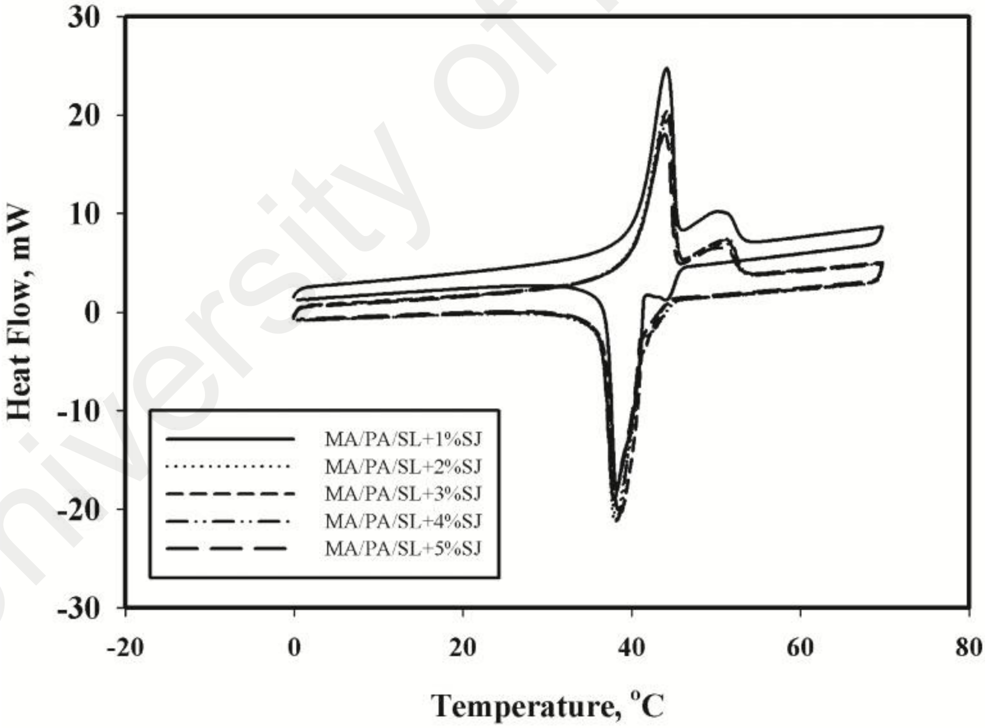


Figure 4.22. DSC curves of thermal properties eutectic MA/PA/SL/SJ

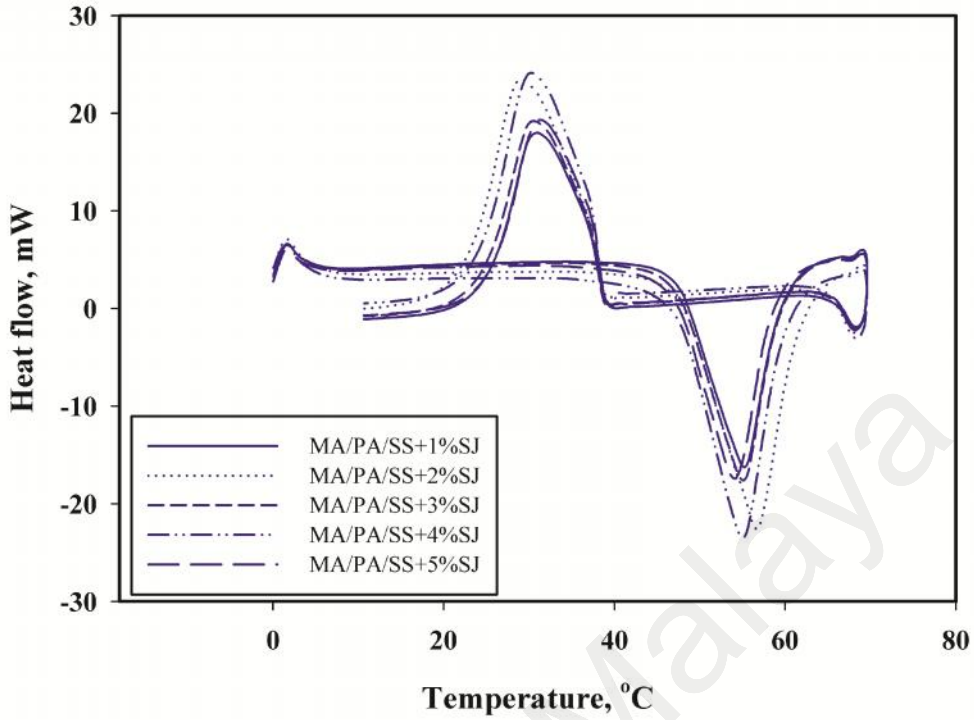


Figure 4.23. DSC curves of thermal properties eutectic MA/PA/SS/SJ

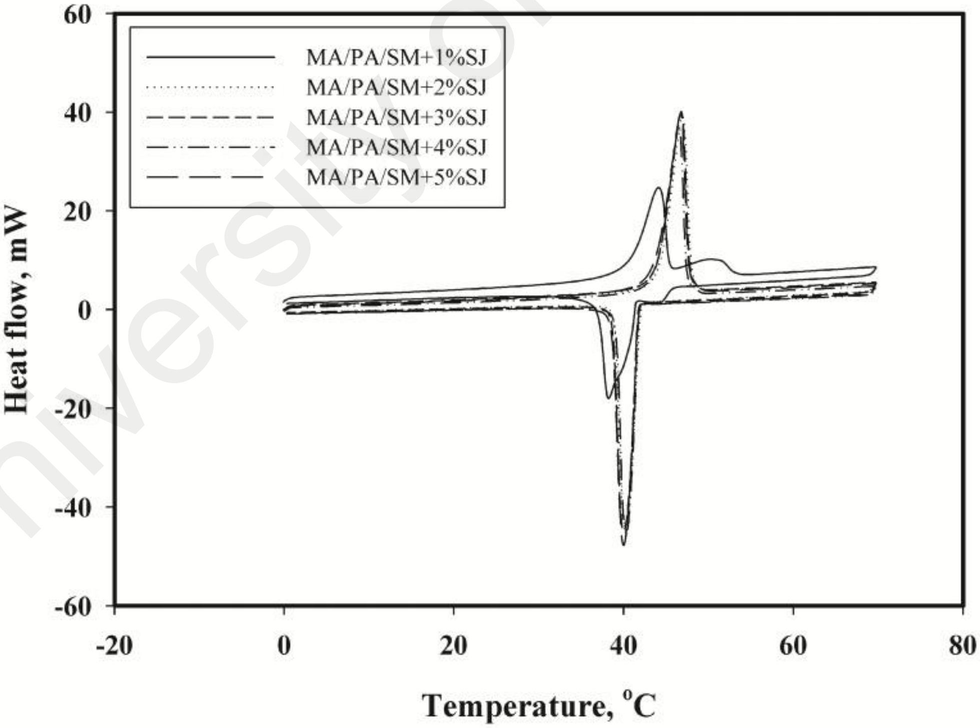


Figure 4.24. DSC curves of thermal properties eutectic MA/PA/SM/SJ

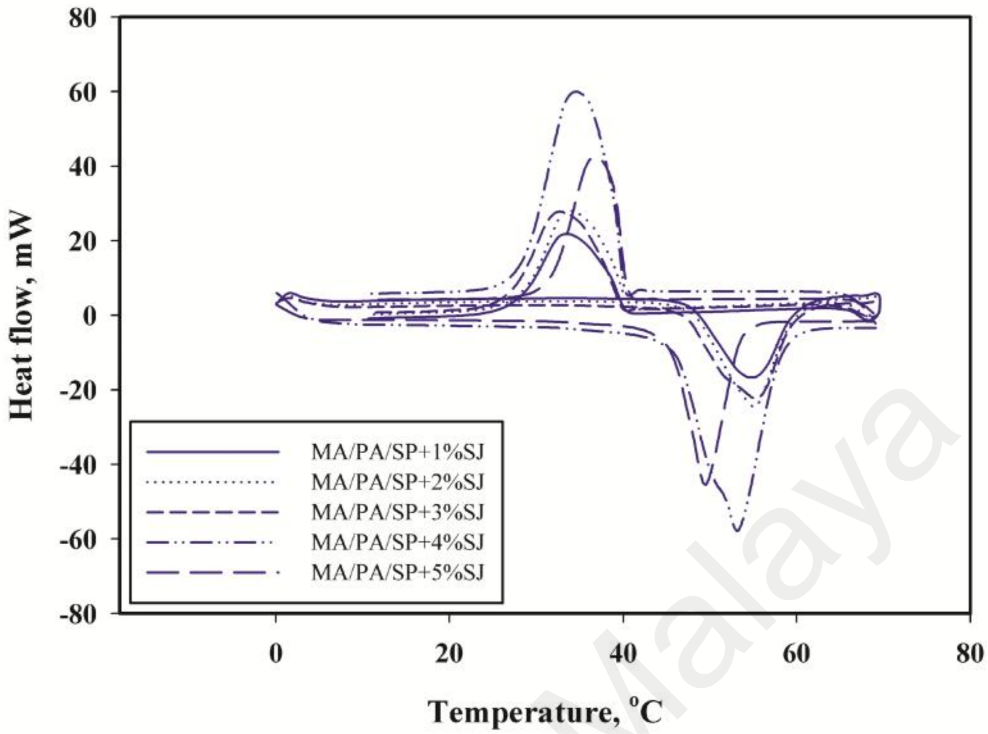


Figure 4.25. DSC curves of thermal properties eutectic MA/PA/SP/SJ

Table 4.11. Thermal properties of MA/PA/SS/SJ eutectic composite

Composite phase change materials (CPCMs)	T_m (^oC)	$\Delta H_{f,m}$ (J/g)	T_s (^oC)	$\Delta H_{f,s}$ (J/g)
MA/PA/SS + 1% SJ	41.96	184.72	39.02	188.18
MA/PA/SS + 2% SJ	42.36	174.21	40.73	181.70
MA/PA/SS + 3% SJ	41.91	176.19	40.80	180.48
MA/PA/SS + 4% SJ	42.10	176.58	40.79	181.32
MA/PA/SS + 5% SJ	41.65	172.72	39.95	179.43

Table 4.12. Thermal properties of MA/PA/SL/SJ eutectic composite

Composite phase change materials (CPCMs)	T_m (^oC)	$\Delta H_{f,m}$ (J/g)	T_s (^oC)	$\Delta H_{f,s}$ (J/g)
MA/PA/SL + 1% SJ	40.64	169.26	41.56	169.70
MA/PA/SL + 2% SJ	41.20	161.27	41.36	159.26
MA/PA/SL + 3% SJ	41.48	158.69	41.50	156.68
MA/PA/SL + 4% SJ	41.26	157.45	41.40	155.68
MA/PA/SL + 5% SJ	42.08	153.91	41.30	153.14

Table 4.13. Thermal properties of MA/PA/SM/SJ eutectic composite

Composite phase change materials (CPCMs)	T_m (°C)	$\Delta H_{f,m}$ (J/g)	T_s (°C)	$\Delta H_{f,s}$ (J/g)
MA/PA/SM + 1% SJ	40.54	179.92	41.46	183.55
MA/PA/SM + 2% SJ	43.20	176.39	41.95	179.95
MA/PA/SM + 3% SJ	43.96	177.45	41.73	180.85
MA/PA/SM + 4% SJ	43.89	169.35	41.75	172.29
MA/PA/SM + 5% SJ	43.75	167.38	41.67	175.63

Table 4.14. Thermal properties of MA/PA/SP/SJ eutectic composite

Composite phase change materials (CPCMs)	T_m (°C)	$\Delta H_{f,m}$ (J/g)	T_s (°C)	$\Delta H_{f,s}$ (J/g)
MA/PA/SP + 1% SJ	42.50	175.26	40.39	179.78
MA/PA/SP + 2% SJ	42.76	176.68	40.64	178.31
MA/PA/SP + 3% SJ	42.92	176.23	39.57	180.22
MA/PA/SP + 4% SJ	42.91	171.19	40.11	175.01
MA/PA/SP + 5% SJ	42.13	169.72	40.52	179.95

As shown in Table 4.15, Table 4.16, Table 4.17, and Table 4.18, the thermal conductivities of MA/PA/SS/SJ, MA/PA/SL/SJ, MA/PA/SM/SJ, and MA/PA/SP/SJ eutectic composites increases with increasing percentages of SJ. The highest thermal conductivity value were obtained with 5 wt. % SJ which were 0.383 $Wm^{-1}K^{-1}$, 0.393 $Wm^{-1}K^{-1}$, 0.396 $Wm^{-1}K^{-1,}$ and 0.394 $Wm^{-1}K^{-1}$, for MA/PA/SS/SJ, MA/PA/SL/SJ, MA/PA/SM/SJ, and MA/PA/SP/SJ eutectic composites respectively. However, the corresponding values of latent heat of fusion for MA/PA/SS/SJ, MA/PA/SL/SJ, MA/PA/SM/SJ, and MA/PA/SP/SJ eutectic composites had shown a significant drop to 172.72 Jg^{-1}, 153.91 Jg^{-1}, 167.38 Jg^{-1}, and 169.72 Jg^{-1}, respectively, from their initial values of 191.85 Jg^{-1}, 174.47 Jg^{-1}, 179.12 Jg^{-1}, and 184.14 Jg^{-1}. This corresponds to a reduction of 9.97%, 11.78%, 6.5%, and 7.8%, respectively.

