Fatty acids based eutectic phase change system for thermal energy storage applications

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HIGHLIGHTS

- Eutectic point and the thermophysical properties of eutectic mixtures are predicted by Schrader equation.
- Solid-liquid phase diagrams for each eutectic phase change material are developed by modeling method.
- DSC analysis shows low melting temperature ∼27–75 °C and high latent heat ∼127–210 kJ⋅kg−1, of eutectics.
- Latent heat decreases with the increase in the number of components in the eutectic mixtures developed.
- PT68 based eutectic PCMs possess superior thermo-physical characteristics with no supercooling.

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ABSTRACT

Multiple fatty acid based eutectic phase change materials are prepared for low to moderate temperature latent heat thermal energy storage applications. In particular, palmitic acid, myristic acid, stearic acid, lauric acid and commercial PureTemp68 are used for making eutectic mixtures. The eutectic point of each eutectic mixture is determined using Schrader equation along with its thermophysical properties. Ten different eutectic mixtures are prepared in accordance with eutectic point obtained from the phase diagrams by melt blending followed by ultra-sonication. The latent heat, melting point as well as the specific heat capacity of the eutectic phase change material are determined by Differential Scanning Calorimetry (DSC). The results revealed that the melting point of these organic phase change materials ranges from ∼27–75 °C, with the latent heat from ∼127 to 210 kJ⋅kg−1 respectively. Chemical structure of these phase change materials is determined by using Fourier Transformation Infrared Spectroscopy (FT-IR) and the presence of carboxylic group in obtained spectra is in accordance with the fatty acids. It is evident that these eutectic phase change materials possess promising characteristics for thermal energy storage ranging from the room temperature to ∼75 °C.

1. Introduction

The technological advancement of the rapidly urbanizing global community in recent decade has widened the demand-supply gap of the energy. With the depleting fossil fuel reserves along with the escalating scenario of global warming, there is an intense need to explore sustainable energy resources [1,2]. The renewable resources such as solar energy provide the most promising source of the thermal energy that can be harvested without harming the environment, but the intermittent nature of the renewable resources is a major obstacle in order to integrate them in the existing systems. Energy storage has recently gained much attention in order to curtail the extent of global warming and overcome the intermittency of the renewable energy resources [3,4]. In this regard, thermal energy storage (TES) systems are integrated with renewables resources such as solar energy, to efficiently utilize and store the solar thermal energy, to bridge the energy demand-supply gap and consequently dispatching the thermal energy during the unavailability of the renewable energy resources [5,6].

TES comprises either of the sensible, latent or thermochemical heat storage. Recently, latent heat thermal energy storage (LHTES) has gained attention due to the flexibility in the operation and a wide range of the materials available for it. Phase change materials (PCMs) store energy in the form of the latent heat. By absorbing the available heat and leading to the phase transformation (charging cycle), once the absorbed heat gets released (discharging cycle) they retain their existing phase. On the basis of phase transformations PCMs for LHTES are
classified as solid-liquid, solid-solid, liquid-gas, solid-gas and vice-versa [7]. Solid-gas and liquid-gas PCMs are usually not employed in the LHTES systems because of large volumetric changes associated with their phase transformations, while solid-solid PCMs possess low latent heat during phase transition. In case of solid-liquid PCMs, various organic and inorganic PCMs have been reported in the literature possessing high energy storage density and flexible operating temperature range for TES applications [8]. However, recently there has been much emphasis on introducing techniques to address the concerns in the extensive commercialization of organic PCMs such as low thermal conductivity, shape stability and suppression of the supercooling [9,10]. In order to resolve these issues, organic eutectic PCMs have been introduced which comprises of proportions of different organic PCMs depending upon their eutectic point along with the nanomaterials additives, these eutectic mixtures help in order to achieve the desired thermophysical properties for a particular application [11–13]. Solid-liquid organic PCMs and their eutectics exhibit the advantages of congruent melting, non-toxic and eco-friendly bio-based nature, low vapor pressure during phase transformation, the minute extent of supercooling, compatibility with the material of construction, reliability and their abundance in nature, makes them suitable for low to moderate temperature TES applications [14]. Moreover, a large number of eutectic PCMs can be tailored, considering the desired thermophysical properties of the LHTES system for increasing the adaptability of the PCMs for TES applications. In this study, a series of organic eutectic PCMs is studied in order to develop the thermophysical characteristics for the application towards LHTES systems.

