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Study on phase diagram of fatty acids mixtures to determine eutectic temperatures and the corresponding mixing proportions

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HIGHLIGHTS

- A series of fatty acids mixtures were prepared by heating-ultrasonic method.
- The phase diagram was plotted and analyzed.
- The thermal data was tested by DSC.
- The theoretical data was obtained by Schroder Van Laar equation.
- The scope to find the ternary eutectic point can be narrowed greatly.

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ABSTRACT

This study was focused on preparation and characterization of fatty acid eutectic mixtures as phase change materials (PCMs). The four common fatty acids: stearic acid (SA), palmitic acid (PA), myristic acid (MA) and lauric acid (LA) were selected as representative to prepare binary and ternary eutectic mixtures by heating-ultrasonic method. The melting points of LA–MA, LA–SA, SA–MA, SA–PA, MA–PA, LA–MA–SA, MA–SA–PA mixtures with varying combination proportions were determined and then analyzed by drawing the phase diagrams to determine the eutectic points and the corresponding mixing proportions. The results showed that the eutectic temperature of ternary fatty acids was lower than binary fatty acids'; ternary mixture possessed the same thermal properties with pseudo-binary mixture in both melting temperature and latent heat of phase change; the Schröeder-Van Laar equation can be taken as a basis for mixing proportion of pseudo-binary fatty acid and ternary fatty acid systems; the ternary eutectic point on the ternary phase diagram was just in the vicinity of a small triangle which was formed by the connection between the three vertices and the three eutectic points of binary fatty acid in the corresponding across flats. Moreover, ternary and pseudo-binary mixtures had advantage in energy conservation applications such as building heating/cooling and indoor temperature controlling especially when the temperature in need was low.

1. Introduction

As a new energy-saving and environment-friendly technique, latent heat thermal energy storage by using phase change materials (PCMs) has achieved an increasing attention. PCMs can be applied widely to the field of energy conservation such as construction, solar energy, waste heat and waste cold as a novel energy conservation material. In the process of the urbanization in some developing countries like China, more and more new buildings and public facilities are needed. Applying to PCMs to building materials can contribute to moderating temperature swings, improving thermal comfort and decrease electrical peak–valley difference [1–6].

Based on their chemical components, PCMs can be classified into two different kinds of categories: (i) organic compounds and (ii) inorganic compounds [6,7]. Most of inorganic PCMs are corrosive to most metals, undergo supercooling and have poor reversibility, while organic PCMs are recommended widely due to their satisfying thermal and heat transfer features. The fatty acids are most promising organic PCMs, due to their advantages of chemical and physical stability, low cost, high latent heat of fusion, non-toxicity, non-flammability, non-subcooling, non-corrosiveness, small volume change and good thermal reliability after a great number of melt/freeze cycles [8,9]. Furthermore, fatty acids can be extracting from the common vegetable and animal oils, therefore they can be supplied continuously

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[5,9–12]. However, the melting point of the single fatty acid is quite high for applications such as building heating/cooling and indoor temperature controlling [13–16]. In general, the low-melting organic mixtures of saturated acids are attained by mixing, namely eutectic mixtures.

Many studies on the preparation and the properties of binary PCMs have been carried out. Shilei et al. [17] investigated wallboard incorporated the eutectic mixture of CA–LA and tested its thermal stability by phase transition cycles; Sari [18] tested the melting points of binary eutectic mixture made with LA–MA, LA–PA, and MA–SA, proving that the mixtures had shown reasonably good thermal properties and thermal reliability; Li et al. [2] prepared a series of binary phase change materials by mixing fatty acids and calculated their phase-transition temperatures and corresponding mixing proportions by Schröeder-Van Laar equation. This calculation method can be taken as a basis for determining mixing proportion of binary phase change materials. Feldman et al. [19] prepared several products by esterification of different commercial mixtures of SA and PA with methyl, butyl and propyl alcohols and investigated heat storage capacity and phase transition temperature.

However, taking the comfortability of the residential surroundings into consideration, single fatty acid and the binary fatty acid mixture, whose phase-transition temperatures are usually high, cannot meet the requirement of moderating the indoor temperature. According to the law of lowering the melting point, the eutectic temperature of mixture is lower than any one of the components in mixture. The mixture of three components has the lower melting point than the corresponding mixture of two components. Study on ternary compounding of fatty acid is yet limited.