Table 4.15. Thermal conductivity of MA/PA/SS/SJ eutectic composite

Composite phase change materials (CPCMs)	**Thermal conductivity, $Wm^{-1}K^{-1}$**
MA/PA/SS + 1% SJ	0.292
MA/PA/SS + 2% SJ	0.317
MA/PA/SS + 3% SJ	0.361
MA/PA/SS + 4% SJ	0.364
MA/PA/SS + 5% SJ	0.383

Table 4.16. Thermal conductivity of MA/PA/SL/SJ eutectic composite

Composite phase change materials (CPCMs)	**Thermal conductivity, $Wm^{-1}K^{-1}$**
MA/PA/SL + 1% SJ	0.273
MA/PA/SL + 2% SJ	0.312
MA/PA/SL + 3% SJ	0.356
MA/PA/SL + 4% SJ	0.387
MA/PA/SL + 5% SJ	0.393

Table 4.17. Thermal conductivity of MA/PA/SM/SJ eutectic composite

Composite phase change materials (CPCMs)	**Thermal conductivity, $Wm^{-1}K^{-1}$**
MA/PA/SM + 1% SJ	0.263
MA/PA/SM + 2% SJ	0.325
MA/PA/SM + 3% SJ	0.388
MA/PA/SM + 4% SJ	0.389
MA/PA/SM + 5% SJ	0.396

Table 4.18. Thermal conductivity of MA/PA/SP/SJ eutectic composite

Composite phase change materials (CPCMs)	**Thermal conductivity, $Wm^{-1}K^{-1}$**
MA/PA/SP + 1% SJ	0.276
MA/PA/SP + 2% SJ	0.343
MA/PA/SP + 3% SJ	0.379
MA/PA/SP + 4% SJ	0.386
MA/PA/SP + 5% SJ	0.394

Reducing the percentage of addition alleviate the significant drop of latent heat of fusion, shown in the results of MA/PA/SS+3%SJ, MA/PA/SL+2%SJ MA/PA/SM+3%SJ, and MA/PA/SP+3%SJ eutectic composites. In term of the thermal conductivity, the eutectic composites of MA/PA/SS+3%SJ, MA/PA/SL+2%SJ MA/PA/SM+3%SJ, and MA/PA/SP+3%SJ show an improvement of 56.95%, 32.76%, 60.33%, and 60.59% higher than the corresponding thermal conductivity values of MA/PA/SS, MA/PA/SL, MA/PA/SM, and MA/PA/SP eutectic mixtures.

Similar results have been described by past researchers. Karaipekli et al. (2007) reported that the thermal conductivity of SA was increased by 27.6%, 58.6%, 179.3%, and 279.3% by adding expended graphite (EG) in mass fractions of 2%, 4%, 7%, and 10%. It was also observed that the addition of carbon fiber (CF) in similar quantities instead of EG, increases the thermal conductivity of SA by 24.1%, 106.9%, 162.1%, and 217.2%, respectively. However, the addition of EG and CF in SA had decreased the latent heat capacity of SA by 7% and 8% respectively as compared to the latent heat capacity value of pure SA. Karaipekli and Sarı (2008) had also investigated the effect of incorporating expended perlite (EP) to capric acid/myristic acid (CA/MA) eutectic PCM. The latent heat value of CA/MA/EP composite PCM was found to be slightly lower than pure CA/MA eutectic mixture. Zhang and Fang (2006) and Sari and Karaipekli (2007) had enhanced the thermal conductivity of paraffin by adding expended graphite (EG) and reported that the melting point of paraffin was increased while its latent heat capacity was decreased as a direct result from the addition EG as compared to pure paraffin.

Fig 4.26 to Fig. 4.29 described the duration of heat storage and heat release of the PCMs and CPCPMs, showing an overall improvement of the heat transfer rates of the eutectic composite phase change materials (CPCMs). The figure shows MA/PA/SS+3%SJ, MA/PA/SL+2%SJ, MA/PA/SM+3%SJ, MA/PA/SP+3%SJ eutectic composites having the shortest time to reach the melting and solidification points as compared to MA/PA/SS, MA/PA/SL, MA/PA/SM, and MA/PA/SP eutectic mixtures, respectively.

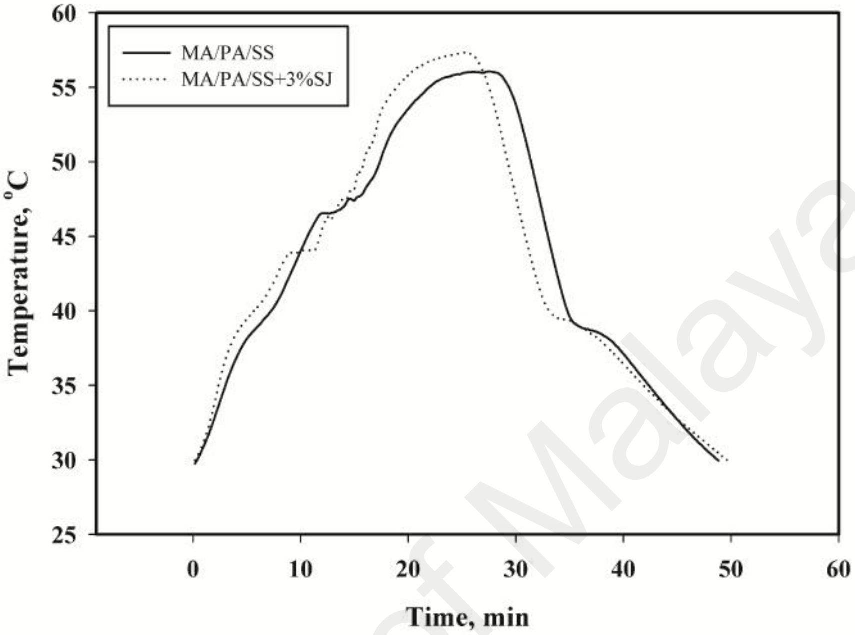


Figure 4.26. Heat storage and release curve of MA/PA/SS and MA/PA/SS/SJ

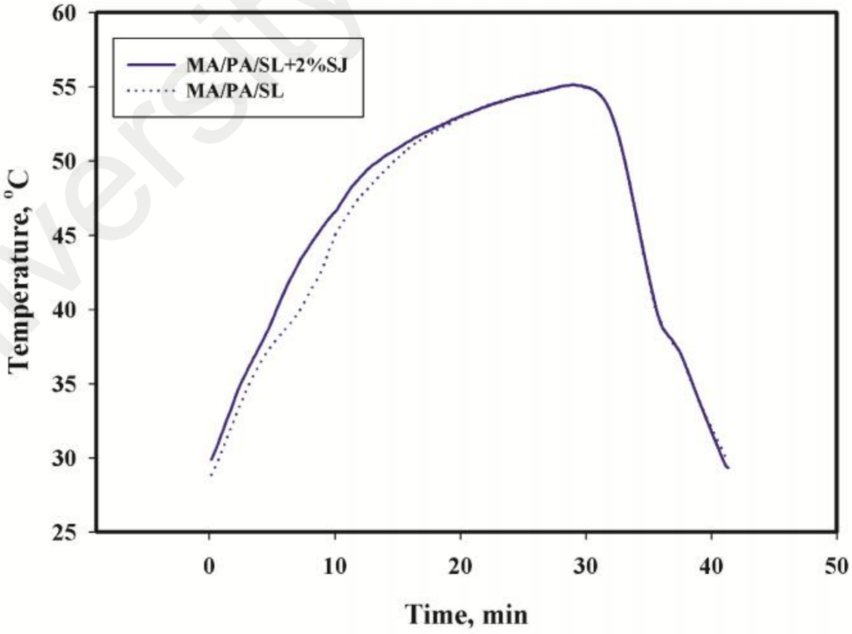


Figure 4.27. Heat storage and release curve of MA/PA/SL and MA/PA/SL/SJ

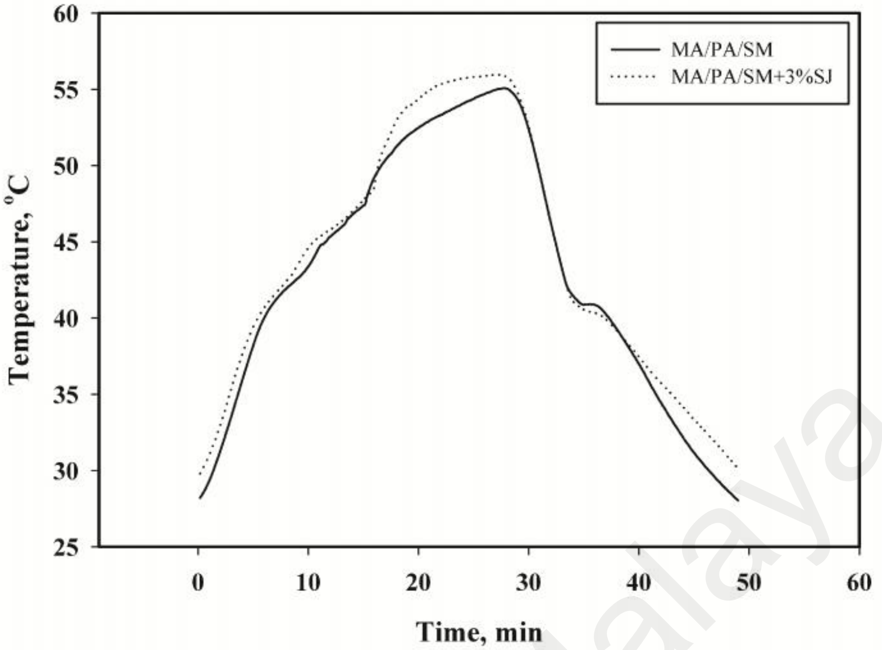


Figure 4.28. Heat storage and release curve of MA/PA/SM and MA/PA/SM/SJ

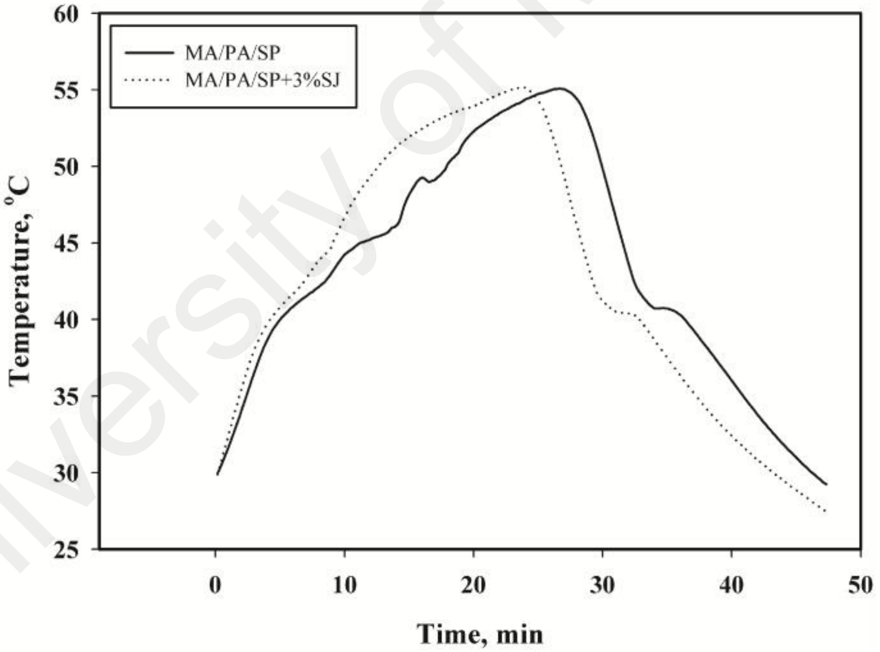


Figure 4.29. Heat storage and release curve of MA/PA/SP and MA/PA/SP/SJ

The improvements of heat transfer rate indicated by the reduction of phase transition duration time have been reported in the literatures. Karaipekli et al (2007), in comparing the melting times of SA/CE and SA/CF composite PCMs with that of pure SA, discovered that the melting times of CPCMs were reduced respectively by 38% and 37% as compared to that of pure SA. Zhang and Fang (2006) and Sarı and Karaipekli

(2007), in comparing the thermal performance of paraffin and paraffin/EG, have shown that paraffin/EG CPCMs were 27.4% and 32% faster in reaching the melting points as compared to pure paraffin.

The results in this study have shown that the heat transfer rate during heat release processes was faster than heat storage processes. This is due to the mechanism of heat transfer, which is by natural convection during heat storage and thermal conduction during heat release. Therefore, it can be said that the increase in thermal conductivity of CPCM had a shows a better enhancement on the heat transfer during heat release than heat storage processes.

4.3.2 Chemical reaction analysis of CPCMs

The FT-IR spectra in Fig. 4.30 to Fig. 4.33.d show the absorbance peaks for each chemical functional group of MA/PA/SS, MA/PA/SS+3%SJ, and SJ; MA/PA/SL, MA/PA/SL+3%SJ, and SJ; MA/PA/SM, MA/PA/SM+3%SJ, and SJ; MA/PA/SP, MA/PA/SP+3%SJ, and SJ, respectively. In general, the spectra showed similar peak occurrences in every range of wavenumber for each eutectic PCMs and eutectic CPCMs after adding *shorea javanica* (SJ).

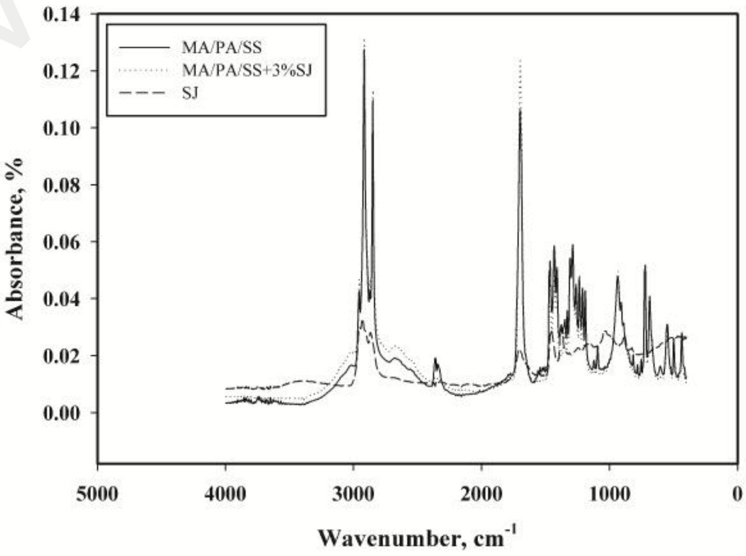


Figure 4.30. FT-IR absorbance curve of MA/PA/SS and MA/PA/SS/SJ

This indicates that the addition of *shorea javanica* (SJ) into the prepared eutectic PCMs did not cause any chemical reactions between eutectic PCMs and SJ in the mixtures. Thus, it can be inferred that changes of thermal properties of MA/PA/SM/SJ eutectic CPCM were not caused by chemical reactions but due to the physical properties of *shorea javanica* (SJ). The increase in melting temperatures and reduction in the latent heat of fusion of eutectic CPCMs is probably due to the high melting temperature and low latent heat of fusion of SJ.

