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Research Paper

Binary mixtures of fatty acid methyl esters as phase change materials for low temperature applications

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HIGHLIGHTS

- Binary mixtures of fatty acid methyl esters are proposed as phase change materials.
- Two binary eutectic mixtures using methyl laurate are investigated.
- The mixtures provide desirable thermal properties for deicing applications.
- The mixtures' high latent heat of fusion provides sufficient energy to reduce ice.
- Solid–liquid phase diagrams for the two mixtures are developed.

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ABSTRACT

Incorporating phase change materials (PCMs) into concrete pavements has been suggested as a means to improve anti-icing practices by reducing the accumulation of snow and ice. This paper reports on the development of two PCMs composed of a binary mixture of fatty acid methyl esters (FAME) at their eutectic composition, which provide a solid–liquid phase transformation with thermal transition temperature slightly above 0 °C and with a high enthalpy of fusion. The phase behavior of binary mixtures of medium length saturated FAME at their eutectic composition demonstrated ideal properties for PCMs. The eutectic binary mixtures and corresponding thermal properties are: (1) methyl laurate (C12) + methyl myristate, $x_{C12} = 0.77$, and (2) methyl laurate + methyl palmitate, $x_{C12} = 0.86$ with eutectic melting temperatures and latent heats of fusion of 0.21 °C and 2.4 °C, and 174.3 J·g^{-1} and 166.5 J·g^{-1}, respectively. Using differential scanning calorimetry, solid–liquid phase diagrams were created, indicating that the phase behavior of these binary mixtures at their eutectic compositions demonstrated useful thermal properties for PCMs. Current findings of this study indicate that these binary mixtures have the necessary properties to be a high performance PCM with the potential to reduce the levels of icing on concrete pavements.

1. Introduction

Phase change materials (PCMs) are latent heat storage materials which have the ability to absorb thermal energy from external sources and release the energy during phase transitions. The use of high latent enthalpy PCMs in concrete infrastructure has been proposed as a possible method for altering anti-icing practices on concrete pavements [1–6]. The energy stored in PCMs can be released during cooling (crystallization) and absorbed during heating (melting). The released energy can reduce the amount of snow and ice on the surface of the pavement thereby decreasing the use of deicing salts and improving the durability of concrete [7–13].

Using PCMs in concrete pavements to melt ice and snow requires specific thermal, physical, and chemical properties to be compatible with the concrete system. The search for a suitable PCM has been directed toward use of low melting organic materials. Fatty acid methyl esters show solid–liquid phase transitions with desirable thermal properties within a narrow temperature range. FAME mixtures can be tailored to include a phase transition temperature that differs from the pure material for the required temperature slightly above 0 °C and high latent energy of fusion (>150 J·g^{-1}). FAME's physical properties include low vapor pressure and small volumetric changes during phase transition. FAMEs are chemically stable, nontoxic, and non-flammable. They are commercially available and are sustainably derived from common vegetable and animal oils providing renewable supply without depending on petroleum [14–16].

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In the present study, the thermal properties of two binary mixtures providing the required thermal properties, methyl laurate + methyl myristate (C12–C14) and methyl laurate + methyl palmitate (C12–C16), were investigated using differential scanning calorimetry. Additionally, solid–liquid phase diagrams for each of the binary mixtures were developed providing information on the *liquidus* line and transitions below the *liquidus* line are reported in the present study.

2. Experimental

2.1. Materials

Methyl laurate (C12:0, 98% pure, CAS: 111-82-0), methyl myristate (C14:0, 98% pure, CAS: 124-10-7), and methyl palmitate (C16:0, 97% pure, CAS: 112-39-0), hereafter referred to as pure, were used for preparation of the binary mixtures. These methyl esters were purchased from SAFC Supply Solutions and Sigma Aldrich. A series of binary mixtures were prepared gravimetrically by heating the methyl esters above their melting point before blending together at various mole fractions within the range of 0.00–1.00.

2.2. Composition analysis

The fatty acid methyl ester composition in each mixture was confirmed using a Thermo Scientific TRACE™ Ultra Gas Chromatograph (GC) equipped with a variable split flow programmable temperature vaporizing injector (PTV), temperature programmable oven, a flame ionization detector (FID) and an AS/AI 3000 auto-sampler and auto-injector. The GC operating conditions were configured to follow the standard method, EN 14103-2011 [17], presented in Table 1, using a polar analytical capillary column, EC™-WAX, 30 m length × 0.25 mm inner diameter × 0.25 µm film thickness. ChromQuest™ 4.2 was used for data collection and the analysis of the chromatographs.

