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Preparation, Phase Diagrams and Characterization of Fatty Acids Binary Eutectic Mixtures for Latent Heat Thermal Energy Storage

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Abstract: A series of fatty acid binary eutectic mixtures were prepared by using capric acid, lauric acid, myristic acid, palmitic acid, and stearic acid (CA, LA, MA, PA, and SA) as raw materials. The phase diagrams of these fatty acid binary eutectic mixtures were drawn using the Schrader equation. The thermal properties and structure were determined using differential scanning calorimetry (DSC). The thermal stability was assessed using thermogravimetric analysis (TGA) and thermal cycling tests. DSC analysis results showed that the phase change temperature of these fatty acid binary eutectic mixtures is between 17.7 °C and 57.1 °C, and the phase change latent heat is between 145.2 J/g and 193.0 J/g. The results of TGA and thermal cycle tests showed that these fatty acid binary eutectic mixtures have good thermal stability and long-term cycle thermal reliability. These results indicated that these binary eutectic mixtures of fatty acids were suitable as thermal energy storage materials for low-temperature systems.

Keywords: fatty acids; eutectic mixtures; phase diagrams; characterization; latent heat thermal energy storage

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1. Introduction

Thermal energy storage (TES) technology offers a wide range of applications in the sectors of solar energy utilization, shifting peaks and valleys of power, industrial waste heat and waste heat recycling, and heating and air conditioning of buildings, and more and more people are paying attention to it [1–4]. Chemical energy storage, sensible heat storage, and latent heat storage are the three main types of thermal energy storage [5–7]. Latent heat thermal energy storage has gained wide attention and application. In addition to having a high energy storage density, latent heat storage also has a small temperature change while storing energy, superior material stability, and a high level of safety [8–11]. Phase change material (PCM) is at the heart of latent thermal energy storage. The fatty acid has attracted much attention due to their favorable phase transition temperature, high phase transition latent heat, non-toxic, non-corrosive, minimal undercooling, no or minor volume change, high thermal reliability, abundant raw materials, easy to get, and other advantages [12,13]. Mainly long-chain saturated fatty acids with even-numbered carbon atoms, C10–C18, are employed as phase change energy storage materials. The general chemical formula is $C_nH_{2n}O_2$ or $CH_3(CH_2)_nCOOH$ (where n is the number of carbon atoms), such as capric acid (CA), lauric acid (LA), myristic acid (MA), palmitic acid (PA), and stearic acid (SA), etc. The chemical formulas for CA, LA, MA, PA, and SA are CH_3–$(CH_2)_8$–COOH, CH_3–$(CH_2)_{10}$–COOH, CH_3–$(CH_2)_{12}$–COOH, CH_3–$(CH_2)_{14}$–COOH, and CH_3–$(CH_2)_{16}$–COOH, respectively, and the main physical properties are shown in Table 1 [14–17]. It can be seen from Table 1 that although the pure fatty acid phase change material has a larger phase transition latent heat, but the phase transition temperature is relatively higher than that of low-temperature building energy-saving applications. Therefore, in order to better meet the temperature of 18–55 °C, multiple fatty acids can be mixed into a eutectic mixture according to the eutectic effect of fatty acids to reduce the phase transition temperature and expand its temperature application range, on which plenty of research has been done [18–23].

Table 1. Physical characteristics of saturated fatty acids commonly used as PCMs.

Fatty Acid	Formula	Temperature of Phase Change /°C	Latent Heat of Phase Change /J·g^{-1}	Density /kg·(m^3)$^{-1}$		Specific Heat /kJ·(kg·°C)$^{-1}$		Thermal Conductivity /W·(m·K)$^{-1}$
				Solid	Liquid	Solid	Liquid	
CA	$C_{10}H_{20}O_2$	30.1–32	149.1–155.5	1004	878	1.9	2.1	0.153
LA	$C_{12}H_{24}O_2$	42.4–44	174.9–186.4	1007	862	1.7	2.3	0.147
MA	$C_{14}H_{28}O_2$	52.2–58	180.5–188.6	990	861	1.7	2.4	0.150
PA	$C_{16}H_{32}O_2$	58.9–64	185.4–212.1	989	850	1.9	2.8	0.162
SA	$C_{18}H_{36}O_2$	68.54–70.8	201.8–222.8	965	848	1.6	2.2	0.172

When two kinds of fatty acids are mixed, the mixtures have different melting points according to the mixing ratio, but the melting point of the mixtures is lower than that of both fatty acids. This phenomenon is called the eutectic effect. Even if the phase transition latent heat of the single fatty acid phase change material is large, but the phase transition temperature is constant and is substantially higher than the application in the field of low-temperature energy saving. Therefore, two fatty acids can be combined in accordance with the eutectic effect to achieve the desired temperature in order to accommodate various applications.