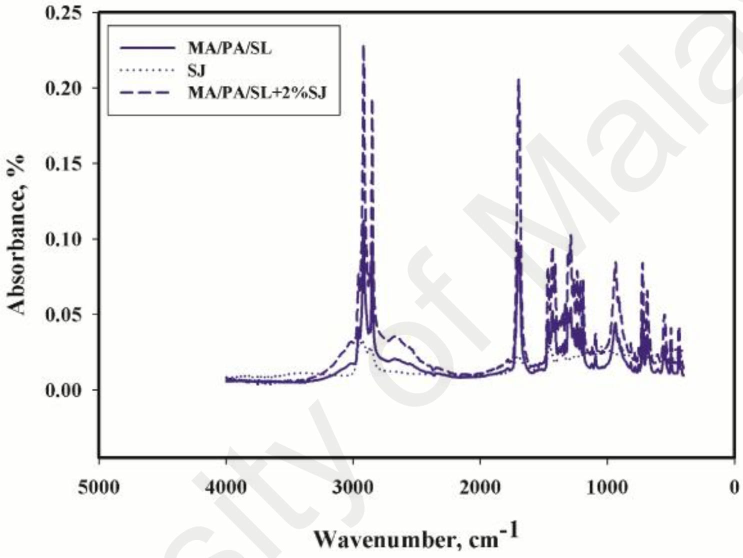


Figure 4.31. FT-IR absorbance curve of MA/PA/SL and MA/PA/SL/SJ

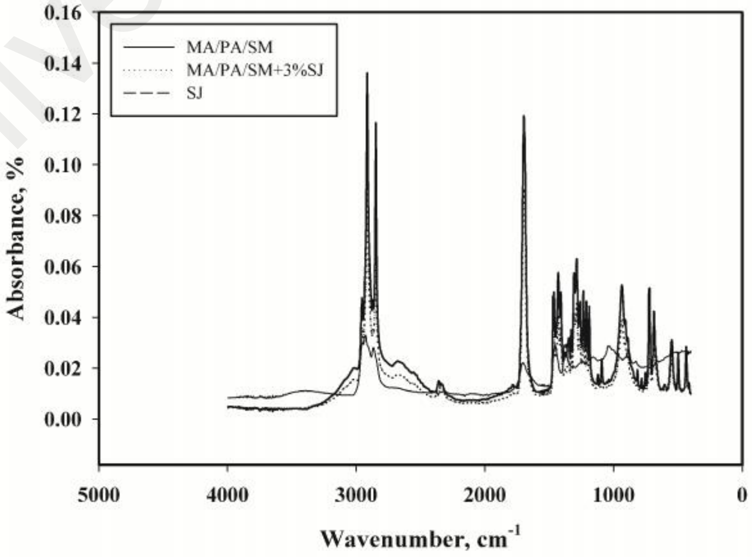


Figure 4.32. FT-IR absorbance curve of MA/PA/SM and MA/PA/SM/SJ

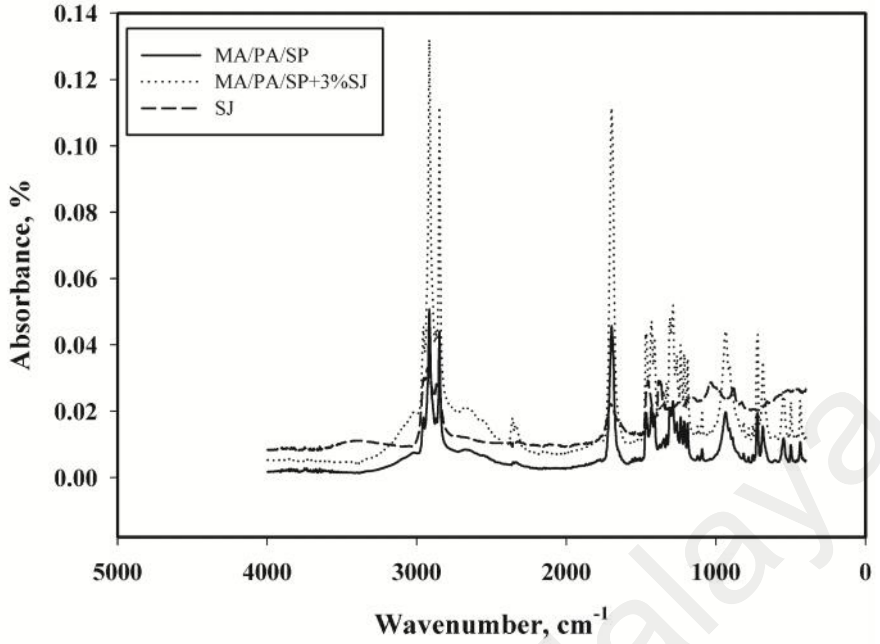


Figure 4.33. FT-IR absorbance curve of MA/PA/SP and MA/PA/SP/SJ

4.3.3 Thermal stability analysis of CPCMs

Fig 4.34 shows no mass degradation of MA/PA/SS+3%SJ, MA/PA/SL+2%SJ, MA/PA/SM+3%SJ, and MA/PA/SP+3%SJ eutectic composites within the working temperatures of 30 to 153 ^{o}C, 30 to 132.38 ^{o}C, 30 to 168.71 ^{o}C, and 30 to 156.19 ^{o}C, respectively, indicating overall high thermal stabilities of the CPCMs. However, the weight degradations of MA/PA/SS+3%SJ, MA/PA/SL+2%SJ, MA/PA/SM+3%SJ, and MA/PA/SP+3%SJ eutectic composite appear once the work temperature reached 153.86 ^{o}C, 133.11 ^{o}C, 169.43 ^{o}C, and 156.93 ^{o}C, respectively. The most significant weight degradations occur once the working temperature of these CPCMs reached 290.4 ^{o}C, 290.06 ^{o}C, 283.39 ^{o}C, and 289.73 ^{o}C, respectively. These results indicate that the MA/PA/SS+3%SJ, MA/PA/SL+2%SJ, MA/PA/SM+3%SJ, and MA/PA/SP+3%SJ eutectic composites show good thermal stabilities and thus suitable to be used as thermal energy storage (TES) application operating at temperatures below 150 ^{o}C.

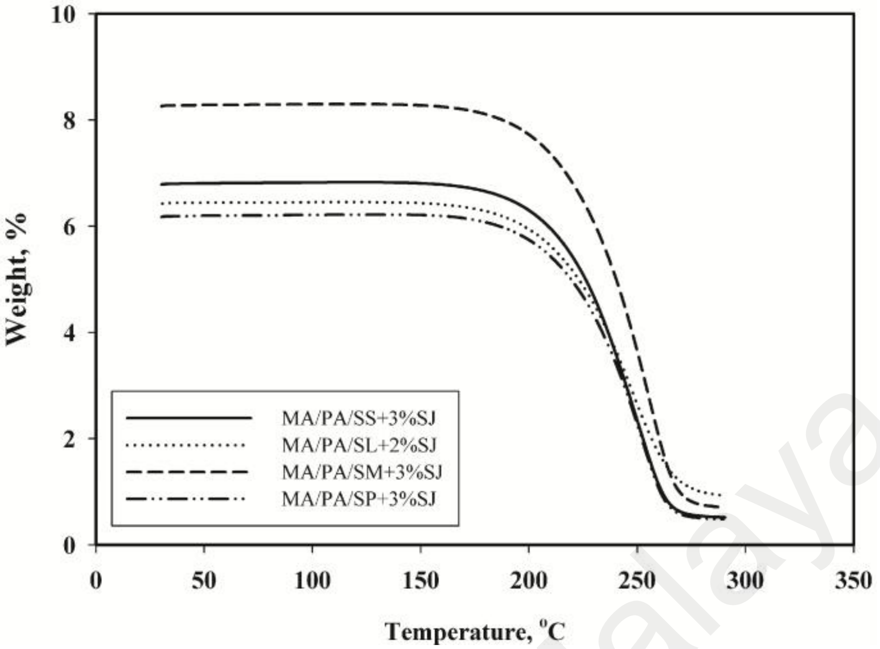


Figure 4.34. STA curves of composite phase change materials (CPCMs)

4.4 Compatibility of eutectic CPCMs with construction materials

Although many organic and inorganic PCM have been developed, there are limited studies on their compatibilities with construction materials such as metals and metal alloys. Corrosion is the most common problem encountered in PCM applications, and the assumptions that corrosion is a general problem requiring no further evaluation is unjustified. The long life utilization of PCMs is not only determined by thermal reliability of PCM, it will also be dependent on the compatibility of the PCMs with construction materials of the TES systems.

Some studies have been conducted on the compatibility of inorganic PCMs with metals. Groll et al. (1990) in their evaluation of the corrosion behavior of steel containers, commented that the corrosion could be affected by waters along with other harmful particles inside the eutectic salt mixtures. A summary of their result has indicated the range of salt eutectics and construction materials available for use in latent heat thermal energy storage (LHTES) applications within the temperatures range of 160-420 ^{o}C. Porosini (1988) presented the corrosion resistance data of metallic alloys such as stainless steel, carbon steel, Al alloys, and Cu, to various hydrated salts for 5650 thermal cycles. It was found that stainless steel was the most corrosion resistant alloy to all the hydrated salts tested. Cabeza et al. (2001) have conducted a study on the corrosion resistance of typical metals such as aluminium, brass, copper, steel, and stainless steel contacting with salt hydrates such as zinc nitrate hexahydrate, sodium hydrogen phosphate dodecahydrate, and calcium chloride hexahydrate. The study reported that the combination of zinc nitrate hexahydrate with stainless steel, sodium hydrogen phosphate dodecahydrate with brass, copper and stainless steel, and calcium chloride hexahydrate with brass and copper exhibited no considerable corrosion in the short term. In another work, Cabeza et al. (2002) have analyzed the corrosion resistance of several commercial metal, namely, aluminium, brass, copper, steel and stainless steel in contact with two salt hydrates, sodium acetate trihydrate and sodium thiosulfate pentahydrate. After test duration of 70 days, it was discovered that brass and copper did not fare well with sodium acetate trihydrate for long-term proposes, although aluminium, steel and stainless steel did not exhibit any corrosion problems.

However, there is a lack of literature on the compatibilities of organic PCMs to container materials. A report by Sari and Kaygusuz (2003), in their evaluations of several construction materials such as stainless steel, carbon steel, aluminum (Al) and copper (Cu) to fatty acids over 910 thermal cycles period, have described that stainless steel and Al are compatible with the investigated fatty acids. However, carbon steel and Cupper (Cu) are less compatible with PCMs.

In this work, evaluation was made on the corrosion resistance behavior of two metal samples, stainless steel (SS 304L) and carbon steel (steel C20), in contact with the prepared eutectic composite phase change materials (CPCMs) of Myristic acid/palmitic acid/ sodium stearate/shorea javanica (MA/PA/SS/SJ), Myristic acid/palmitic acid/

sodium laurate/shorea javanica (MA/PA/SL/SJ), Myristic acid/palmitic acid/ sodium myristate/shorea javanica (MA/PA/SM/SJ), and Myristic acid/palmitic acid/ sodium palmitate/shorea javanica (MA/PA/SP/SJ), subjected to 300, 700, 1200, and 1800 thermal cycles. Gravimetric analysis was used to quantify weight losses and corrosion rate of metal samples is contact with the CPCMs.

4.4.1 Corrosion behavior of metals with CPCMs

Gravimetric analysis were measured by weight loss (mg.cm^{-2}) and corrosion rate (mg.d^{-1}) for both SS 304L and steel C20 in contact with prepared eutectic CPCMs (MA/PA/SS/SJ, MA/PA/SL/SJ, MA/PA/SM/SJ, and MA/PA/SP/SJ) subjected to 300, 700, 1200, and 1800 thermal cycles. The result of the analysis is summarized in Table 4.19 and Table 4.20.

Table 4.19. Gravimetric analysis results of SS 304L with eutectic CPCMs subjected to thermal cycles

Thermal cycles number	**MA/PA/SS/SJ**		**MA/PA/SL/SJ**		**MA/PA/SM/SJ**		**MA/PA/SP/SJ**	
	ΔW, mg.cm^{-2}	**K_{corr}, mg.d^{-1}**	**ΔW, mg.cm^{-2}**	**K_{corr}, mg.d^{-1}**	**ΔW, mg.cm^{-2}**	**K_{corr}, mg.d^{-1}**	**ΔW, mg.cm^{-2}**	**K_{corr}, mg.d^{-1}**
300	0.193	14. 10^{-4}	0.105	7.6. 10^{-4}	0.120	8.6. 10^{-4}	0.178	12.9. 10^{-3}
700	0.316	9.8. 10^{-4}	0.225	7.0. 10^{-4}	0.244	7.5. 10^{-4}	0.265	8.2. 10^{-4}
1200	0.447	8.1. 10^{-4}	0.393	7.1. 10^{-4}	0.335	6.0. 10^{-4}	0.425	7.7. 10^{-4}
1800	0.615	7.4. 10^{-4}	0.433	5.2. 10^{-4}	0.411	4.9. 10^{-4}	0.452	6.5. 10^{-4}

Table 4.20. Gravimetric analysis results of Steel C20 with eutectic CPCMs subjected to thermal cycles

Thermal cycles number	**MA/PA/SS/SJ**		**MA/PA/SL/SJ**		**MA/PA/SM/SJ**		**MA/PA/SP/SJ**	
	ΔW, mg.cm^{-2}	**K_{corr}, mg.d^{-1}**	**ΔW, mg.cm^{-2}**	**K_{corr}, mg.d^{-1}**	**ΔW, mg.cm^{-2}**	**K_{corr}, mg.d^{-1}**	**ΔW, mg.cm^{-2}**	**K_{corr}, mg.d^{-1}**
300	6.011	4.4. 10^{-2}	7.742	5.7. 10^{-2}	10.265	7.6. 10^{-2}	8.905	6.6. 10^{-2}
700	7.225	2.2. 10^{-2}	9.680	3.0. 10^{-2}	12.571	3.4. 10^{-2}	10.811	3.4. 10^{-2}
1200	8.811	1.6. 10^{-2}	11.665	2.1. 10^{-2}	14.480	2.6. 10^{-2}	13.153	2.4. 10^{-2}
1800	10.43	1.2. 10^{-2}	14.615	1.8. 10^{-2}	16.011	1.9. 10^{-2}	14.724	1.8. 10^{-2}

