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Stable, low-cost phase change material for building applications: The eutectic mixture of decanoic acid and tetradecanoic acid

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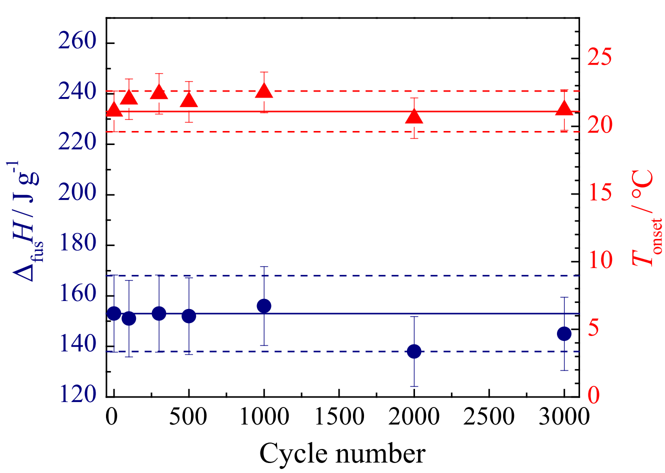
HIGHLIGHTS

- Decanoic/tetradecanoic acid eutectic at 0.82 ± 0.02 mole fraction (78 ± 2 mass%) decanoic acid.
- Melting of eutectic at 20.5 ± 1.5 °C, useful for building applications.
- High enthalpy change, 153 ± 15 J g^{-1}, is promising.
- Negligible change in stability after 3000 melt–freeze cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

We present a thorough characterization of the thermal properties and thermal reliability of the eutectic mixture of decanoic acid with tetradecanoic acid, as a phase change material (PCM) of potential interest for passive temperature control in buildings. From the temperature-composition binary phase diagram we found that the eutectic composition is 0.82 ± 0.02 mole fraction (78 ± 2 mass%) decanoic acid. We thoroughly characterized the thermal properties of the eutectic mixture. The eutectic composition has a high latent heat of fusion $\Delta_{fus}H$ = 153 ± 15 J g^{-1} and a melting temperature T_{onset} = 20.5 ± 1.5 °C. The heat capacity measured as a function of temperature for the solid and liquid phases just below and above the melting point is 1.9 and 2.1 ± 0.2 J K^{-1} g^{-1}, respectively. The average value of the thermal conductivity of the solid phase measured between −33 and 9 °C is κ_s = 0.20 ± 0.02 W m^{-1} K^{-1} and for the liquid phase, the thermal conductivity is κ_l = 0.23 ± 0.03 W m^{-1} K^{-1} for 28 and 38 °C. The mixture has a good long-term thermal stability as indicated by negligible changes in $\Delta_{fus}H$ and T_{onset} after 3000 melt–freeze cycles. The parameters determined in this work allow more accurate modeling and optimization of the behavior of the eutectic mixture in preparation for implementation as a thermal energy storage PCM.

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Nomenclature

C10	decanoic acid (aka capric acid)
C14	tetradecanoic acid (aka myristic acid)
C_p	heat capacity at constant pressure
$C_{p,l}$	heat capacity at constant pressure of liquid phase
$C_{p,s}$	heat capacity at constant pressure of solid phase
$\Delta_{fus}H$	latent heat of fusion
DSC	differential scanning calorimetry
κ_l	thermal conductivity of the liquid phase
κ_s	thermal conductivity of the solid phase
α_l	thermal diffusivity of the liquid phase
α_s	thermal diffusivity of the solid phase
ρ_l	mass density of the liquid phase
ρ_s	mass density of the solid phase
PCM	phase change material
PPMS	Physical Property Measurement System
T_{onset}	onset of DSC thermal anomaly
T_{peak}	peak of DSC thermal anomaly
T_{mpt}	melting point temperature
x_{C10}	mole fraction of decanoic acid
x_{C14}	mole fraction of tetradecanoic acid

1. Introduction

Thermal energy storage using the latent heat of fusion of phase change materials (PCMs) has developed into an important method to improve energy efficiencies in thermal systems by enhancing the capture of otherwise wasted heat; these characteristics have been of particular interest in building-comfort control and solar thermal applications [1–10]. For example, PCM can be added to an existing structure or directly incorporated into building materials such as wallboards, ceiling tiles, or insulation materials to absorb excess heat. The stored energy is released later, e.g. during solidification when the freezing point of the PCM is reached. As a result, PCM-infiltrated building materials can moderate temperature fluctuations within the space and reduce utility costs by easing the load on the air conditioning system during the peak hours of the day. PCMs also can compactly store solar energy during the day and use it to heat the building space at night.