As we all known, LA, MA, SA and PA, as common fatty acids, are often employed in preparing fatty acids eutectic mixtures. In this work, under different combination ratios, eutectic mixtures of LA–MA, LA–SA, SA–MA, SA–PA, MA–PA, LA–MA–SA, MA–SA–PA mixtures were prepared by using heating-ultrasonic method as representative of fatty acids eutectic mixtures, and then the thermal properties were measured by differential scanning calorimetry (DSC) and Binocular microscope melting point apparatus. Based on the test results, the comparison of pseudo-binary fatty acid system and ternary fatty acid system were discussed; the phase diagrams of LA–MA, LA–SA, SA–MA, SA–PA, MA–PA, LA–MA–SA, MA–SA–PA mixtures were plotted and investigated; the location of eutectic point in phase diagrams were determined. The novel way to narrow the scope of the ternary eutectic point on the ternary phase diagram would make the work of finding the ternary eutectic point more effectively. In addition, the research conclusions about LA–SA–MA and SA–MA–PA ternary eutectic mixture were promoted into general rules about fatty acids eutectic mixtures. This research would provide some theoretical support and application reference for the future works about compounding polynary eutectic mixtures of fatty acids as PCM, and make up for the vacancy of existing research.

2. Materials and methods

2.1. Raw materials

Fatty acids including stearic acid (SA, 0.94 g/mL, min 98% pure), palmitic acid (PA, 0.85 g/mL, min 98% pure), myristic acid (MA, 0.86 g/mL, min 98% pure) and lauric acid (LA, 0.88 g/mL, min 98% pure) were all obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai). All the four fatty acids had good chemical stability, good thermal stability, non-flammability, low corrosion and non-toxicity. The basic thermal properties are listed in Table 1.

2.2. Characterization

The melting points of the mixtures were obtained by using Binocular microscope melting point apparatus (XT-4 Beijing No. 000,000,113 Beijing Tech Instrument Co., Ltd.). Samples were heated at a heating rate of 0.2 °C per min. The uncertainty of the measurements was less than 1.0 °C.

Differential scanning calorimetry (METTLER TOLEDO DSC1 STAR^e system) was used to test the thermal properties of fatty acid mixtures. Samples were heated from 10 °C to 70 °C at a heating rate of 2–5 °C per min in a static nitrogen atmosphere. The latent heat of fusion was attained by calculating the area under the peak by numerical integration. Drawing a line at the point of maximum slope of the leading edge of the DSC peak and extrapolating the base line on the same side as the leading edge of the peak, the onset temperature was obtained, which was the temperature that mixture started to melt obviously. It can be regarded as the melting point. The uncertainty of the melting temperature was estimated to be lower than 0.2 °C. The calorimetric sensitivity was 0.04 μW.

Due to the experimental conditions, the melting points of majority samples were measured by Binocular microscope melting point apparatus in order to save time.

2.3. Preparation of fatty acid mixtures

Fatty acid mixtures were prepared by heating-ultrasonic method. The fatty acids were weighed according to the certain proportion on an analytical balance (AL204 METTLER TOLEDO, made by Metter-Toledo Group) with a ±0.2 mg accuracy: certain intervals (10%) from 0% to 100%, and uniformly mixed together. The mixtures were vacuumed firstly, then melted and blended in the drying oven. Then the mixtures were cooled to the room temperature and conserved under sealed condition.

3. Results and analysis

3.1. Characteristics of eutectic system

Eutectic system has the following characteristics [20]: 1. Components do not react with each other; 2. Different components are completely immiscible in solid state, while completely miscible in liquid state; 3. Phase transition of every single component occurs only when it reaches the specific phase transition temperatures, especially for solid-liquid phase transition.

3.1.1. Properties of typical binary eutectic system

A typical and the simplest binary eutectic phase diagram is shown in Fig. 1 [21]. The A and B represent the different crystals. j and g represent the solid state of A and B, respectively. Point C stands for the melting point of pure A, with the dosage of B increasing, melting point of A gradually decreases until it reached point E along line CE. Point D stands for the melting point of pure B, and when more and more A is added to B, the changing trend of B is similar with that of A. A and B melt or crystallize at the same point of E. Point E is regarded to the eutectic point. Because the mixed phase change medium in eutectic point proportioning has stable performance, a defined single melting point and heat of fusion, it is popular in application.

The proportion and the corresponding phase-transition temperature can be calculated through an empirical formula: the equation of Schröeder-Van Laar [12].

$$\ln x_i = H_i/R(1/T_i - 1/T) \quad (1)$$

Note: H_i is the molar melting heat of component i at the melting point T (J/mol), T_i is the melting point of component i (K); the