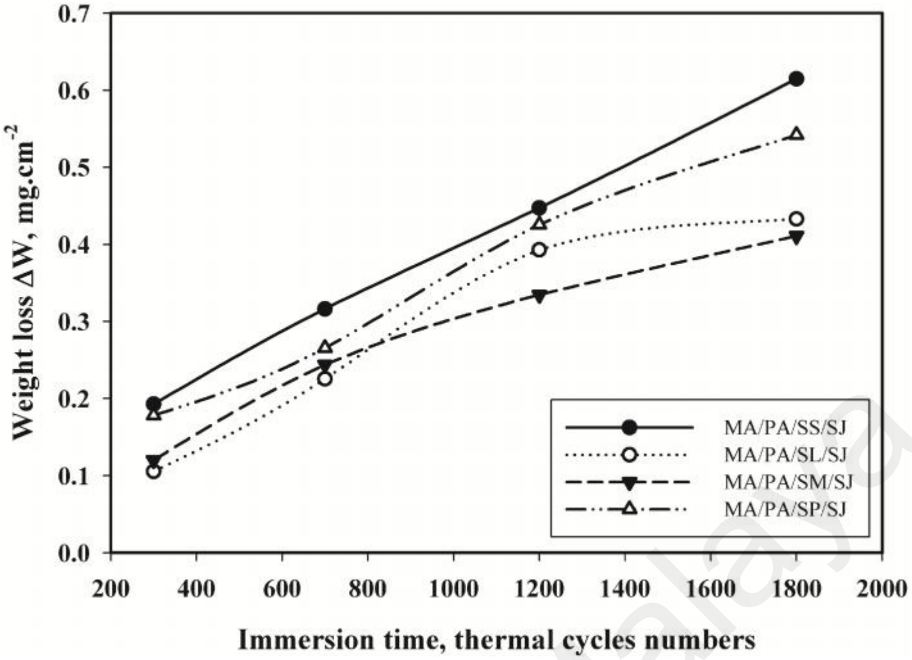


Figure 4.35. The variation of weight loss as a function of immersion time (thermal cycles) of SS 304L immersed in prepared eutectic composite phase change materials (CPCMs)

The weight losses, ΔW of SS 304L and steel C20, were calculated using Eq. 3.1 as a function of immersion time of these metal samples. Fig. 4.35 and Fig. 4.36 shows that the weight losses of SS 304L and steel C20 in eutectic CPCMs mixtures increases with increasing number of thermal cycles immersion times.

Fig. 4.35 shows the weight losses of SS 304L samples immersed in the prepared eutectic CPCMs at immersion times of 300 and 700 thermal cycles. The lowest weight loss value were calculated to be 0.105 mg.cm^{-2} at 300 thermal cycle and 0.225 mg.cm^{-2} at 700 thermal cycle for SS 304L immersed in MA/PA/SL/SJ, as compared to SS 304L immersed in other eutectic composite mixtures of MA/PA/SM/SJ, MA/PA/SP/SJ, and MA/PA/SS/SJ. Similarly, at 1200 and 1800 thermal cycles, the SS 304L with MA/PA/SM/SJ eutectic composite mixture showed the lowest weight losses value of 0.335 mg.cm^{-2} and 0.441 mg.cm^{-2}, respectively, followed by MA/PA/SL/SJ, MA/PA/SP/SJ, and MA/PA/SS/SJ.

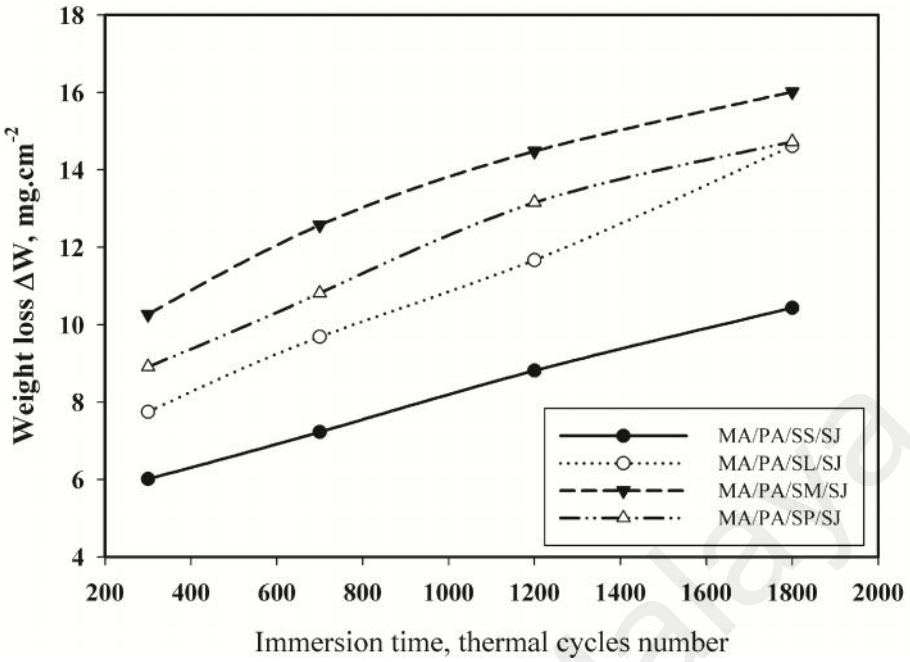


Figure 4.36. The variation of weight loss as a function of immersion time (thermal cycles) of steel C20 immersed in prepared eutectic composite phase change materials (CPCMs)

Fig 4.36 show the variation of weight losses for steel C20, subjected to immersion times of 300, 700, 1200, and 1800 thermal cycles. The figure indicates that steel C20 samples immersed with MA/PA/SS/SJ had the lowest weight losses of 6.011 mg.cm^{-2}, 7.225 mg.cm^{-2}, 8.811 mg.cm^{-2}, and 10.43 mg.cm^{-2} at 300, 700, 1200, and 1800 thermal cycles, respectively. The most significant weight losses were obtained for steel C20 immersed in MA/PA/SM/SJ eutectic composite mixture, followed by MA/PA/SP/SJ and MA/PA/SL/SJ eutectic composite mixtures, respectively.

The corrosion rate, K_{corr} value of metal samples, SS 304L and steel C20 in the prepared eutectic composites mixtures were calculated from their weight loss test results using Eq. 3.2 (Astm, 2006). Fig. 4.37 and Fig. 4.38 show that the corrosion rate of metals samples, SS 304L and steel C20, decreases as the immersion times were increased, and tapers to a constant value.

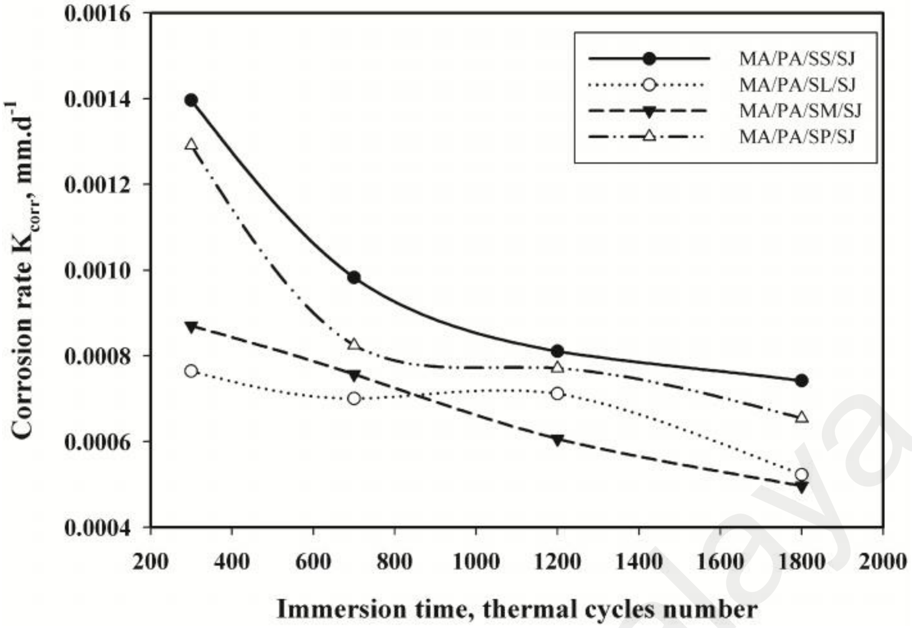


Figure 4.37. The changes of corrosion rate as a function of immersion time (thermal cycles) of SS 304L immersed in prepared eutectic composite phase change materials (CPCMs)

Fig. 4.37 shows that the SS 304L samples with MA/PA/SL/SJ eutectic composite mixture gave the lowest corrosion rates of 7.6 10^{-4} mg.d^{-1} and 7.0 mg.d^{-1} for the immersion times of 300 and 700 thermal cycles, respectively. There is a slight increase at 1200 thermal cycles and decrease at 1800 thermal cycles. The lowest corrosion rates of 6.0 mg.d^{-1} and 4.9 mg.d^{-1} were obtained for SS 304L with MA/PA/SM/SJ eutectic composite at immersion times of 1200 and 1800 thermal cycles, respectively. The highest corrosion rate value were obtained for SS 304L samples immersed in MA/PA/SS/SJ and followed by MA/PA/SP/SJ, subjected to immersion times of 300, 700, 1200, and 1800 thermal cycles, respectively.

In addition, Fig. 4.38 also shows that C20 samples immersed with MA/PA/SS/SJ eutectic composite mixture has the lowest corrosion rate values for immersion times of 300, 700, 1200, and 1800 thermal cycles, as compared to its corrosion rate immersed with MA/PASL/SJ, MA/PA/SP/SJ, and MA/PA/SM/SJ eutectic composite mixtures, respectively.

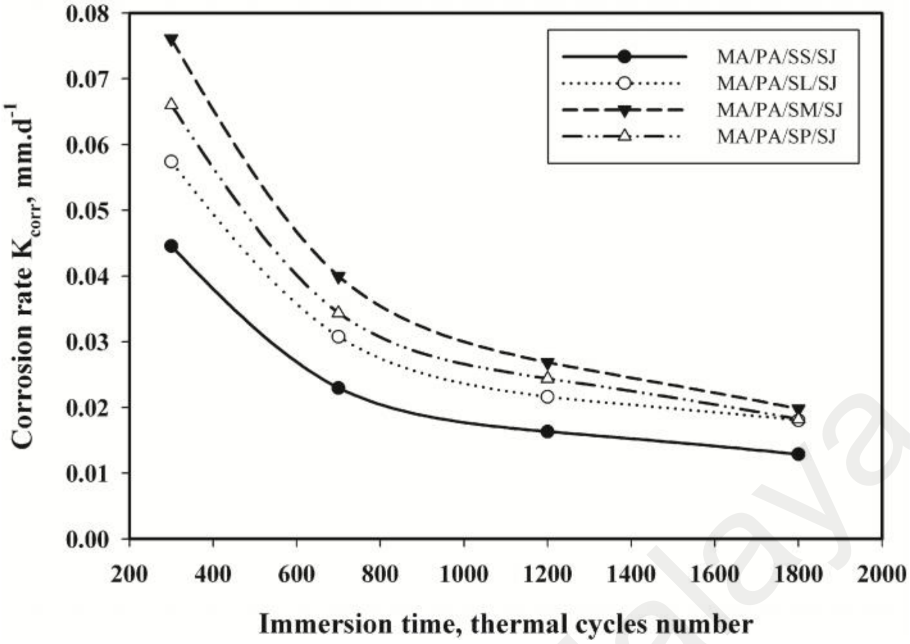


Figure 4.38. The changes of corrosion rate as a function of immersion time (thermal cycles) of steel C20 immersed in prepared eutectic composite phase change materials (CPCMs)

Studies on the compatibility of metal samples with PCM have been conducted in the past by several researchers. Sari and Kaygusuz (2003) investigated the weight loss and corrosion rate of selected metal samples of SS 304L, steel C20, Al, and Cu immersed with stearic acid (SA), palmitic acid (PA), myristic acid (MA), and lauric acid (LA). The results have shown that SS 304L and Al were resistant to corrosion, immersed in SA, PA, MA, and LA, respectively. Steel C20 was shown to be corrosion resistant to SA, MA, and LA, but have slightly corroded to PA. Cu has shown slight corrosion with all PCMs of SA, PA, MA, and LA. The study has reported the highest corrosion rate calculated were 3.4 10^{-2} and 4.9 10^{-2} mg/d for steel C20 in contact with myristic acid and Cu in contact with stearic acid, respectively. The lowest corrosion was also determined in the level of 10^{-4} mg/d for all metal samples (Sari & Kaygusuz, 2003).

This study has indicated the compatibility of prepared CPCMs of (MA/PA/SS/SJ), (MA/PA/SL/SJ), (MA/PA/SM/SJ), and (MA/PA/SP/SJ) with container construction materials of stainless steel (SS 304L) and carbon steel (steel C20). These two materials have shown good chemical resistivity and are deemed suitable for long time use in LHTES systems.

Abhat, A. (1983). Low temperature latent heat thermal energy storage: Heat storage materials. *Solar Energy, 30*(4), 313-332. doi:10.1016/0038-092x(83)90186-x

Alkan, C., & Sari, A. (2008). Fatty acid/poly(methyl methacrylate) (PMMA) blends as form-stable phase change materials for latent heat thermal energy storage. *Solar Energy, 82*(2), 118-124. doi:http://dx.doi.org/10.1016/j.solener.2007.07.001

Astm, E. (2006). 06a Standard Test Method for Measurement of Fracture Toughness. *Annual Book of Astm Standards. Philadelphia PA: American Society for Testing and Materials*.

Bo, H., Gustafsson, E. M., & Setterwall, F. (1999). Tetradecane and hexadecane binary mixtures as phase change materials (PCMs) for cool storage in district cooling systems. *Energy, 24*(12), 1015-1028. doi:10.1016/s0360-5442(99)00055-9

Dodd, J. W., Tonge, K. H., & Currell, B. R. (1987). *Thermal methods*.