2.3. Thermal analysis

The heat flow and temperature associated with phase transitions for each mixture were determined using a TA Instruments Q2000 low temperature differential scanning calorimetry (LT-DSC) instrument. The thermograms were analyzed using TA Instruments Universal Analysis 2000. Indium was used for the DSC calibration. Dry nitrogen was used for the sample purge gas with the flow rate regulated at 50 mL·min^{-1}. A sample (10 ± 2 mg) was weighed into a Tzero stainless steel high volume pan and sealed hermetically. Using the protocol of Costa et al. [18], the sample was heated at a rate of 5 °C·min^{-1} to 15 °C above the melting temperature of the highest melting temperature component and held for 20 min. The cooling thermogram was then recorded by cooling the sample at a rate of 1 °C·min^{-1} to 25 °C below the melting temperature of the lowest melting component. Then, the sample was held isothermally for 30 min. The heating thermogram was obtained by increasing the temperature at a rate of 1 °C·min^{-1} to the initial heated temperature. This program was repeated three times for each sample.

The peak top temperatures, the temperature associated with the point of maximum heat flow, were determined using a Universal Analysis 2000 program of TA Instruments (New Castle, DE) for the melting (T_{melt}), eutectic reaction (T_{eut}), peritectic reaction (T_{peri}), and metatectic reaction (T_{meta}) temperatures. The eutectic, peritectic and metatectic reactions were identified by an endothermic peak appearing at the invariant reaction's temperature. The peak top temperatures were also used for determining the temperature for phase transitions (T_{trans1}, T_{trans2}, and $T_{trans.pure}$) associated with overlapping peaks to avoid errors on temperature evaluation, a common method for evaluating mixtures of FAME, fatty acids and fatty alcohols [14,19–29]. The onset temperature (T_{onset}) and end of melting temperature (T_{end}) were measured as the point of intersection from the line tangential to the point of maximum slope and the horizontal baseline. The total enthalpy values (ΔH_{melt}) were obtained by numerical integration of the area under all the peaks in the corresponding heat flow versus temperature curves.

Table 1
GC operating conditions.

Inlet		Carrier		
Temperature	250 °C	Column flow (He)	1.4 mL·min^{-1}	
Split flow	70 mL·min^{-1} (50:1 ratio)	Flow mode	Constant	
FID		**Oven program**		
Temperature	270 °C	Initial	110 °C	Hold 0.5 min
Air flow	300 mL·min^{-1}	Ramp 1	20 °C min^{-1} to 130 °C	Hold 0.5 min
H_2 flow	30 mL·min^{-1}	Ramp 2	30 °C min^{-1} to 220 °C	Hold 1 min
Make-up (He) flow	30 mL·min^{-1}	Ramp 3	10 °C min^{-1} to 250 °C	Hold 7 min

3. Results and discussion

3.1. Mixtures composition

The composition of each of the binary mixtures and the pure FAME used in this study are presented based on mole fractions in Tables 2 and 3. A particular mixture will be referred to by its methyl laurate mole fraction such as $x_{C12} \approx 0.77$.

3.2. Methyl laurate and methyl myristate binary mixtures

The melting temperature, transition temperatures under the *liquidus* line and enthalpy for each methyl laurate + methyl myristate binary mixture are presented in Table 4. The DSC melting thermograms for a select number of the C12–C14 mixtures are plotted in Fig. 1.

The melting curves show the complex melting behavior of this binary system. The binary mixtures of methyl esters form non-ideal solutions exhibiting freezing point depression. With increasing the methyl myristate composition, the melting temperature of the system decreases and multiple overlapping peaks form, relating to polymorphic behavior.

Table 2
Composition of C12–C14 binary mixtures.[a]

C12:0 (mole fraction)	C14:0 (mole fraction)	Others (mole fraction)[d]
0.9927[b]	0.0017	0.0057
0.9036	0.0913	0.0050
0.8591	0.1372	0.0028
0.8123	0.1822	0.0055
0.7674	0.2273	0.0052
0.7222	0.2762	0.0016
0.6764	0.3214	0.0021
0.6253	0.3731	0.0016
0.5817	0.4164	0.0020
0.5245	0.4722	0.0033
0.4274	0.5601	0.0120
0.3386	0.6592	0.0022
0.2229	0.7756	0.0016
0.1155	0.8839	0.0006
0.0022[c]	0.9921	0.0057

[a] Values represent an average of at least three replicates. Standard deviations are all less than ±0.010.
[b] Pure methyl laurate (C12:0).
[c] Pure methyl myristate (C14:0).
[d] Others include methyl palmitate, methyl 10-heptadecanoate, methyl stearate, methyl oleate, methyl linoleate.