Thermophysical properties of organic PCMs such as paraffin, non-paraffin and their eutectics have been widely investigated for the potential application of TES [15,16]. Among the range of organic PCMs, fatty acids have precedence of widespread availability, environmental benignity and above all less expensive as compared to other organic PCMs [17–20]. In addition, they also offer the advantages of superior thermal and chemical stability, congruent melting behavior, biodegradability and suitable operating temperature range for low to moderate temperature (LHTES) applications such as district water heating, photovoltaic/thermal hybrid systems, space heating, thermal management of the buildings, thermo-regulating fibers and solar thermal water heating [11,21–25]. Various investigations have been performed on the fatty acids and their eutectics as a potential candidate for LHTES [26,27]. Cai et al. [28] investigated the thermophysical properties of the prepared form stable fatty acid based eutectics fiber comprising of polytetrafluoroethylene (PET), the operating temperature range of the eutectic PCMs with varying amount of PET is reported as 35–53 °C. Kant et al. [29] developed ternary eutectics comprising of fatty acids for low temperature TES applications and experimentally determined their operating temperature range to be 14–21 °C. Kahlwaij et al. [22] studied the thermophysical properties of the individual fatty acids as a potential PCMs for LHTES and identified their optimum operating temperature range. Authors performed the thermal analysis of these individual fatty acids and their eutectic PCMs after 3000 melt/freeze cycles and reported them as thermally stable, and suitable for the application in the thermal management of the buildings [30]. Ke [31] prepared multiple fatty acids based eutectic PCMs using prediction method and compared their theoretical and experimentally determined thermophysical properties. Sharma et al. [32] reported myristic acid and palmitic acid to be thermally reliable for long-term usage by performing the thermal analysis of these fatty acids after 1500 melt/freeze cycles. From the literature, it is evident that pristine fatty acids possess promising thermophysical properties with thermal stability. However, a very limited data on the modeling and prediction of the thermophysical properties, eutectic mass ratios, phase diagrams and the experimentally determined thermophysical properties of fatty acids based eutectic PCMs are available in the literature [33,34]. Design of LHTES system requires optimal information of thermophysical properties for efficient utilization of the technology, the prerequisites include the optimum operating temperature range, melting enthalpies, chemical stability and cyclic reliability [35]. The present study also gives extended theoretical and experimental insights on this subject by developing eutectic mass ratios, phase diagrams and evaluating the thermophysical properties of fatty acid based binary, ternary, quaternary and quinary eutectic PCMs. Furthermore, the effect of the components in the eutectic mixture on the thermophysical properties is also analyzed.

The present study focuses on modeling, designing and developing of fatty acid eutectic mixtures as solid-liquid PCMs with minimal supercooling specifically for LHTES. For this purpose, four different fatty acid namely myristic acid (MA), lauric acid (LA), stearic acid (SA), palmitic acid (PA) and a commercial bio-based PCM product PureTemp68 (PT68) are utilized to achieve a goal of developing multiple eutectics PCM with a lower operating temperature and higher latent heat, consequently diversifying the options of the organic eutectic PCMs for LHTES. PT68 has not been investigated for the preparation of eutectic PCMs in the past, which is the part of this study. In particular, eutectics LA/PT68, MA/PT68, SA/PT68, PA/PT68, SA/PA/PT68, SA/PA/LA/PT68, and SA/PA/LA/MA/PT68 have not been reported in the literature.

The overall framework of the study comprises of mathematical modeling for determining eutectic point by plotting phase diagrams and estimating the thermo-physical properties of particular eutectic PCMs. Multiple eutectic samples were prepared based on molar ratios by melt blending all the constituents followed by ultra-sonication. A comprehensive comparison of determined eutectic mass ratios, eutectic temperature, melting behavior and the melting enthalpies with the experimental outcomes obtained from DSC has been carried out. Moreover, the chemical structure of prepared eutectics is discussed by obtaining FTIR spectra [36]. The specific heat capacity of the eutectic PCMs are estimated and compared with the measured values from the DSC data. Experimental outcomes provide the necessary data for designing the LHTES systems comprising of prepared eutectic PCMs particularly for district water heating, thermo-regulating and smart textiles, thermal management of the buildings and electronic components and photovoltaic/thermal systems. Various aspects of the thermophysical properties of these PCMs as obtained through DSC are discussed in detail. The determined optimum eutectic mass ratios along with the latent heat values, melting temperatures, melting behavior and the degree of supercooling of these eutectics are useful additions in the thermal analysis of the PCMs. In this context, the fatty acid based eutectic PCMs are useful for LHTES applications due to their promising characteristics for thermal energy storage ranging from the room temperature to ~75 °C.

2. Experimental

2.1. Materials

Properties of the pure PCMs as provided by the suppliers are consolidated in Table 1. Laboratory grade fatty acids; SA by Acros Organics, PA by TCI Chemicals, LA, and MA by Alfa Aesar of purity 97%, 99.1%, 99.2% and 99.2% respectively and a bio-based commercially available PCM PT68 manufactured by Entropy Solutions LLC., are procured and used without any further purification.

2.2. Determination of eutectic point for fatty acids eutectic phase change materials

The ideal eutectic mixture has a common melting point which is lower than that of its constituents. To determine the eutectic point, two methods are usually practiced: the proportioning test or the prediction method. In the proportioning test, series of samples with varying mass proportions are prepared, such as component A-B (90-10%), A-B (80-20%) and so on. The optimum proportion of the particular eutectic PCM is identified by comparing the heat flow curves obtained from DSC test
for prepared eutectic mixture with variant proportions. In prediction method, optimum mass ratios of eutectic mixture are determined by drawing phase diagrams for the binary and pseudo-binary mixtures. The mole fraction of the individual components of eutectics mixture is plotted against the temperature obtained from the Schrader equation [37,38]. The point of intersection of two curves represent the optimum proportion for a particular eutectics mixture and is termed as eutectic point identified from the phase diagram [31]. For a pseudo-binary mixture A-B/C, the optimum mass proportion of component A and B is determined from the eutectic point of the plotted phase diagram. Whereas the composition of the components A and B for eutectic A-B/C is calculated by manipulating the mass proportions of A and B in binary eutectic A/B obtained from its phase diagram.