Farid, M. M., Khudhair, A. M., Razack, S. A. K., & Al-Hallaj, S. (2004). A review on phase change energy storage: materials and applications. *Energy Conversion and Management, 45*(9–10), 1597-1615. doi:10.1016/j.enconman.2003.09.015

Fauzi, H., Metselaar, H. S. C., Mahlia, T. M. I., & Silakhori, M. (2014). Thermo-physical stability of fatty acid eutectic mixtures subjected to accelerated aging for thermal energy storage (TES) application. *Applied Thermal Engineering, 66*(1–2), 328-334. doi:http://dx.doi.org/10.1016/j.applthermaleng.2014.02.014

Fauzi, H., Metselaar, H. S. C., Mahlia, T. M. I., Silakhori, M., & Nur, H. (2013). Phase change material: Optimizing the thermal properties and thermal conductivity of myristic acid/palmitic acid eutectic mixture with acid-based surfactants. *Applied Thermal Engineering, 60*(1–2), 261-265. doi:http://dx.doi.org/10.1016/j.applthermaleng.2013.06.050

Hasan, A., & Sayigh, A. A. (1994). Some fatty acids as phase-change thermal energy storage materials. *Renewable Energy, 4*(1), 69-76. doi:http://dx.doi.org/10.1016/0960-1481(94)90066-3

Hasnain, S. M. (1998). Review on sustainable thermal energy storage technologies, Part I: heat storage materials and techniques. *Energy Conversion and Management, 39*(11), 1127-1138. doi:http://dx.doi.org/10.1016/S0196-8904(98)00025-9

Karaipekli, A., & Sarı, A. (2008). Capric–myristic acid/expanded perlite composite as form-stable phase change material for latent heat thermal energy storage. *Renewable Energy, 33*(12), 2599-2605. doi:http://dx.doi.org/10.1016/j.renene.2008.02.024

Karaıpeklı, A., Sarı, A., & Kaygusuz, K. (2009). Thermal Properties and Thermal Reliability of Capric Acid/Stearic Acid Mixture for Latent Heat Thermal Energy Storage. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 31*(3), 199-207. doi:10.1080/15567030701522369

Kim, S., & Drzal, L. T. (2009). High latent heat storage and high thermal conductive phase change materials using exfoliated graphite nanoplatelets. *Solar Energy Materials and Solar Cells, 93*(1), 136-142. doi:http://dx.doi.org/10.1016/j.solmat.2008.09.010

Lane, G. A. (1980). Low temperature heat storage with phase change materials. *International Journal of Ambient Energy, 1*(3), 155-168. doi:10.1080/01430750.1980.9675731

Matsui, T., Yoshida, M., Yamasaki, H., & Hatate, Y. (2007). Thermal Properties of Multicomponent Fatty Acids as Solid-Liquid Phase Change Materials for Cooling Applications. *Chemical Engineering Communications, 194*(1), 129-139. doi:10.1080/00986440600715920

Mehling, H., & Cabeza, L. (2008). Basic thermodynamics of thermal energy storage *Heat and cold storage with PCM* (pp. 1-10): Springer Berlin Heidelberg.

Nomura, T., Okinaka, N., & Akiyama, T. (2009). Impregnation of porous material with phase change material for thermal energy storage. *Materials Chemistry and Physics, 115*(2–3), 846-850. doi:http://dx.doi.org/10.1016/j.matchemphys.2009.02.045

Sarı, A. (2003). Thermal reliability test of some fatty acids as PCMs used for solar thermal latent heat storage applications. *Energy Conversion and Management, 44*(14), 2277-2287. doi:10.1016/s0196-8904(02)00251-0

Sarı, A. (2005). Eutectic mixtures of some fatty acids for low temperature solar heating applications: Thermal properties and thermal reliability. *Applied Thermal Engineering, 25*(14–15), 2100-2107. doi:http://dx.doi.org/10.1016/j.applthermaleng.2005.01.010

Sarı, A., & Karaipekli, A. (2007). Thermal conductivity and latent heat thermal energy storage characteristics of paraffin/expanded graphite composite as phase change material. *Applied Thermal Engineering, 27*(8–9), 1271-1277. doi:http://dx.doi.org/10.1016/j.applthermaleng.2006.11.004

Sarı, A., & Kaygusuz, K. (2003). Some fatty acids used for latent heat storage: thermal stability and corrosion of metals with respect to thermal cycling. *Renewable Energy, 28*(6), 939-948. doi:http://dx.doi.org/10.1016/S0960-1481(02)00110-6

Sarı, A., Sarı, H., & Önal, A. (2004). Thermal properties and thermal reliability of eutectic mixtures of some fatty acids as latent heat storage materials. *Energy Conversion and Management, 45*(3), 365-376. doi:http://dx.doi.org/10.1016/S0196-8904(03)00154-7

Sharma, A., Sharma, S. D., & Buddhi, D. (2002). Accelerated thermal cycle test of acetamide, stearic acid and paraffin wax for solar thermal latent heat storage applications. *Energy Conversion and Management, 43*(14), 1923-1930. doi:10.1016/s0196-8904(01)00131-5

Sharma, S. D., Buddhi, D., & Sawhney, R. L. (1999). Accelerated thermal cycle test of latent heat-storage materials. *Solar Energy, 66*(6), 483-490. doi:http://dx.doi.org/10.1016/S0038-092X(99)00045-6

Zalba, B., Marín, J. M., Cabeza, L. F., & Mehling, H. (2003). Review on thermal energy storage with phase change: materials, heat transfer analysis and applications. *Applied Thermal Engineering, 23*(3), 251-283. doi:10.1016/s1359-4311(02)00192-8

Zhang, J.-J., Zhang, J.-L., He, S.-M., Wu, K.-Z., & Liu, X.-D. (2001). Thermal studies on the solid–liquid phase transition in binary systems of fatty acids. *Thermochimica Acta, 369*(1–2), 157-160. doi:http://dx.doi.org/10.1016/S0040-6031(00)00766-8

Zhang, Z., & Fang, X. (2006). Study on paraffin/expanded graphite composite phase change thermal energy storage material. *Energy Conversion and Management, 47*(3), 303-310. doi:http://dx.doi.org/10.1016/j.enconman.2005.03.004

Zhou, D., & Zhao, C. Y. (2011). Experimental investigations on heat transfer in phase change materials (PCMs) embedded in porous materials. *Applied Thermal Engineering, 31*(5), 970-977. doi:http://dx.doi.org/10.1016/j.applthermaleng.2010.11.022

Zhou, D., Zhao, C. Y., & Tian, Y. (2012). Review on thermal energy storage with phase change materials (PCMs) in building applications. *Applied Energy, 92*(0), 593-605. doi:http://dx.doi.org/10.1016/j.apenergy.2011.08.025

Zhou, M., Bi, H., Lin, T., Lü, X., Wan, D., Huang, F., & Lin, J. (2014). Heat transport enhancement of thermal energy storage material using graphene/ceramic composites. *Carbon, 75*(0), 314-321. doi:10.1016/j.carbon.2014.04.009

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The performance of a latent heat thermal energy storage (LHTES) system is dependent on its thermal energy storage material, which is normally in the form of a phase change material (PCM). A high-performing PCM is characterized with good thermo-physical and chemical characteristics for it to be able to store and release large amount of thermal energy. It is expected that the PCM possess the required thermo-physical properties such as having the phase transition temperature suitable for the required application, high latent heat capacity, high thermal conductivity, minimal undercooling, and small volume changes. Similarly, the chemical characteristic required is for the PCM materials to have no phase separation, non-toxic, and compatible with the container materials.

The proposed Phase Change Material (PCM) in this study is designed to be used in domestic solar water heating applications for tropical countries such as Malaysia, Indonesia, and other ASEAN countries, with an operating temperature in the range of 40-45 ^{o}C. The phase change material chosen is based on the combination of fatty acids with subsequent improvement in the form of additives and impregnations of porous materials.

The proposed PCM is based on a eutectic binary mixture of two kinds of fatty acids, namely, myristic acids (T_m: 54.70^{o}C, T_s: 52.58^{o}C; $\Delta H_{f,m}$: 161.37 J.g^{-1}, $\Delta H_{f,s}$: 161.14 J.g^{-1}) and palmitic acid (T_m: 63.08^{o}C, T_s: 61.90^{o}C; $\Delta H_{f,m}$: 173.69 J.g^{-1}, $\Delta H_{f,s}$: 172.92 J.g^{-1}). 5 - 20 wt.% of acid based surfactant such as sodium stearate (SS), sodium laurate (SL), sodium myristate (SM), and sodium palmitate (SP) were subsequently added to the eutectic mixture improve the latent heat capacity of the material and to decrease the phase transition temperature to within the range of the required application. The surfactants added also control the undercooling problems present during thermal absorbing/releasing processes.

The eutectic PCM with the best composition of surfactants was evaluated using a thermal cyclic test to assess the stability of thermal properties, chemical structure, and physical change of the eutectic PCM after a prolonged heating/cooling cycles. A composite phase change material (CPCM) were subsequently developed by impregnation of a porous material in the form of 1 – 5 wt.% of *shorea javanica* derived from damar gum trees. Finally, the compatibility of the composite phase change material (CPCM) with container materials of stainless steel (SS 304L) and carbon steel (steel C20) were tested using gravimetric analysis to measure weight loss and corrosion rate of the CPCMs.

The conclusions for this study are summarised as follows:

i. A novel eutectic phase change material (PCM), having the thermal characteristics near to the phase transition temperature range for domestic water heating application, was successfully developed based on a binary mixture of pure myristic acid (MA) and palmitic acid (PA). The eutectic PCM has a composition ratio of 70 wt.% myristic acid and 30 wt.% palmitic acid. Furthermore, the addition of acid based surfactants, sodium stearate (SS) 5 wt.%, sodium laurate (SL) 10 wt.%, sodium myristate (SM) 5 wt.%, and sodium palmitate (SP) 5 wt.%, showed a significant effect on reducing the under cooling temperature by 0.81 ^{o}C, 0.43 ^{o}C, 0.34 ^{o}C, and 0.4 ^{o}C, and the phase transition temperatures of the eutectic PCM by 4.92 ^{o}C, 4.73 ^{o}C, 5.37 ^{o}C, 5.15 ^{o}C, respectively. The addition of 5 wt.% sodium stearate (SS), 10 wt.% sodium laurate (SL), 5 wt.% sodium myristate (SM), and 5 wt.% sodium palmitate (SP), had also enhanced the latent heat capacity and thermal conductivity of the eutectic PCM, which were increased by 36.42 J.g^{-1}, 15.14 J.g^{-1}, 23.69 J.g^{-1}, and 28.71 J.g^{-1}, and 0.005 W m^{-1} K^{-1}, 0.010 W m^{-1} K^{-1}, 0.017 W m^{-1} K^{-1}, and 0.011 W m^{-1} K^{-1}, respectively.

ii. The thermo-physical stability of MA/PA/SS, MA/PA/SL, MA/PA/SM, and MA/PA/SP eutectic mixtures were better than MA/PA eutectic mixtures after a prolonged period of thermal reliability test. This was evident from the small decrease on latent heat of fusion and acceptable levels of irregular changes in the phase transition temperature of the materials. These also confirm by the volume expansion of the prepared MA/PA/SS, MA/PA/SL, MA/PA/SM, and MA/PA/SP eutectic mixture were small and are acceptable to be considered as a PCM in thermal energy storage (TES) applications.

iii. The impregnations of *shorea javanica* in amounts of 3 wt.% into MA/PA/SS, 2 wt.% into MA/PA/SL, 3 wt.% into MA/PA/SM, and 3 wt.% into MA/PA/SP eutectic mixture, forming the eutectic composite phase change materials (CPCMs), have improved the thermal conductivity and enhanced the heat transfer characteristic of the CPCMs without significant decrease in their thermal properties. The *shorea javanica* also does not show any chemical reaction with each component in the eutectic composite mixtures. The developed eutectic CPCMs with *shorea javanica* have a good thermal stability, as indicated by zero weight degradation within the working temperature envelope of 30 to 170 ºC.

iv. A gravimetric analysis has shown that the prepared CPCMs have good compatibility with stainless steel (SS 304L) and carbon steel (steel C20) as container materials after immersion length of 1,800 thermal cycles, corresponding to 5 years utilization period.

Therefore, it can be concluded that the novel composite phase change material formulated from fatty acids and suitable additives, as proposed in this study, have met all the important characteristic of thermal properties, physical properties, and chemical properties as required for usage in domestic water heating applications.

5.2 Recommendations

The following recommendation are offered as possible way to complete this study in future work.

i. A shape-stabilized method proposed to handle the physical leakage possibility of prepared composite phase change materials (CPCMs) in thermal energy storage devises container.

ii. Development a lab model, prototype, and pilot unit of heat exchanger which is applicable to solar water heater application and calculate the exactly volume of container that allow CPCMs to keep enough heat to use during sun light off.

iii. Analysis the heat transfer phenomena and thermodynamic performance of CPCM in heat exchanger prototype during heat absorbing and heat releasing processes.

iv. Analysis of mathematical simulation and models to predict performance of solar water heating system and compare it with prototype performance.

REFERENCES

¹ùÇ¿, Í. (2014). Preparation and Characterization of Sodium Sulfate/Silica Composite as a Shape-stabilized Phase Change Material by Sol-gel Method. *Chinese Journal of Chemical Engineering, 22*(3), 360-364.

Abhat, A. (1983). Low temperature latent heat thermal energy storage: Heat storage materials. *Solar Energy, 30*(4), 313-332.

Absi Halabi, M., Al-Qattan, A., & Al-Otaibi, A. (2015). Application of solar energy in the oil industry—Current status and future prospects. *Renewable and Sustainable Energy Reviews, 43*(0), 296-314.

Agency, I. E. (2013). Key World Energy Statistics. 82.

Alkan, C., & Sari, A. (2008). Fatty acid/poly(methyl methacrylate) (PMMA) blends as form-stable phase change materials for latent heat thermal energy storage. *Solar Energy, 82*(2), 118-124.

Arkar, C., & Medved, S. (2015). Optimization of latent heat storage in solar air heating system with vacuum tube air solar collector. *Solar Energy, 111*(0), 10-20.

Birchenall, C. E., & Riechman, A. F. (1980). Heat storage in eutectic alloys. *Metallurgical and Materials Transactions A, 11*(8), 1415-1420.

Biswas, D. P. (1977). Thermal energy storage using sodium sulfate decahydrate and water. *Solar Energy, 19*, 99.

Bo, H., Gustafsson, E. M., & Setterwall, F. (1999). Tetradecane and hexadecane binary mixtures as phase change materials (PCMs) for cool storage in district cooling systems. *Energy, 24*(12), 1015-1028.

Buddhi, D., Sawhney, R., Sehgal, P., & Bansal, N. (1987). A simplification of the differential thermal analysis method to determine the latent heat of fusion of phase change materials. *Journal of Physics D: Applied Physics, 20*(12), 1601.