Experimental studies and numerical simulations have demonstrated a substantial increase in thermal energy storage capacity when a PCM is integrated into existing systems. In solar thermal applications, for example, a recent study showed that a conventional flat-plate solar thermal collector with a tank filled with a PCM can absorb 20% more thermal energy than a water storage system [11]. Many organic (paraffin and non-paraffin) and inorganic (salt hydrate) PCMs have been intensively studied for comfort-control applications by integration of the PCM in building materials such as in gypsum and concrete [12–18], and several commercial products are readily available and used in different climates around the world. In a Mediterranean climate, it has been shown that the temperature fluctuations inside a structure built with bricks integrated with commercial PCMs are reduced and the peak temperature decreases, yielding a 17% reduction in energy consumption during the cooling period [19]. In New Zealand, a commercial PCM with a melting temperature range 18–22 °C was tested during the heating season, demonstrating the effectiveness of the PCM in peak load shifting, resulting in 31% decrease in energy consumption [20]. A study in China also showed that the addition of a mixture of fatty acid PCMs to gypsum wallboards reduced the temperature fluctuations [21].

Different methods for the incorporation of PCMs into construction materials have been investigated, including [22]: direct incorporation, where the PCM is directly mixed with the construction materials; immersion, where the building materials are impregnated with the liquid PCM; encapsulation, where either small particles (1–1000 μm) of PCM are enclosed in thin shells (microencapsulation) or several liters of PCMs are packed in containers (macroencapsulation) such as tubes, spheres and panels before being introduced into the building materials. The preparation of composite materials, such as concrete with macro-encapsulated paraffin [23] and concrete with paraffin/expanded perlite [24], are frequently reported in the literature along with their thermal performance. A panel made with the concrete and macro-encapsulated paraffin composite was shown to reduce the temperature inside a room by 3 °C by effectively absorbing part of the heat load [23].

An extensive list of PCMs suitable for building-comfort applications, along with some of their thermophysical properties, can be found in Ref. [5]. Among those PCMs, fatty acids possess several characteristics that make them particularly desirable for building applications [25–27]: they are non-toxic, biodegradable and easily recyclable, with a low commodity cost, and they can be derived from renewable sources in a sustainable way such that the payback time to recoup their embodied energy is only a matter of months in solar thermal applications [28]. Fatty acids also have good thermophysical properties, especially high volumetric latent heats of fusion ($\geqslant$150 kJ L^{-1}), congruent melting and little or no supercooling, and good chemical and thermal stability after many thermal cycles. However, a major limitation of fatty acids as PCMs is that their transition temperatures are considerably higher than the 20–28 °C range that is typically required for comfort-control applications in buildings. However, by combining two or more fatty acids with different compositions, it is possible to form eutectic mixtures with phase transition temperatures within the desired range. While eutectic mixtures of fatty acids lower the melting temperature relative to the pure components, the eutectic can maintain a sharp phase transition and a high latent heat of fusion.

In this study, we present a comprehensive characterization of the thermal properties of the eutectic mixture of high-purity decanoic acid (also known as capric acid) and tetradecanoic acid (also known as myristic acid) PCMs, along with an investigation of its thermal stability. This eutectic was chosen because its transition temperature is at a very useful temperature for building applications (~21 °C). However, the reports concerning this binary mixture presented a range of compositions (0.72–0.80 mole fraction decanoic acid) and of transition temperatures (21–25 °C) [29–34]. The nature of a eutectic is such that the precise composition is required for consistent performance over many thousands of melt–freeze cycles, as required for PCM applications in building materials. Off-eutectic compositions would eventually lead to phase inhomogeneity, and a consequent temperature range of transition, and thereby reduced efficiency for energy storage. Furthermore, important thermophysical information such as the heat capacity and the thermal conductivity of both the solid and liquid phases was not reported for this eutectic. When a PCM is considered for integration into a structure, such information is required to model the effectiveness of the PCM and to optimize the quantity needed and placement within the space [18,35]. We also determined the long-term thermal stability of this eutectic as a PCM, as an important contributor to its economic viability. As we show, the eutectic of decanoic acid and tetradecanoic acid offers considerable promise as a stable, low-cost phase change material for building applications.