Sari et al. investigated the thermal stability of SA, PA, MA, and LA PCMs, and the results showed that after 0, 120, 560, 850 and 1200 accelerated thermal cycles, the change of PCM melting temperature is in the range of 0.07–7.87 °C, and the change of PCM melting latent heat is in the range of −1–−27.7%, and all PCMs melting latent heat decreases irregularly with the increase of the number of thermal cycles [24]. Sari et al. also studied the long-term thermal stability of binary eutectic fatty acids, and the results showed that the phase change temperature and latent heat changed little before and after the thermal cycle, but there was no law to follow [25]. Sari et al. further studied the creation of a cheap and environmentally friendly composite PCM made of wood fiber and CA-SA and its performance on a lab scale in terms of thermoregulation [26]. Ke Huichen prepared multiple binary, ternary, quaternary, and quinary fatty acid eutectic compounds with five kinds of single fatty acids as raw materials and carried out experimental research, and the results show that these fatty acids are suitable for low-temperature TES systems [27]. Yang L et al. selected LA, MA, PA, and SA fatty acids to perform 10,000 thermal cycles for characterization, and the results showed that as the number of thermal cycles increases, the phase change temperature and phase change latent heat of PCMs both showed a downward trend, the specific heat and thermal conductivity did not change significantly, and nothing changed in the chemical structure, therefore, it is believed that these PCMs have high thermal reliability and can last a very long period [28]. Zhou et al. prepared the CA–MA binary eutectic and investigated its properties, and the results revealed that the mixture (72/28 wt%) has a suitable phase transition temperature (T_m: 18.21 °C; T_f: 17.40 °C) and high phase transition enthalpy (ΔH_m: 148.5 J/g; ΔH_f: 134.0 J/g), and it is an excellent PCM for TES [29]. Mailhe Clement et al. obtained a phase diagram of the PA-SA binary system containing over a hundred data sets, and the results' reliability is evaluated by comparing them to results of DSC or from other standard methods, as well as a thermodynamic model for solid-liquid equilibria [30]. Samer Kahwaji et al. created a mathematical tool based on a thermodynamic model in Microsoft Excel to calculate the composition, T_{mpt}, and ΔH_{fus} of 105 binary mixtures formed by 15 fatty acids, and the computed properties demonstrated that eutectics significantly broaden the range of uses for fatty acids as PCMs for TES by both extending the range of T_{mpt} and providing a wide range of new T_{mpt} values that are impossible to obtain from single fatty acids [31,32].

In the low-temperature TES such as building energy conservation, solar energy storage, and waste heat recovery, the temperature range is generally between 15 °C and 60 °C. However, the above pure fatty acid phase transition temperature is constant. Therefore, different phase transition temperatures can be obtained by mixing two kinds of pure fatty acids with different mass ratios according to the eutectic effect to adapt to different applications. As can be seen from the above, most of the literature only focuses on a few binary eutectic mixtures, and systematic theoretical research and experimental characterization have not been carried out. In this paper, ten fatty acid binary eutectic mixtures, capric acid–lauric acid (CA–LA), capric acid–myristic acid (CA–MA), capric acid–palmitic acid (CA–PA), capric acid–stearic acid (CA–SA), lauric acid–myristic acid (LA–MA), lauric acid–palmitic acid (LA–PA), lauric acid–stearic acid (LA–SA), myristic acid–palmitic acid (MA–PA), myristic acid–stearic acid (MA–SA), and palmitic acid–stearic acid (PA–SA), were prepared with five fatty acids of CA, LA, MA, PA, and SA, and the phase diagrams of ten fatty acid binary eutectic mixtures were calculated, and the theoretical eutectic points were calculated and deduced, and the thermal properties, structure and thermal stability of the binary eutectic mixtures were systematically studied.

2. Experiments

2.1. Materials

Capric acid (CA, ≥98.5% purity), Lauric acid (LA, ≥99% purity), Myristic acid (MA, ≥98% purity), Palmitic acid (PA, ≥98.5% purity), and stearic acid (SA, ≥98.5% purity) were supplied by Shanghai Zhunyun Chemical Co, Ltd., China.

2.2. Characterization

Differential scanning calorimeter (DSC, NETSZCH 214Polyma, Germany) is used to determine the phase transition temperature (melting and freezing, T_m and T_f) and latent heat (melting and freezing, ΔH_m and ΔH_f) of pure fatty acids and their eutectic mixtures. The sample is packaged in an aluminum crucible, and the mass of the sample is about 5–10 mg, cooled with liquid nitrogen. The accuracy of phase change temperature and latent heat are ±0.1% and ±4%, respectively. The temperature range is 0–80 °C, and the heating speed is 5 °C per minute based on the effect of different heating speeds on the DSC results by references [33]. To make sure the test is accurate, the average value is taken after multiple tests, and the extrapolated starting temperature on the DSC curve is set as the phase transition temperature.