Buddhi, D., & Sharma, S. (1999). Measurements of transmittance of solar radiation through stearic acid: a latent heat storage material. *Energy Conversion and Management, 40*(18), 1979-1984.

Bugaje, I. (1997). Enhancing the thermal response of latent heat storage systems. *International Journal of Energy Research, 21*(9), 759-766.

Cabeza, L., Illa, J., Roca, J., Badia, F., Mehling, H., Hiebler, S., & Ziegler, F. (2001). Immersion corrosion tests on metal-salt hydrate pairs used for latent heat storage in the 32 to 36° C temperature range. *Materials and Corrosion, 52*(2), 140-146.

Cabeza, L., Roca, J., Nogués, M., Mehling, H., & Hiebler, S. (2002). Immersion corrosion tests on metal-salt hydrate pairs used for latent heat storage in the 48 to 58° C temperature range. *Materials and Corrosion, 53*(12), 902-907.

Cabeza, L. F., Castell, A., Barreneche, C., de Gracia, A., & Fernández, A. I. (2011). Materials used as PCM in thermal energy storage in buildings: A review. *Renewable and Sustainable Energy Reviews, 15*(3), 1675-1695.

Cabeza, L. F., Ibáñez, M., Sole, C., Roca, J., & Nogués, M. (2006). Experimentation with a water tank including a PCM module. *Solar Energy Materials and Solar Cells, 90*(9), 1273-1282.

Cabeza, L. F., Svensson, G., Hiebler, S., & Mehling, H. (2003). Thermal performance of sodium acetate trihydrate thickened with different materials as phase change energy storage material. *Applied Thermal Engineering, 23*(13), 1697-1704.

Canseco, V., Anguy, Y., Roa, J. J., & Palomo, E. (2014). Structural and mechanical characterization of graphite foam/phase change material composites. *Carbon, 74*(0), 266-281.

Chaiyasat, P., Noppalit, S., Okubo, M., & Chaiyasat, A. (2015). Do encapsulated heat storage materials really retain their original thermal properties? *Physical Chemistry Chemical Physics*.

Chandra, D., Chellappa, R., & Chien, W.-M. (2005). Thermodynamic assessment of binary solid-state thermal storage materials. *Journal of Physics and Chemistry of Solids, 66*(2), 235-240.

Chen, Y., Zhang, S., Zhang, Q., Chen, Y., & Zhang, Y. (2014). Composite phase change materials prepared by encapsuling paraffin in PVC macrocapsules. *Thermochimica Acta, 578*(0), 10-14.

Delgado, M., Lázaro, A., Mazo, J., & Zalba, B. (2012). Review on phase change material emulsions and microencapsulated phase change material slurries: materials, heat transfer studies and applications. *Renewable and Sustainable Energy Reviews, 16*(1), 253-273.

Dimaano, M. N. R., & Watanabe, T. (2002). The capric–lauric acid and pentadecane combination as phase change material for cooling applications. *Applied Thermal Engineering, 22*(4), 365-377.

Dincer, I. (2002). On thermal energy storage systems and applications in buildings. *Energy and Buildings, 34*(4), 377-388.

Dincer, I., & Rosen, M. (2002). *Thermal energy storage: systems and applications*: John Wiley & Sons.

Dodd, J. W., Tonge, K. H., & Currell, B. R. (1987). *Thermal methods*.

Elgafy, A., & Lafdi, K. (2005). Effect of carbon nanofiber additives on thermal behavior of phase change materials. *Carbon*, *43*(15), 3067-3074.

Ettouney, H., Alatiqi, I., Al-Sahali, M., & Al-Hajirie, K. (2006). Heat transfer enhancement in energy storage in spherical capsules filled with paraffin wax and metal beads. *Energy Conversion and Management*, *47*(2), 211-228.

Ettouney, H. M., Alatiqi, I., Al-Sahali, M., & Al-Ali, S. A. (2004). Heat transfer enhancement by metal screens and metal spheres in phase change energy storage systems. *Renewable Energy, 29*(6), 841-860.

Fang, G., Li, H., Chen, Z., & Liu, X. (2011). Preparation and properties of palmitic acid/SiO2 composites with flame retardant as thermal energy storage materials. *Solar Energy Materials and Solar Cells, 95*(7), 1875-1881.

Farid, M. M., & Husian, R. M. (1990). An electrical storage heater using the phase-change method of heat storage. *Energy Conversion and Management*, *30*(3), 219-230.

Farid, M. M., Khudhair, A. M., Razack, S. A. K., & Al-Hallaj, S. (2004). A review on phase change energy storage: materials and applications. *Energy Conversion and Management*, *45*(9–10), 1597-1615.

Farid, M. M., Kim, Y., & Kansawa, A. (1990). Thermal performance of a heat storage module using PCM's with different melting temperature; Experimental. *Journal Name: Journal of Solar Energy Engineering; (USA); Journal Volume: 112:2*, Medium: X; Size: Pages: 125-131.

Farid, M. M., & Mohamed, A. K. (1987). Effect Of Natural Convection On The Process Of Melting and Solidification of Paraffin Wax. *Chemical Engineering Communications*, *57*(1-6), 297-316.

Farrell, A. J., Norton, B., & Kennedy, D. M. (2006). Corrosive effects of salt hydrate phase change materials used with aluminium and copper. *Journal of materials processing technology, 175*(1), 198-205.

Feldman, D., Shapiro, M. M., Banu, D., & Fuks, C. J. (1989). Fatty acids and their mixtures as phase-change materials for thermal energy storage. *Solar Energy Materials, 18*(3–4), 201-216.

Fiedler, T., Öchsner, A., Belova, I. V., & Murch, G. E. (2008). *Thermal conductivity enhancement of compact heat sinks using cellular metals.* Paper presented at the Defect and Diffusion Forum.

Fukai, J., Hamada, Y., Morozumi, Y., & Miyatake, O. (2002). Effect of carbon-fiber brushes on conductive heat transfer in phase change materials. *International Journal of Heat and Mass Transfer, 45*(24), 4781-4792.

Fukai, J., Hamada, Y., Morozumi, Y., & Miyatake, O. (2003). Improvement of thermal characteristics of latent heat thermal energy storage units using carbon-fiber brushes: experiments and modeling. *International Journal of Heat and Mass Transfer, 46*(23), 4513-4525.

Fukai, J., Kanou, M., Kodama, Y., & Miyatake, O. (2000). Thermal conductivity enhancement of energy storage media using carbon fibers. *Energy Conversion and Management, 41*(14), 1543-1556.

Ge, Z., Ye, F., & Ding, Y. (2014). Composite Materials for Thermal Energy Storage: Enhancing Performance through Microstructures. *ChemSusChem*.

Gibbs, B., & Hasnain, S. (1995). *DSC study of technical grade phase change heat storage materials for solar heating applications*.

Gil, A., Medrano, M., Martorell, I., Lázaro, A., Dolado, P., Zalba, B., & Cabeza, L. F. (2010). State of the art on high temperature thermal energy storage for power generation. Part 1—Concepts, materials and modellization. *Renewable and Sustainable Energy Reviews, 14*(1), 31-55.

Giro-Paloma, J., Barreneche, C., Delgado, M., Martínez, M., Fernández, A. I., & Cabeza, L. F. (2014). Physicochemical and Thermal Study of a MPCM of PMMA Shell and Paraffin Wax as a Core. *Energy Procedia, 48*(0), 347-354.

Gong, Z.-X., & Mujumdar, A. S. (1996). Enhancement of energy charge-discharge rates in composite slabs of different phase change materials. *International Journal of Heat and Mass Transfer, 39*(4), 725-733.

Groll, M., Brost, O., & Heine, D. (1990). Corrosion of steels in contact with salt eutectics as latent heat storage materials: Influence of water and other impurities. *Heat Recovery Systems and CHP, 10*(5–6), 567-572.

Hadjieva, M., & Argirov, J. (1992). Thermophysical properties of some paraffins applicable to thermal energy storage. *Solar Energy Materials and Solar Cells, 27*(2), 181-187.

Haillot, D., Py, X., Goetz, V., & Benabdelkarim, M. (2008). Storage composites for the optimisation of solar water heating systems. *chemical engineering research and design, 86*(6), 612-617.

Hamada, Y., & Fukai, J. (2005). Latent heat thermal energy storage tanks for space heating of buildings: comparison between calculations and experiments. *Energy Conversion and Management, 46*(20), 3221-3235.

Hamada, Y., Ohtsu, W., & Fukai, J. (2003). Thermal response in thermal energy storage material around heat transfer tubes: effect of additives on heat transfer rates. *Solar Energy, 75*(4), 317-328.

Hamada, Y., Otsu, W., Fukai, J., Morozumi, Y., & Miyatake, O. (2005). Anisotropic heat transfer in composites based on high-thermal conductive carbon fibers. *Energy, 30*(2), 221-233.

Hasan, A., & Sayigh, A. A. (1994). Some fatty acids as phase-change thermal energy storage materials. *Renewable Energy, 4*(1), 69-76.

Hasnain, S. M. (1998). Review on sustainable thermal energy storage technologies, Part I: heat storage materials and techniques. *Energy Conversion and Management, 39*(11), 1127-1138.

Heine, D. (1981). *The chemical compatibility of construction materials with latent heat storage materials.* Paper presented at the Proceedings of the International Conference on Energy Storage, Brighton, UK.

Himran, S., Suwono, A., & Mansoori, G. A. (1994). Characterization of Alkanes and Paraffin Waxes for Application as Phase Change Energy Storage Medium. *Energy Sources, 16*(1), 117-128.

Inagaki, M., Kaburagi, Y., & Hishiyama, Y. (2014). Thermal Management Material: Graphite. *Advanced Engineering Materials*.

International, A. (2011). *Standard test method for measurement of fracture toughness*: ASTM International.

IRENA, I.-E. a. (2013). Thermal Energy Storage, Technology Brief.

Jäger, K., Isabella, O., Smets, A., van Swaaij, R., & Zeman, M. (2014). Solar Energy. Fundamentals, Technology, and Systems. *Delft University of Technology*.

Jeong, S.-G., Jeon, J., Lee, J.-H., & Kim, S. (2013). Optimal preparation of PCM/diatomite composites for enhancing thermal properties. *International Journal of Heat and Mass Transfer, 62*(0), 711-717.

Jeong, S.-G., Lee, J.-H., Seo, J., & Kim, S. (2014). Thermal performance evaluation of Bio-based shape stabilized PCM with boron nitride for energy saving. *International Journal of Heat and Mass Transfer, 71*(0), 245-250.

Jian, Y., Falcoz, Q., Neveu, P., Bai, F., Wang, Y., & Wang, Z. (2015). Design and optimization of solid thermal energy storage modules for solar thermal power plant applications. *Applied Energy, 139*(0), 30-42.

Karaipekli, A., Sari, A., & Kaygusuz, K. (2008). Thermal Properties and Long-term Reliability of Capric Acid/Lauric Acid and Capric Acid/Myristic Acid Mixtures for Thermal Energy Storage. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 30*(13), 1248-1258.

Karaıpeklı, A., Sarı, A., & Kaygusuz, K. (2009). Thermal Properties and Thermal Reliability of Capric Acid/Stearic Acid Mixture for Latent Heat Thermal Energy Storage. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 31*(3), 199-207.

Kauranen, P., Peippo, K., & Lund, P. D. (1991). An organic PCM storage system with adjustable melting temperature. *Solar Energy, 46*(5), 275-278.

Kaygusuz, K., & Sari, A. (2007). High density polyethylene/paraffin composites as form-stable phase change material for thermal energy storage. *Energy Sources, Part A, 29*(3), 261-270.

Kenisarin, M., & Mahkamov, K. (2007). Solar energy storage using phase change materials. *Renewable and Sustainable Energy Reviews, 11*(9), 1913-1965.

Khodadadi, J., & Hosseinizadeh, S. (2007). Nanoparticle-enhanced phase change materials (NEPCM) with great potential for improved thermal energy storage. *International Communications in Heat and Mass Transfer, 34*(5), 534-543.

Khodadadi, J. M., Fan, L., & Babaei, H. (2013). Thermal conductivity enhancement of nanostructure-based colloidal suspensions utilized as phase change materials for thermal energy storage: A review. *Renewable and Sustainable Energy Reviews, 24*(0), 418-444.

Kim, S., & Drzal, L. T. (2009). High latent heat storage and high thermal conductive phase change materials using exfoliated graphite nanoplatelets. *Solar Energy Materials and Solar Cells, 93*(1), 136-142.

Kim, T., France, D. M., Yu, W., Zhao, W., & Singh, D. (2014). Heat transfer analysis of a latent heat thermal energy storage system using graphite foam for concentrated solar power. *Solar Energy, 103*(0), 438-447.

KMGroup, U. (2012). Solar Update. *The Newsletter of the IEA Solar Heating and Cooling Programme, 55*, 12.

KMGroup, U. (2013). Solar Update. *The Newsletter of the IEA Solar Heating and Cooling Programme, 57*, 10.

Krishnan, S., Murthy, J. Y., & Garimella, S. V. (2005). A two-temperature model for solid-liquid phase change in metal foams. *Journal of Heat Transfer, 127*(9), 995-1004.

Lachheb, M., Karkri, M., Albouchi, F., Mzali, F., & Nasrallah, S. B. (2014). Thermophysical properties estimation of paraffin/graphite composite phase change material using an inverse method. *Energy Conversion and Management, 82*(0), 229-237.

Lane, G. A. (1980). Low temperature heat storage with phase change materials. *International Journal of Ambient Energy, 1*(3), 155-168.

Lane, G. A. (1983). *Solar heat storage: Latent heat materials*.

Li, G., Zhang, B., Li, X., Zhou, Y., Sun, Q., & Yun, Q. (2014). The preparation, characterization and modification of a new phase change material: CaCl2·6H2O–MgCl2·6H2O eutectic hydrate salt. *Solar Energy Materials and Solar Cells, 126*(0), 51-55.

Li, X., Sanjayan, J. G., & Wilson, J. L. (2014). Fabrication and stability of form-stable diatomite/paraffin phase change material composites. *Energy and Buildings, 76*(0), 284-294.

Liu, M., Saman, W., & Bruno, F. (2012). Review on storage materials and thermal performance enhancement techniques for high temperature phase change thermal storage systems. *Renewable and Sustainable Energy Reviews, 16*(4), 2118-2132.