In this study, the theoretical prediction method is used for the preparation of the multiple binary eutectic mixture PCMs for minimizing the number of test samples as well as the cost associated with the characterization. Theoretical eutectic mass ratios of multiple fatty acid eutectic mixtures are determined through the phase diagram. Schrader equation derived from the second law of thermodynamics and phase equilibrium theory [28,38,39], relates the thermophysical properties of the eutectic PCMs with varying composition, is used for this purpose as mentioned below:

$$T_M = \left[ \frac{1}{T_{on,A}} - R \frac{\ln X_A}{\Delta H_{m,A}} \right]^{\frac{1}{T}}$$ (1)

$$T_M = \left[ \frac{1}{T_{on,B}} - R \frac{\ln X_B}{\Delta H_{m,B}} \right]^{\frac{1}{T}}$$ (2)

where $T_M$ represents the melting temperature of the eutectic mixture in K, $T_{on,A}$ and $T_{on,B}$ represents the onset melting temperature in K, $X_A$ and $X_B$ represent the mole fraction, while $\Delta H_{m,A}$ and $\Delta H_{m,B}$ represents the molar latent heat in kJ·mol$^{-1}$, of component A and B respectively. $R$ is the general gas constant (8.314 kJ·mol$^{-1}$·K$^{-1}$) used in Eqs. (1) and (2).

The specific heat capacity for liquid and solid states of the individual fatty acids and PT68 involved in this study are shown in Table 1. The specific heat capacities for the liquid and solid states of the eutectic mixture are predicted by using following formula [31,40]:

$$C_{p_{liq}} = \sum X_i C_{p_i} \quad (i = A, B, \ldots, n)$$ (3)

where $C_{p_{liq}}$ represents the specific heat capacity of the particular fatty acid eutectic mixture and $C_{p_i}$ represents the specific heat capacity of component $i$ in the eutectic mixture in kJ·kg$^{-1}$·C$^{-1}$. $X_i$ represents the mole fraction of component $i$ in the eutectic mixture.

Melting enthalpy is another important thermal property of the PCMs and the formula employed for the estimation of melting enthalpies of the fatty acid eutectic mixture is shown below [31]:

$$H_{m,i} = T_{m,i} \sum_{i=1}^{n} X_i \cdot C_{p_{liq}} \cdot \Delta H_{m,i} \cdot \left( \frac{T_{m,i}}{T_i} \right) - T_{m,i} \cdot C_{p_{liq}}$$ (4)

where $H_{m,i}$ represents the melting enthalpy of the eutectic mixture in kJ·mol$^{-1}$, $T_{m,i}$ represents the melting temperature of the eutectic mixture in K (determined through the Schrader equation by plotting the phase diagrams). $X_i$ represents the mole fraction of component $i$, $H_i$ represents the melting enthalpy of component i in kJ·mol$^{-1}$, $T_i$ represents the melting point of component i in the eutectic mixture in K, whereas $C_{p_{liq}}$ and $C_{p_{sol}}$ represent the specific heat capacity of liquid and solid phase of component $i$ respectively in kJ·kg$^{-1}$·C$^{-1}$.

2.3. Preparation of fatty acid based multi-component eutectics

A series of fatty acid eutectic PCMs is prepared through melt-blending followed by ultra-sonication technique [37]. Multiple fatty acid eutectic mixtures are prepared on the basis of eutectic mass ratios obtained from the particular phase diagram, as given in Table 2. Firstly, the selected fatty acids are carefully weighed as per their weight percent in a particular eutectic mixture, using a precision balance (XS603S Mettler Toledo, weighing precision ± 0.5 mg) to prepare a 30 g sample and all the components of the eutectic mixture, are mixed together into a beaker. Homogenous eutectic mixture was obtained by heating (60 min) and stirring (45 min) at ~80 °C followed by sonication (15 min) at ~70 °C and is slowly cooled to room temperature for uniform solidification. All the eutectic mixtures are prepared in a similar manner.

2.4. Chemical and thermal characterization

Fourier transform infrared spectroscopy (FT-IR, Bruker IFS66V/S) is employed for obtaining the spectra of the eutectic mixtures in the range of 5000–400 cm$^{-1}$, in order to investigate the chemical structure. The chemical bonds in organic compounds absorb electromagnetic radiations of frequencies in the range of wavenumber ~4000–400 cm$^{-1}$ and their recorded absorption spectrum is analyzed in order to identify the organic compounds.

Thermal properties of the eutectic mixtures are measured by using DSC instrument (TA 2920 MDC V2.6A, accuracy ± 0.1 °C). The temperature and heat flow calibrations of DSC are performed using known quantity of high purity Indium (Observed melting point: 157.2 °C vs 156.6 °C). For each eutectic PCM, DSC tests are conducted in the

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**Table 1** Properties of individual fatty acids and PureTemp68 from suppliers’ data.

<table>
<thead>
<tr>
<th>Trade name</th>
<th>IUPAC name</th>
<th>Formula (CAS #)</th>
<th>Supplier</th>
<th>Purity</th>
<th>Molecular weight (g·mol$^{-1}$)</th>
<th>Melting point (°C)</th>
<th>Specific heat capacity (J·g$^{-1}$·K$^{-1}$)</th>
<th>Latent heat of fusion (kJ·kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric acid (LA)</td>
<td>Dodecanoic acid</td>
<td>C12H24O2 (143- 07-7)</td>
<td>Alfa Aesar</td>
<td>99.2%</td>
<td>200.31</td>
<td>43–45</td>
<td>2.2</td>
<td>1.6</td>
</tr>
<tr>
<td>Myristic acid (MA)</td>
<td>Tetradecanoic acid</td>
<td>C14H28O2 (544- 63-8)</td>
<td>Alfa Aesar</td>
<td>99.2%</td>
<td>228.37</td>
<td>53–56</td>
<td>2.3</td>
<td>1.7</td>
</tr>
<tr>
<td>Palmitic acid (PA)</td>
<td>Hexadecanoic acid</td>
<td>C16H32O2 (57- 10-3)</td>
<td>TCI Chemicals</td>
<td>99.1%</td>
<td>256.42</td>
<td>62–66</td>
<td>2.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Stearic acid (SA)</td>
<td>Octadecanoic acid</td>
<td>C18H36O2 (57- 11-4)</td>
<td>Acros Organics</td>
<td>97%</td>
<td>284.47</td>
<td>67–69</td>
<td>2.4</td>
<td>1.7</td>
</tr>
<tr>
<td>PureTemp68 (PT68)</td>
<td>–</td>
<td>–</td>
<td>Entropy Solutions, LLC</td>
<td>–</td>
<td>–284</td>
<td>68–71</td>
<td>1.91</td>
<td>1.85</td>
</tr>
</tbody>
</table>

* Purity is determined by GC as indicated by the suppliers.
temperature range of 0–80 °C. The scanning rate for both heating and cooling cycles is set at 4 °C min\(^{-1}\) under a constant flow rate of nitrogen at 80 ml min\(^{-1}\). Eutectic PCMs samples weighing ∼3–7 mg are hermetically sealed in the standard aluminum pan/lid for conducting the thermal analysis. Heat flow and temperature data with respect to time are obtained for prepared eutectic PCMs, an in-depth thermal analysis is performed and results are discussed in Section 4. The specific heat capacity of the eutectic PCMs is determined as per ASTM E1269-11, while the SA/PT68 has the highest onset melting point (58.2 °C) among various eutectic combinations evaluated, respectively. A comparison of the calculated eutectic point, specific heat capacity, and latent heat value with the literature values are given in Table 2. The theoretical eutectic point and the specific heat capacity are in accordance with the reported literature values. Ten samples are prepared in accordance with the eutectic mass composition determined from the phase diagrams and the DSC thermal analysis for these eutectic PCMs is performed. The thermophysical properties are discussed in Section 3.4, along with their comparison with the respective theoretical values.

### 3.2. Fourier transform infrared spectroscopy analysis

The chemical structure of the prepared eutectic mixture is characterized by performing FT-IR spectroscopy analysis. The FT-IR spectra of prepared binary eutectic PCMs (LA-PT68, MA-PT68, PA-PT68, SA-PT68 and SA-PA), ternary eutectic PCMs (SA-PA-LA and SA-PA-PT68), quaternary eutectic PCMs (SA-PA-LA-MA and SA-PA-LA-PT68) and quinary eutectic PCMs (SA-PA-LA-MA-PT68) obtained are shown in Fig. 2. A common trend appears on the spectra of eutectics and the fingerprint region in the lower right part of each spectrum gives a unique pattern representing the particular group of organic materials. Stretching vibrations of C=O are evident in the form of a strong peak at 1692.9 cm\(^{-1}\) [39,41], while the peak observed at 1299.5 cm\(^{-1}\) indicates the presence of C–O. The stretching vibrations of –OH bond is evident from the peak at 3939.4 cm\(^{-1}\) [39]. The observed peaks indicate the presence of C–O, C=O and –OH bonds of the carboxyl group (–COOH) present in the fatty acids [42]. Symmetric and asymmetric stretching vibrations of the C–H bond in the alkane are recorded in the form of absorption peaks at 2846.6 and 2919.9 cm\(^{-1}\), respectively [31]. Medium absorption peaks at 1432.9 and 1466.2 cm\(^{-1}\) are related to deformation vibration of the –CH\(_2\) and –CH\(_3\) groups respectively [31,39], while the weak absorption peak at 725.9 cm\(^{-1}\) indicates the rocking vibrations of the –CH\(_2\) group. C–H bending in the molecule is evident from the strong peak observed at 685.9 cm\(^{-1}\). After comparing the FT-IR absorption spectrum of the prepared eutectic mixture with the spectrum in the literature, a similarity with the absorption peaks of the individual fatty acids is observed [43]. The smaller absorption peaks observed in the spectra also suggests that they have high molecular mass, while the fingerprint region of the spectrum confirms the organic nature of the eutectics. The obtained FT-IR spectra of the eutectics LA-PT68, MA-PT68, PA-PT68, SA-PT68, SA-PA-LA, SA-PA-PT68, SA-PA-LA-MA and SA-PA-LA-MA-PT68 displays the characteristics peaks similar to the individual fatty acids SA, PA, LA and MA as reported in the literature [31,36,39,44].