Matsui, T., Yoshida, M., Yamasaki, H., & Hatate, Y. (2007). Thermal Properties of Multicomponent Fatty Acids as Solid-Liquid Phase Change Materials for Cooling Applications. *Chemical Engineering Communications, 194*(1), 129-139.

Mehling, H., & Cabeza, L. F. (2007). Phase change materials and their basic properties *Thermal energy storage for sustainable energy consumption* (pp. 257-277): Springer.

Mehling, H., & Cabeza, L. F. (2008). *Heat and cold storage with PCM*: Springer.

Mehling, H., Cabeza, L. F., & Yamaha, M. (2007). Phase change materials: application fundamentals *Thermal Energy Storage for Sustainable Energy Consumption* (pp. 279-313): Springer.

Mehling, H., Hiebler, S., & Ziegler, F. (2000). *Latent heat storage using a PCM-graphite composite material.* Paper presented at the Proceedings of TERRASTOCK.

Mesalhy, O., Lafdi, K., Elgafy, A., & Bowman, K. (2005). Numerical study for enhancing the thermal conductivity of phase change material (PCM) storage using high thermal conductivity porous matrix. *Energy Conversion and Management, 46*(6), 847-867.

Mettawee, E.-B. S., & Assassa, G. M. (2007). Thermal conductivity enhancement in a latent heat storage system. *Solar Energy, 81*(7), 839-845.

Moeini Sedeh, M., & Khodadadi, J. M. (2013). Thermal conductivity improvement of phase change materials/graphite foam composites. *Carbon, 60*(0), 117-128.

Nakaso, K., Teshima, H., Yoshimura, A., Nogami, S., Hamada, Y., & Fukai, J. (2008). Extension of heat transfer area using carbon fiber cloths in latent heat thermal energy storage tanks. *Chemical Engineering and Processing: Process Intensification, 47*(5), 879-885.

Nikolić, R., Marinović-Cincović, M., Gadžurić, S., & Zsigrai, I. J. (2003). New materials for solar thermal storage—solid/liquid transitions in fatty acid esters. *Solar Energy Materials and Solar Cells, 79*(3), 285-292.

Nomura, T., Okinaka, N., & Akiyama, T. (2009). Impregnation of porous material with phase change material for thermal energy storage. *Materials Chemistry and Physics, 115*(2–3), 846-850.

Paksoy, H. (2012). International Energy Agency Energy Conservation through Energy Storage Programme. *IEA ECES.*

Pielichowska, K., & Pielichowski, K. (2014). Phase change materials for thermal energy storage. *Progress in Materials Science, 65*(0), 67-123.

Pielichowski, K., & Flejtuch, K. (2003a). Binary blends of polyethers with fatty acids: a thermal characterization of the phase transitions. *Journal of applied polymer science, 90*(3), 861-870.

Pielichowski, K., & Flejtuch, K. (2003b). Differential scanning calorimetry study of blends of poly (ethylene glycol) with selected fatty acids. *Macromolecular Materials and Engineering, 288*(3), 259-264.

Pillai, K., & Brinkworth, B. (1976). The storage of low grade thermal energy using phase change materials. *Applied Energy, 2*(3), 205-216.

Pincemin, S., Olives, R., Py, X., & Christ, M. (2008). Highly conductive composites made of phase change materials and graphite for thermal storage. *Solar Energy Materials and Solar Cells, 92*(6), 603-613.

Pincemin, S., Py, X., Olives, R., Christ, M., & Oettinger, O. (2008). Elaboration of conductive thermal storage composites made of phase change materials and graphite for solar plant. *Journal of solar energy engineering, 130*(1), 011005.

Porisini, F. C. (1988). Salt hydrates used for latent heat storage: Corrosion of metals and reliability of thermal performance. *Solar Energy, 41*(2), 193-197.

Rathod, M. K., & Banerjee, J. (2013). Thermal stability of phase change materials used in latent heat energy storage systems: A review. *Renewable and Sustainable Energy Reviews, 18*(0), 246-258.

Renyun, S. J. Z. (2005). Review of Thermal Energy Storage with Metal Phase Change Materials [J]. *Materials Review, 8*, 027.

Roxas-Dimaano, M., & Watanabe, T. (2002). The capric and lauric acid mixture with chemical additives as latent heat storage materials for cooling application. *Energy, 27*(9), 869-888.

Rozanna, D., Chuah, T. G., Salmiah, A., Choong, T. S. Y., & Sa'ari, M. (2005). Fatty Acids as Phase Change Materials (PCMs) for Thermal Energy Storage: A Review. *International Journal of Green Energy, 1*(4), 495-513.

Sahan, N., & Paksoy, H. O. (2014). Thermal enhancement of paraffin as a phase change material with nanomagnetite. *Solar Energy Materials and Solar Cells, 126*(0), 56-61.

Sarı, A. (2003a). Thermal characteristics of a eutectic mixture of myristic and palmitic acids as phase change material for heating applications. *Applied Thermal Engineering, 23*(8), 1005-1017.

Sarı, A. (2003b). Thermal reliability test of some fatty acids as PCMs used for solar thermal latent heat storage applications. *Energy Conversion and Management, 44*(14), 2277-2287.

Sarı, A. (2005). Eutectic mixtures of some fatty acids for low temperature solar heating applications: Thermal properties and thermal reliability. *Applied Thermal Engineering, 25*(14–15), 2100-2107.

Sarı, A. (2006). Eutectic mixtures of some fatty acids for latent heat storage: Thermal properties and thermal reliability with respect to thermal cycling. *Energy Conversion and Management, 47*(9–10), 1207-1221.

Sarı, A., & Karaipekli, A. (2007). Thermal conductivity and latent heat thermal energy storage characteristics of paraffin/expanded graphite composite as phase change material. *Applied Thermal Engineering, 27*(8–9), 1271-1277.

Sarı, A., & Karaipekli, A. (2012). Fatty acid esters-based composite phase change materials for thermal energy storage in buildings. *Applied Thermal Engineering, 37*(0), 208-216.

Sarı, A., Karaipekli, A., & Alkan, C. (2009). Preparation, characterization and thermal properties of lauric acid/expanded perlite as novel form-stable composite phase change material. *Chemical Engineering Journal, 155*(3), 899-904.

Sari, A., Karaipekli, A., & Kaygusuz, K. (2008). Capric Acid and Myristic Acid for Latent Heat Thermal Energy Storage. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 30*(16), 1498-1507.

Sari, A., & Kaygusuz, K. (2001). Thermal energy storage system using stearic acid as a phase change material. *Solar Energy, 71*(6), 365-376.

Sari, A., & Kaygusuz, K. (2002a). Thermal performance of a eutectic mixture of lauric and stearic acids as PCM encapsulated in the annulus of two concentric pipes. *Solar Energy, 72*(6), 493-504.

Sari, A., & Kaygusuz, K. (2002b). Thermal performance of palmitic acid as a phase change energy storage material. *Energy Conversion and Management, 43*(6), 863-876.

Sarı, A., & Kaygusuz, K. (2001). Thermal performance of myristic acid as a phase change material for energy storage application. *Renewable Energy, 24*(2), 303-317.

Sarı, A., & Kaygusuz, K. (2002). Thermal and heat transfer characteristics in a latent heat storage system using lauric acid. *Energy Conversion and Management, 43*(18), 2493-2507.

Sarı, A., & Kaygusuz, K. (2003). Some fatty acids used for latent heat storage: thermal stability and corrosion of metals with respect to thermal cycling. *Renewable Energy, 28*(6), 939-948.

Sarı, A., Sarı, H., & Önal, A. (2004). Thermal properties and thermal reliability of eutectic mixtures of some fatty acids as latent heat storage materials. *Energy Conversion and Management, 45*(3), 365-376.

Seeniraj, R., Velraj, R., & Narasimhan, N. L. (2002). Heat transfer enhancement study of a LHTS unit containing dispersed high conductivity particles. *Journal of solar energy engineering, 124*(3), 243-249.

Setianingsih, N. (1992). Pemurinian Damar Shorea javanica dengan Menggunakan pelarut Organik dan Bahan Pemucat.

Sharif, M. K. A., Al-Abidi, A. A., Mat, S., Sopian, K., Ruslan, M. H., Sulaiman, M. Y., & Rosli, M. A. M. (2015). Review of the application of phase change material for heating and domestic hot water systems. *Renewable and Sustainable Energy Reviews, 42*(0), 557-568.

Sharma, A., Sharma, S. D., & Buddhi, D. (2002). Accelerated thermal cycle test of acetamide, stearic acid and paraffin wax for solar thermal latent heat storage applications. *Energy Conversion and Management, 43*(14), 1923-1930.

Sharma, A., Sharma, S. D., Buddhi, D., & Sawhney, R. L. (2001). Thermal cycle test of urea for latent heat storage applications. *International Journal of Energy Research, 25*(5), 465-468.

Sharma, A., Tyagi, V. V., Chen, C. R., & Buddhi, D. (2009). Review on thermal energy storage with phase change materials and applications. *Renewable and Sustainable Energy Reviews, 13*(2), 318-345.

Sharma, S. D., Buddhi, D., & Sawhney, R. L. (1999). Accelerated thermal cycle test of latent heat-storage materials. *Solar Energy, 66*(6), 483-490.

Sharma, S. D., & Sagara, K. (2005). Latent Heat Storage Materials and Systems: A Review. *International Journal of Green Energy, 2*(1), 1-56.

Shi, J.-N., Ger, M.-D., Liu, Y.-M., Fan, Y.-C., Wen, N.-T., Lin, C.-K., & Pu, N.-W. (2013). Improving the thermal conductivity and shape-stabilization of phase change materials using nanographite additives. *Carbon, 51*(0), 365-372.

Shilei, L., Neng, Z., & Guohui, F. (2006). Eutectic mixtures of capric acid and lauric acid applied in building wallboards for heat energy storage. *Energy and Buildings, 38*(6), 708-711.

Shukla, A., Buddhi, D., & Sawhney, R. L. (2008). Thermal cycling test of few selected inorganic and organic phase change materials. *Renewable Energy, 33*(12), 2606-2614.

Shukla, A., Buddhi, D., & Sawhney, R. L. (2009). Solar water heaters with phase change material thermal energy storage medium: A review. *Renewable and Sustainable Energy Reviews, 13*(8), 2119-2125.

Solé, A., Miró, L., Barreneche, C., Martorell, I., & Cabeza, L. F. (2014). Corrosion Test of Salt Hydrates and Vessel Metals for Thermochemical Energy Storage. *Energy Procedia, 48*(0), 431-435.

Solé, A., Neumann, H., Niedermaier, S., Cabeza, L. F., & Palomo, E. (2014). Thermal Stability Test of Sugar Alcohols as Phase Change Materials for Medium Temperature Energy Storage Application. *Energy Procedia, 48*(0), 436-439.

Sun, J., Zhang, R., Liu, Z., & Lu, G. (2007). Thermal reliability test of Al–34% Mg–6% Zn alloy as latent heat storage material and corrosion of metal with respect to thermal cycling. *Energy Conversion and Management, 48*(2), 619-624.

Tunçbilek, K., Sari, A., Tarhan, S., Ergüneş, G., & Kaygusuz, K. (2005). Lauric and palmitic acids eutectic mixture as latent heat storage material for low temperature heating applications. *Energy, 30*(5), 677-692.

Tyagi, V. V., & Buddhi, D. (2007). PCM thermal storage in buildings: a state of art. *Renewable and Sustainable Energy Reviews, 11*(6), 1146-1166.

Velraj, R., Seeniraj, R. V., Hafner, B., Faber, C., & Schwarzer, K. (1999). Heat Transfer Enhancement In a Latent Heat Storage System. *Solar Energy, 65*(3), 171-180.

Yin, H., Gao, X., Ding, J., & Zhang, Z. (2008). Experimental research on heat transfer mechanism of heat sink with composite phase change materials. *Energy Conversion and Management, 49*(6), 1740-1746.

Yuan, Y., Yuan, Y., Zhang, N., Du, Y., & Cao, X. (2014). Preparation and thermal characterization of capric–myristic–palmitic acid/expanded graphite composite as phase change material for energy storage. *Materials Letters, 125*(0), 154-157.

Yuan, Y., Zhang, N., Tao, W., Cao, X., & He, Y. (2014). Fatty acids as phase change materials: A review. *Renewable and Sustainable Energy Reviews, 29*(0), 482-498.

Zalba, B., Marín, J. M., Cabeza, L. F., & Mehling, H. (2003). Review on thermal energy storage with phase change: materials, heat transfer analysis and applications. *Applied Thermal Engineering, 23*(3), 251-283.

Zeng, J.-L., Zhu, F.-R., Yu, S.-B., Xiao, Z.-L., Yan, W.-P., Zheng, S.-H., . . . Cao, Z. (2013). Myristic acid/polyaniline composites as form stable phase change materials for thermal energy storage. *Solar Energy Materials and Solar Cells, 114*(0), 136-140.

Zeng, J., Sun, L., Xu, F., Tan, Z., Zhang, Z., Zhang, J., & Zhang, T. (2006). Study of a PCM based energy storage system containing Ag nanoparticles. *Journal of Thermal Analysis and Calorimetry, 87*(2), 371-375.

Zeng, J. L., Cao, Z., Yang, D. W., Sun, L. X., & Zhang, L. (2010). Thermal conductivity enhancement of Ag nanowires on an organic phase change material. *Journal of Thermal Analysis & Calorimetry, 101*(1), 385-389.

Zhang, J.-J., Zhang, J.-L., He, S.-M., Wu, K.-Z., & Liu, X.-D. (2001). Thermal studies on the solid–liquid phase transition in binary systems of fatty acids. *Thermochimica Acta, 369*(1–2), 157-160.