The presence of the PT68 in the samples indicate strong peaks in the
spectra which are coherent with the spectra of individual fatty acids. Any new absorption peak is not observed in the spectrum indicating, no chemical reaction has occurred between the eutectic components. A structural similarity of the prepared eutectic PCMs with the individual fatty acids is indicated and no additional product is formed during formation of eutectic mixture PCMs.

3.3. Differential scanning calorimetry analysis

Fig. 3a and b presents the heat flow curves of the eutectic mixtures, obtained from the DSC. It is evident from single melting peaks in the heat flow diagrams for each eutectic PCMs that eutectic PCMs can be designed to operate in the desired temperature range, by carefully selecting the constituent organic components as predicted by the mathematical model. Onset, peak end and the peak temperatures along with the latent heat values for both the melting and solidification of the prepared eutectic PCMs, as obtained from the DSC are consolidated in Table 3. The Onset temperatures are determined by following the GEFTA standards. The latent heat values measured for the binary eutectic PCMs are the highest among ternary, quaternary and quinary eutectic PCMs, respectively. The heat flow curves of the binary eutectic PCMs (PA/PT68, MA/PT68, LA/PT68, SA/PA and SA/PT68) indicate a sharp well-defined melting and solidification temperature peaks, (see Fig. 3a and b) implying heat absorption and release over a narrow temperature range, which also depicts that the binary mixtures melt congruently. The onset melting and solidification temperatures are also in line with each other, indicating no extent of supercooling, as a consequence the nucleation gets triggered very close to the onset melting temperature of the eutectic PCMs. However, with the addition of more components in the binary eutectic PCMs, a reduction of about 20–40% is observed in the latent heat values as consolidated in Table 3.

Eutectic PCMs containing LA showed a sharp decrease in their onset melting temperatures which suggest that they can be employed to design eutectics PCMs for a temperature range of ~27–38 °C. Peak broadening is demonstrated from the DSC heat flow curves (see Fig. 3a) for both heat absorption/release cycles of quaternary (SA-PA-LA/PT68 and SA-PA-LA/MA) and quinary (SA-PA-LA-MA/PT68) eutectic PCMs particularly. It might be attributed to a number of factors including higher heating rate, low thermal conductivity and incongruent melting/solidification of the eutectic PCMs due to the slight deviation of actual eutectic point value from the theoretically calculated values. It is clear that the peak broadening phenomenon is more obvious in the eutectics having a greater number of components.

Fig. 3a demonstrates two distinct peaks in the solidification process of SA-PA-LA-MA/PT68 due to the incomplete phase transformation at peak solidification temperature, this severely affects the thermal performance of the PCMs and is, therefore, avoided [45]. As shown in Fig. 3b, smaller peak broadening is observed during the melting cycle of ternary eutectic SA-PA/LA but its corresponding solidification curve shows a smoother phase transformation implying zero degree of supercooling. The slight peak broadening in the absorption cycle might be due to the presence of either impurities or humidity in the sample during the first run of the experiment. The heat flow curve of the ternary eutectic PCM SA-PA/PT68 shows a sharp peak for both melting
and solidification cycles implying the fact that it has a common melting point. The single solidification peaks in Fig. 3a and b clearly demonstrate that the crystallization of the eutectics PCMs is complete during the solidification process. The onset solidification temperature observed is well below the onset melting temperature in the heat flow curves of particular eutectics PCMs. Furthermore, on lowering the temperature of particular PCMs to 0 °C no other transition peak is observed apart from the major clearly identifiable single solidification peak. Latent heat values obtained from solidification peaks are lower compared to that of the melting for all the PCMs (see Table 3), which is mainly due to the heat losses associated with the release of heat by PCMs to the surroundings. Considering these key findings along with a decrease in heat flow with the temperature reaching 0 °C for all the eutectics, the complete crystallization of the eutectics is evidenced through Fig. 3a and b.

The DSC outcomes summarized in Table 3 indicate that the onset melting temperature of the prepared quaternary and quinary eutectic PCMs is lower as compared to the binary and ternary eutectic PCMs. Moreover, with the increase in the number of constituents in the eutectic mixture, lower latent heat values are obtained. A decrease in the onset melting temperature of eutectic PCMs is also observed upon increasing the number of the constituents. The fatty acid based eutectic PCMs SA-PA/MA, SA-PA/MA/PT68 and SA-PA/MA/PT68 can be successfully integrated with low temperature LHTES systems as their melting temperature ranges from ~27 to 30 °C. However, the melting temperature of prepared binary (MA/PT68, PA/PT68, SA/PA and SA-PT68) and ternary (SA-PA/PT68) eutectic PCMs ranges from ~46 to 68 °C with the exception of LA/PT68 and SA-PA/LA as shown in Table 3. These binary and ternary eutectic PCMs possess high latent heat ranging from ~168 to 211 kJ·kg⁻¹, therefore are considered as promising LHTES medium for integrating into district water heating, photovoltaic/thermal, space heating and solar water heating applications. Melting temperature of LA/PT68 and SA-PA/LA are 38 and 32 °C, respectively which is comparatively low due to the presence of the constituent LA. While their latent heat values are ~180 and 160 kJ·kg⁻¹, respectively this makes them the appropriate candidate for the thermal management of the buildings due to their higher latent heat values and moderate operating temperature range. The comparison of the measured thermophysical properties in this study with the literature values is presented in Table 3 [31,46]. A small deviation in the measured thermophysical properties with the literature values is present and this difference can be associated with the factors such as a difference in the purity of the materials, the mass of the materials and

Table 3
Thermal properties of the eutectic phase change materials as measure through DSC at 101.9 kPa. The notation a/b/c/d/e indicates the associated wt.% of corresponding component in eutectic mixture.

<table>
<thead>
<tr>
<th>Eutectic PCMs</th>
<th>Eutectic composition (wt. %)</th>
<th>Melting</th>
<th>Solidification</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Onset temp (°C)</td>
<td>Peak temp (°C)</td>
<td>End temp (°C)</td>
</tr>
<tr>
<td>LA/PT68</td>
<td>80/20</td>
<td>38.3</td>
<td>40.3</td>
</tr>
<tr>
<td>MA/PT68</td>
<td>69/31</td>
<td>46.3</td>
<td>48.8</td>
</tr>
<tr>
<td>PA/PT68</td>
<td>58/42</td>
<td>54.9</td>
<td>57.2</td>
</tr>
<tr>
<td>SA/PT68</td>
<td>47/53</td>
<td>68.7</td>
<td>70.0</td>
</tr>
<tr>
<td>SA/PA</td>
<td>59/61 [37.01/62.99]</td>
<td>55.1 [53.69]</td>
<td>56.0</td>
</tr>
<tr>
<td>SA/PA/PT68</td>
<td>43.92/28.08/28</td>
<td>52.1</td>
<td>57.8</td>
</tr>
<tr>
<td>SA/PA/LA</td>
<td>15.6/24.4/60 [6.77/20.97/72.26]</td>
<td>32.2 [32.02]</td>
<td>35.5</td>
</tr>
<tr>
<td>SA/PA/MA/PT68</td>
<td>14.04/21.96/54/10</td>
<td>30.0</td>
<td>36.9</td>
</tr>
<tr>
<td>SA/PA/MA/PT68</td>
<td>17.4/11.1/42.9/22.6/6</td>
<td>27.8</td>
<td>34.8</td>
</tr>
</tbody>
</table>

Standard uncertainties u are; Pressure u(p) = 1.3 kPa, Composition u(x) = 0.1 wt%, Temperature u(T) = 0.6 °C and Latent heat u(ΔH_m) = 3%.

* Ref. [31].
** Ref. [43].
heating rate while performing the DSC. A comprehensive comparison of the estimated and measured thermophysical properties of the prepared eutectic PCMs along with their constituent eutectic mass compositions are consolidated in Table 4. Estimated values of the thermophysical properties for the prepared eutectic PCMs are in agreement with their measured values through DSC. The disparities observed between the estimated and measured thermophysical values are mainly due to the experimental errors while conducting the DSC and can be attributed to the impurities in the PCMs. A relative difference of approximately < 4% is observed between the theoretical and measured onset melting temperature for LA-PT68, MA-PT68, PA-PT68, SA-PA, and SA-PA-LA-MA, while a relative difference of ~8% is observed for SA-PA-LA and SA-PA-PT68. SA/PT68 comprises the constituents having very close melting temperatures and its estimated onset melting temperature comes well below the measured value. The absolute difference of ~3 °C is observed in the case of SA-PA-LA-MA-PT68 as shown in Table 4. The negligible difference is observed between the estimated and measured value of latent heat for the prepared eutectic SA-PT68. The increase in the relative difference between the estimated and measured latent heat values for the eutectic PCMs having a greater number of components can be attributed to the cumulative errors while computing Eq. (4).

Table 4
Comparison of the estimated thermophysical properties and the measured through DSC at pressure p = 101.9 kPa. The notation a/b/c/d/e indicates the associated wt.% of corresponding component in eutectic mixture.