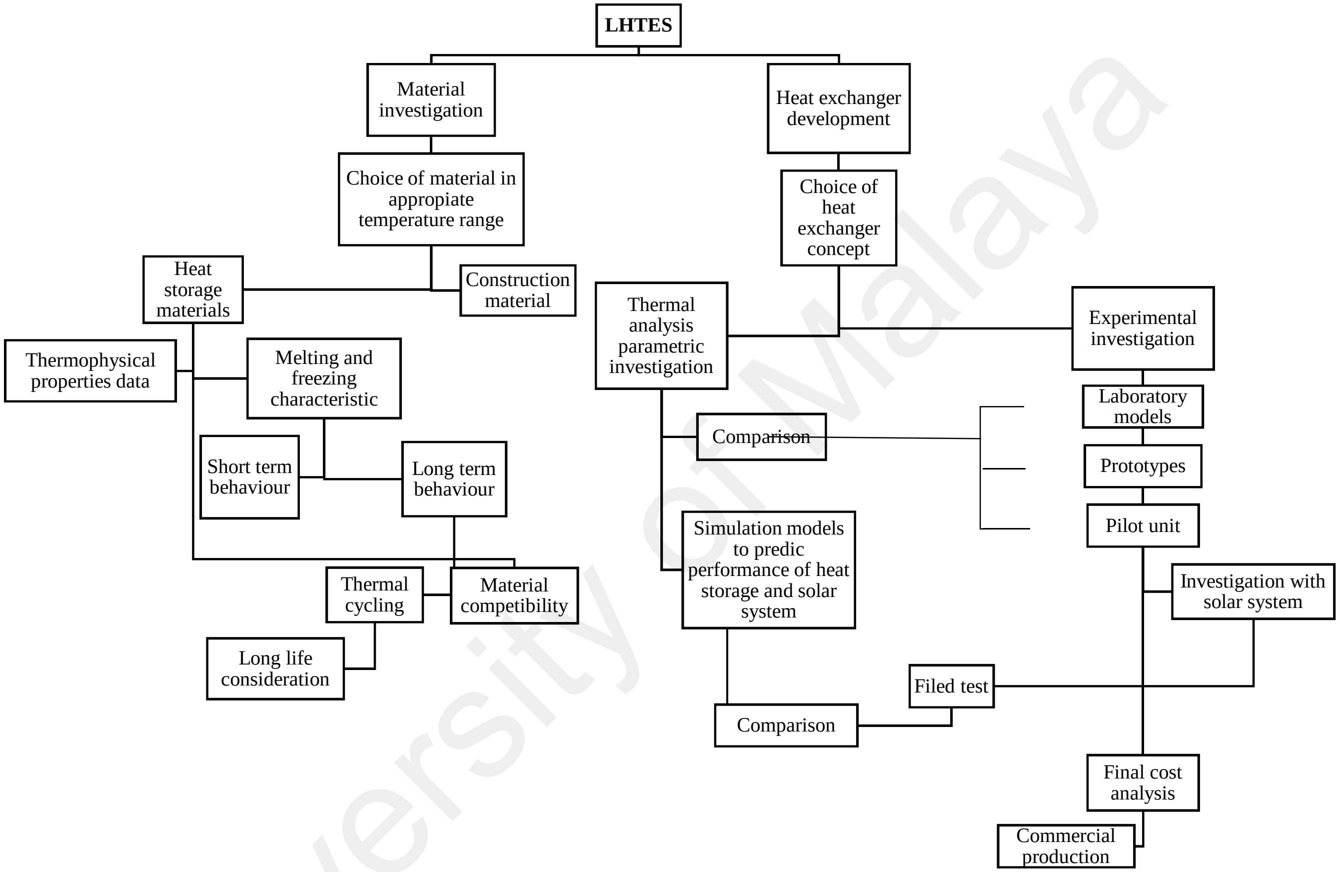
Zhang, N., Yuan, Y., Du, Y., Cao, X., & Yuan, Y. (2014). Preparation and properties of palmitic-stearic acid eutectic mixture/expanded graphite composite as phase change material for energy storage. *Energy, 78*(0), 950-956.

Zhang, Z., & Fang, X. (2006). Study on paraffin/expanded graphite composite phase change thermal energy storage material. *Energy Conversion and Management, 47*(3), 303-310.

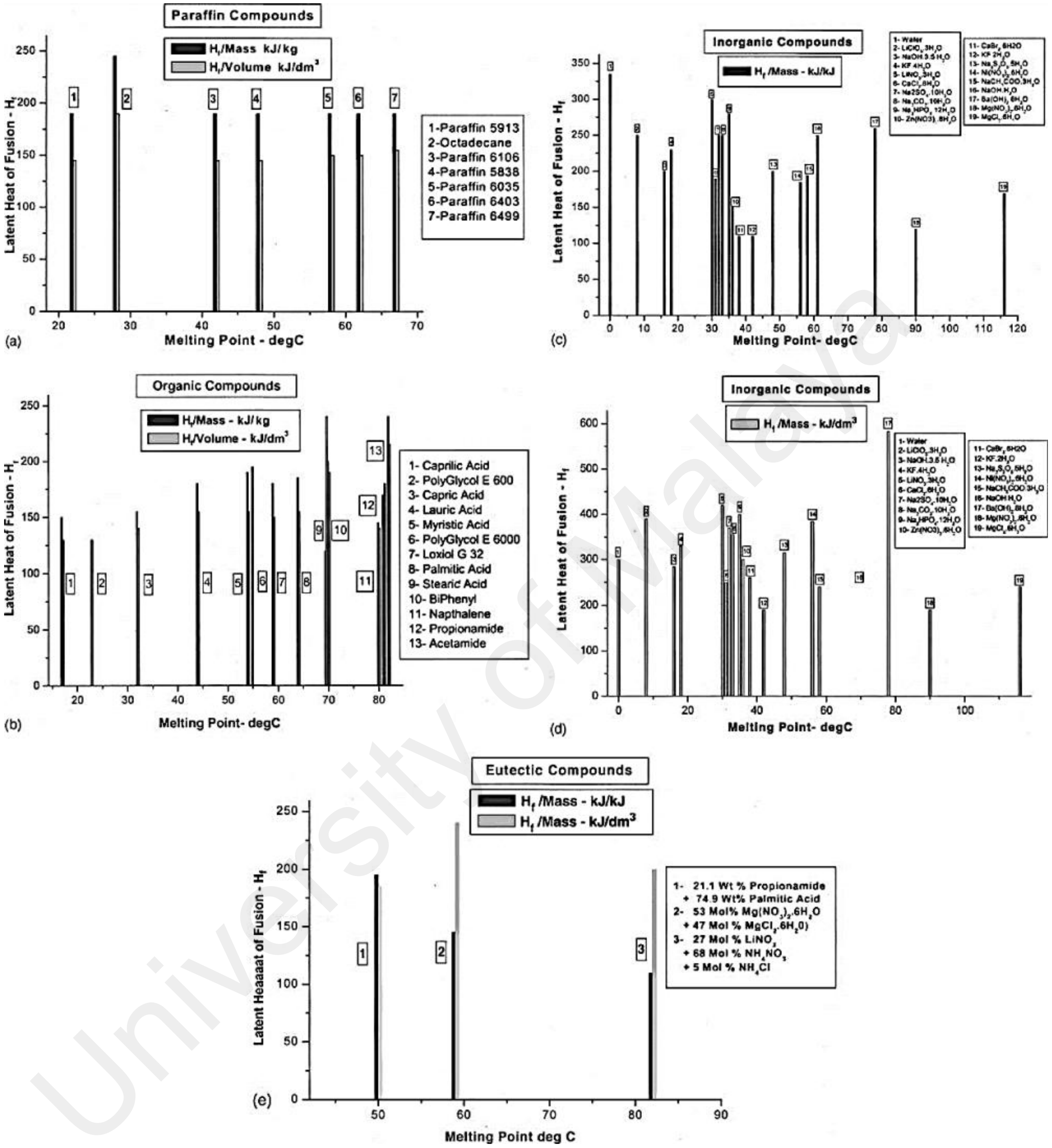
Zhou, D., & Zhao, C. Y. (2011). Experimental investigations on heat transfer in phase change materials (PCMs) embedded in porous materials. *Applied Thermal Engineering, 31*(5), 970-977.

Zhou, D., Zhao, C. Y., & Tian, Y. (2012). Review on thermal energy storage with phase change materials (PCMs) in building applications. *Applied Energy, 92*(0), 593-605.

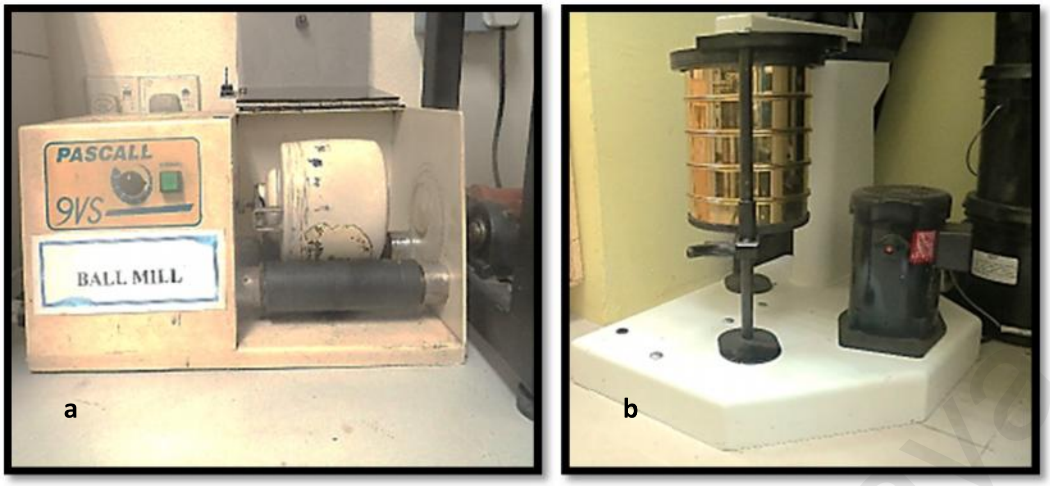
Zhou, M., Bi, H., Lin, T., Lü, X., Wan, D., Huang, F., & Lin, J. (2014). Heat transport enhancement of thermal energy storage material using graphene/ceramic composites. *Carbon, 75*(0), 314-321.



Appendix A.1. Two areas fundamental aspect in LHTES system



Appendix A.2. Classification of PCMs: (a) Latent heat of melting of paraffin compounds (Abhat, 1983; Farid et al., 2004). (b) Latent heat of melting of non-paraffin organic compounds (Abhat, 1983; Farid et al., 2004). (c) Latent heat of melting/mass of inorganic compounds (Abhat, 1983; Farid et al., 2004). (d) Latent heat of melting/volume of inorganic compounds (Abhat, 1983; Farid et al., 2004). (e) Latent heat of melting of eutectic compounds (Abhat, 1983; Farid et al., 2004).



Appendix A.3. a) Rotary ball mill b) Sieve shaker

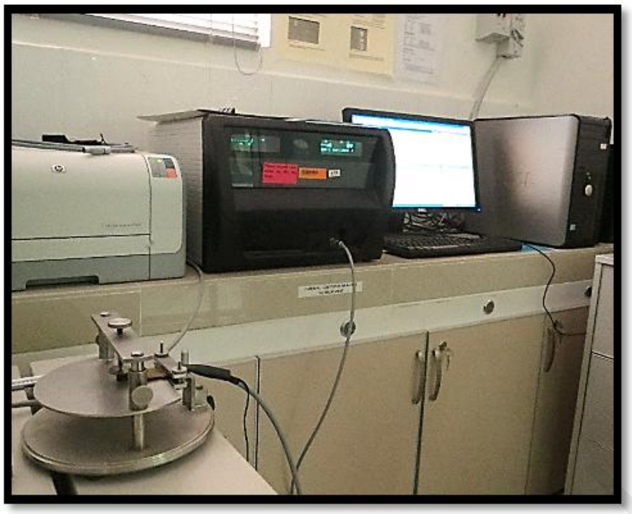
Appendix A.4. Differential Scanning Calorimetric (DSC) thermal analysis (Metler Toledo, DSC1 Star^{e} system)

Appendix A.5. KD2Pro measurements; a) single needles sensor (TR-1); b) measurements setup

Appendix A.6. Differential Scanning Calorimetric (DSC, Perkin Elmer DSC 8000)

Appendix A.7. Fourier transform infrared spectroscopy (FT-IR, Bruker IFS 66/S)

Appendix A.8. Fourier transform infrared spectroscopy (FT-IR, Bruker Tensor 27)



Appendix A.9. Thermal conductivity analyzer, Hot Disc TPS 2500 S

Appendix A.10. Simultaneous thermal analyzer, STA 6000-Perkin Elmer

LIST OF PUBLICATIONS

Fauzi, H., Metselaar, H. S. C., Mahlia, T. M. I., Chyuan Ong, H., Nasruddin, & Khanlou, H. M. (2016). Preparation and thermal characteristics of eutectic fatty acids/Shorea javanica composite for thermal energy storage. *Applied Thermal Engineering, 100*, 62-67.

Fauzi, H., Metselaar, H. S., Mahlia, T., Silakhori, M., & Ong, H. C. (2015). Thermal characteristic reliability of fatty acid binary mixtures as phase change materials (PCMs) for thermal energy storage applications. *Applied Thermal Engineering*.

Fauzi, H., Metselaar, H. S. C., Mahlia, T. M. I., & Silakhori, M. (2014a). Sodium laurate enhancements the thermal properties and thermal conductivity of eutectic fatty acid as phase change material (PCM). *Solar Energy, 102*(0), 333-337.

Fauzi, H., Metselaar, H. S. C., Mahlia, T. M. I., & Silakhori, M. (2014b). Thermal Reliability of Myristic Acid/Palmitic Acid/Sodium Laurate Eutectic Mixture: A Feasibility Study of Accelerated Aging for Thermal Energy Storage Application. *Energy Procedia, 61*(0), 49-54.

Fauzi, H., Metselaar, H. S. C., Mahlia, T. M. I., & Silakhori, M. (2014c). Thermo-physical stability of fatty acid eutectic mixtures subjected to accelerated aging for thermal energy storage (TES) application. *Applied Thermal Engineering, 66*(1–2), 328-334.

Fauzi, H., Metselaar, H. S. C., Mahlia, T. M. I., Silakhori, M., & Nur, H. (2013). Phase change material: Optimizing the thermal properties and thermal conductivity of myristic

acid/palmitic acid eutectic mixture with acid-based surfactants. *Applied Thermal Engineering, 60*(1–2), 261-265.

Fauzi, H., Metselaar, H. S. C., Silakori, M., & Mahlia, T. M. I. (2014). Thermal characteristic of fatty acid/shorea javanica as composite phase change material (PCM). *2014 Renewable Energy and Green Technology International Conference (REEGETECH).*

Fauzi, H., Metselaar, H. S. C. Mahlia, T. M. I., Silakori, M., Ong, H. C. Investigation of thermal characteristic of eutectic fatty acid/damar gum as a composite phase change material (CPCM). 7th International Exergy, Energy and Environment Symposium (IEEES-7).