<table>
<thead>
<tr>
<th>Eutectic PCMs based on individual components (wt.%)</th>
<th>Estimated using model (°C)</th>
<th>Measureda (°C)</th>
<th>Absolute difference</th>
<th>Relative difference (%)</th>
<th>Estimated using model (kJ kg⁻¹)</th>
<th>Measureda (kJ kg⁻¹)</th>
<th>Absolute difference (kJ kg⁻¹)</th>
<th>Relative difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LA/PT68 80/20</td>
<td>40.2</td>
<td>38.3</td>
<td>1.9</td>
<td>4.8</td>
<td>182.4</td>
<td>180.3</td>
<td>2.1</td>
<td>1.2</td>
</tr>
<tr>
<td>MA/PT68 69/31</td>
<td>48.2</td>
<td>46.3</td>
<td>1.9</td>
<td>4.02</td>
<td>195.9</td>
<td>182.2</td>
<td>13.7</td>
<td>7.3</td>
</tr>
<tr>
<td>PA/PT68 58/42</td>
<td>53.7</td>
<td>54.9</td>
<td>1.2</td>
<td>2.2</td>
<td>204.1</td>
<td>184.5</td>
<td>19.6</td>
<td>10.1</td>
</tr>
<tr>
<td>SA/PT68 47/53</td>
<td>58.2</td>
<td>68.7</td>
<td>10.5</td>
<td>16.5</td>
<td>211.4</td>
<td>210.6</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>SA/PA 39/61</td>
<td>54.5</td>
<td>55.1</td>
<td>0.6</td>
<td>1.1</td>
<td>207.7</td>
<td>181</td>
<td>26.7</td>
<td>13.7</td>
</tr>
<tr>
<td>SA/PA/PT68 43.92/28.08/28</td>
<td>48.1</td>
<td>52.1</td>
<td>4</td>
<td>7.9</td>
<td>204.0</td>
<td>167.9</td>
<td>36.1</td>
<td>19.4</td>
</tr>
<tr>
<td>SA/PA/LA 15.6/24.4/60</td>
<td>35.1</td>
<td>32.2</td>
<td>2.9</td>
<td>8.6</td>
<td>183.8</td>
<td>159.9</td>
<td>23.9</td>
<td>13.9</td>
</tr>
<tr>
<td>SA/PA/LA/MA 14.04/21.96/54/10</td>
<td>31.8</td>
<td>30.0</td>
<td>1.8</td>
<td>5.8</td>
<td>184.3</td>
<td>157.9</td>
<td>26.4</td>
<td>15.4</td>
</tr>
<tr>
<td>SA/PA/LA/MA/PT68 11.86/18.54/45.6/24</td>
<td>27.2</td>
<td>27.4</td>
<td>0.2</td>
<td>0.7</td>
<td>179.6</td>
<td>127.7</td>
<td>51.9</td>
<td>33.8</td>
</tr>
<tr>
<td>SA/PA/LA/MA/PT68 17.4/11.1/42.9/22.6/6</td>
<td>25.1</td>
<td>27.8</td>
<td>2.7</td>
<td>10.2</td>
<td>179.2</td>
<td>160.8</td>
<td>18.4</td>
<td>10.8</td>
</tr>
</tbody>
</table>

Standard uncertainties u are; Pressure u(p) = 1.3 kPa, Composition u(x) = 0.1 wt%, Temperature u(Tm) = 0.6 °C and Latent heat u(ΔHm) = 3%.

Fig. 4. Specific heat capacity of fatty acids ((a)-(j)) based eutectic phase change materials.
sharp increase in Cp value of prepared eutectic PCMs indicates the absorption of heat and consequent phase transition from solid to liquid during the melting cycle as shown in Fig. 4a-j. This trend is due to the increase in kinetic energy resulting from molecular collisions. The collision of molecules provides the energy for molecular rotation and subsequent increase in Cp. It is evident from Fig. 4a-j that the Cp is significantly higher for the liquid as compared to the solid state of PCMs. An increase of ~30% in Cp values for the liquid state as compared to the solid states with respect to the temperature range is observed.

The Cp values for the LA-PT68, MA-PT68, PA-PT68 and SA-PT68 in the solid state as represented in Fig. 4a-d, range from 1.16–1.80, 1.27–1.78, 1.18–1.76 and 1.64–2.15 J·g⁻¹·C⁻¹, for the liquid state of the mentioned PCMs it ranges from 1.72–1.88, 1.83–1.89, 1.77–1.83 and 2.23–2.65 J·g⁻¹·C⁻¹ respectively. Cp value increases drastically in the phase transition of the PCMs as shown in Fig. 4a-j. As the specific heat capacity deals with the sensible heat so it is usually not considered in the phase transition of the PCMs, therefore this thermal property is studied for either of the liquid and solid phase of particular species for better understanding. The increase in the Cp with respect to temperature is more prominent in the solid phase as compared to the liquid phase, since the molecules have a restricted motion in solids and relatively lower entropy. Similar trend is evident from the results (see Fig. 4a-j).

The low heat flow in melting of the eutectics SA-PA, SA-PA-PT68, SA-PA-LA and SA-PA-LA-PT68 as shown in Fig. 3a and b is also consistent with their Cp values (see Fig. 4e–h), for the solid phase of these eutectics PCMs Cp value ranges from 0.32–1.35, 1.2–1.9, 0.96–1.62 and 1.21–1.61 J·g⁻¹·C⁻¹, for the liquid phase it ranges from 2.18–2.20,
1.78–1.84, 1.12–1.26 and 1.65–1.91 J·g⁻¹·C⁻¹, for the above-mentioned eutectics respectively. A deviation in the Cp at 70 °C of SA-PA-LA-MA PT68 is also indicated in Fig. 4j which corresponds to the minute transition peak in Fig. 3a. This peak corresponds to the molecular re-organization due to the presence of minor component PT68 in eutectic SA-PA-LA-MA PT68 and may be resulted due to the artifacts while running the DSC as the Cp value beyond this point does not deviate well from the observed trend. It is solely noted that a broader melting peak of the SA-PA-LA-MA PT68 is observed in its heat flow (see Fig. 3a). The temperature dependency of the Cp for the eutectics, SA-PA-LA-MA and SA-PA-LA-MA PT68 is shown in Fig. 4i-j. Cp of their liquid phase is greater than solid phase, which comes in agreement with the above-mentioned results. For the solid phase of the SA-PA-LA-MA and SA-PA-LA-MA PT68, value ranges from 0.73–1.01 and 1.47–1.9 J·g⁻¹·C⁻¹ respectively, while for their liquid phase it ranges from 0.96–1.1 and 2.01–2.22 J·g⁻¹·C⁻¹ respectively.

Cp is an important characteristic for the optimum design of the LHTES system and also useful in the determination of the thermophysical property such as thermal diffusivity of the PCMs. This property is usually negotiated by the researchers while performing the thermal analysis of the PCMs for LHTES. This indeed creates complexities in the design process for the LHTES system, due to the lack of the thermophysical data. And the engineers have to rely on the estimated values along with discrete design assumptions which decrease the performance efficiency of the LHTES system.

Performance characteristics of the eutectic fatty acids evaluated in the present study is compared with that reported in the literature and is given in Table 5. As evident from Table 5, binary eutectic PCMs comprising PT68 (LA/PT68, MA/PT68, SA/PT68 and PA/PT68) showed the most promising thermophysical properties compared with the other fatty acid based binary eutectic PCMs reported in the literature. Moreover, the thermophysical properties of binary eutectic SA/PA, ternary eutectic SA/PA/LA, and quaternary eutectic SA/PA/LA/MA are also validated with the existing findings in the literature. Quinary eutectic SA/PA/LA/MA/PT68 possesses a high latent heat value around room temperature compared with the existing study in the literature, as shown in Table 5. The main advantage of the quinary eutectics is the greater operating temperature window which does not exist for the pristine fatty acids and eutectic PCMs with a smaller number of components. In addition, the uncertainty analysis of the measurements was also performed and are given as footnotes of Tables 3 and 4, in the form of standard uncertainty “u” accordingly.

As evident from Fig. 5 that the operating temperature of SA-PA-LA-MA, SA-PA-LA-MA PT68, SA-PA-La, SA-PA-LA-PT68 and LA-PT68 ranges from ~27 to 38 °C with melting enthalpy ranging from ~128 to 181 kJ·kg⁻¹ which makes them suitable for the development of thermo-regulating textiles and in temperature management of the buildings.

The operating temperature of MA-PT68 ranges from ~46 to 50 °C with a latent heat of 182 kJ·kg⁻¹. Moreover, the melting temperature of SA-PA-PT68, PA-PT68, SA-PA and SA-PT68 ranges from ~52 to 75 °C with melting enthalpy ranging from 168 to 211 kJ·kg⁻¹ which makes them promising candidate in developing LHTES for solar water heating, district heating, and photovoltaic/thermal applications. The prepared eutectic PCMs covers the operating temperature range from 27 to 75 °C and can be employed in the TES systems integrated with renewables resources such as solar energy for the efficient performance. Consequently decreasing the fossil fuels consumption and greenhouse gas emissions thus providing cleaner and sustainable energy to the end user.

4. Conclusions

Various fatty acids like palmitic acid, myristic acid, stearic acid, lauric acid, and PureTemp68 are used for developing eutectic PCMs for thermal energy storage applications. The eutectic points of the 10 fatty acid mixtures prepared by melt blending followed by ultra-sonication are obtained from DSC and found to be in agreement with that obtained through Schröder equation. The specific heat capacities are also calculated from the data obtained from the DSC. The results revealed that the melting point of these organic phase change materials ranges from ~27 to 75 °C, with the latent heat from ~127 to 210 kJ·kg⁻¹ respectively. Chemical structure of the phase change materials is determined using FTIR Spectroscopy, by identifying the functional groups. The eutectic phase change materials showed exceptional thermal energy storage characteristics up to ~75 °C and are suitable for thermo-regulating textiles, solar water heating, thermal management in buildings, photovoltaic/thermal and space heating applications.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.appthermeng.2018.07.025.

References


[Q. Wei, Phase diagrams, eutectic mass ratios and thermal energy storage properties of multiple fatty acid eutectics as novel solid-liquid phase change materials for storage and retrieval of thermal energy, Appl. Therm. Eng. 113 (2017) 1319–1331.


[M. Iten, S. Liu, A work procedure of utilising PCMs as thermal storage systems based on air-TES systems, Energy Convers. Manage. 77 (2014) 608–627.