The thermal stability of the samples was studied by using Thermogravimetric analysis (TGA, TA TGA5000IR, USA). In the nitrogen atmosphere, the characteristics of the samples were measured from room temperature to the set temperature at the heating rate of 10 °C/min with an error of ±0.2%. High and low temperature test chamber (LINPIN, LRHS-101-LH, Shanghai Linpin Instrument Co., Ltd., China) is used for accelerated thermal cycle test. The preset temperature is 10–60 °C, the heating rate is 2 °C/min, and the cooling rate is 2 °C/min. Fourier transform infrared spectrometer (FT–IR, Thermo Scientific Nicolet iS5, USA) was used to examine the chemical composition of the substance. After the background test, the samples were put into the test. The test resolution is 4 cm^{-1} and the frequency is 4000–400 cm^{-1} and the number of sample scans is 16. In order to reduce the error of repeated sample loading, it is generally necessary to determine multiple times and calculate the average spectrum.

2.3. Preparation of the Acid Binary Eutectic Mixtures

Using CA, LA, MA, PA, and SA as raw materials, the binary eutectic mixtures of fatty acids were prepared by melt mixing and ultrasonic oscillation. Two solid fatty acid mixtures with a certain mass ratio are put into a beaker, and the weight error of the sample was controlled within 0.1 mg. Then the beaker was placed in a vacuum drying oven at 80 °C for 2 h at a constant temperature. After all of the fatty acids had dissolved, the magnetic stirrer with constant temperature heating was used to stir for 30 min at 500 rpm to make them fully fused. After that, the beaker was put into an ultrasonic water bath with a 60 °C temperature setting, and the ultrasonic vibration time was set to about 2 min to make sure the fatty acids were always molten and fully fused. Finally, after cooling and solidification, the binary eutectic mixture of fatty acids was obtained.

3. Results and Discussion

3.1. Phase Diagram of Fatty Acid Binary Eutectic Mixtures

The phase transition temperature and latent heat are two important thermal performance parameters of PCMs. The phase transition temperature and latent heat determine the use scene and thermal storage capabilities of the PCM, respectively. The DSC curves for CA, LA, MA, PA, and SA are shown in Figure 1. It is evident that the phase change point of a pure fatty acid keeps constant, and the lowest phase change temperature is higher than 30 °C. Therefore, it is required to create eutectic mixtures by mixing multiple pure fatty acids with different phase transition temperatures, where the phase transition points of eutectic mixtures are lower than that of any component.

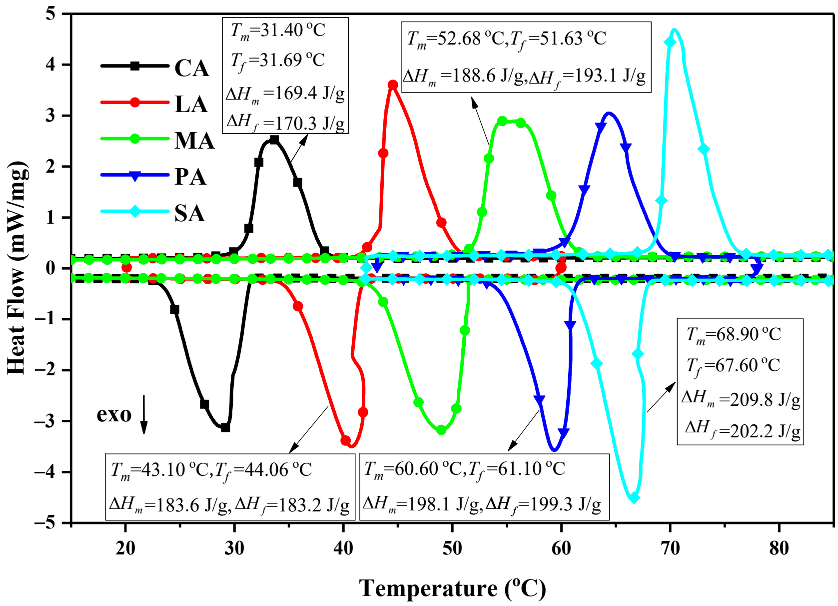

Figure 1. DSC curves of five pure fatty acids.

When two kinds of fatty acids are mixed in a certain proportion, there will be the lowest melting point, which is called the low eutectic point. Figure 2 shows a simple A–B binary phase diagram with a low eutectic point. The lines *aE* and *bE* are the liquidus, which respectively represents the equilibrium between the solid phases A and B and the corresponding liquid phases at different temperatures. Point *a* is the melting point of solid phase A, point *b* is the melting point of solid phase B, and point *E* is the intersection point of two liquids, which is the equilibrium point of the coexistence of the liquid phase (the composition is point *E*) with solid phase A and solid phase B. The equilibrium point is called the eutectic point, and the solid mixture precipitated at this point is called the eutectic mixture.

The law of thermodynamics and the theory of phase equilibrium are useful resources for forecasting the chemical makeup and thermal characteristics of eutectic mixtures. The Schroder equation can be obtained by substituting melting point temperature for three-phase point temperature, as shown in Equation (1) [14,34–36].

$$x_i = \exp\left[\frac{\Delta H_{mi}}{R}\left(\frac{1}{T_{mi}} - \frac{1}{T}\right)\right] \tag{1}$$

where: x_i is the mole fraction of the ith component, $\sum x_i = 1$; ΔH_m is the melting latent heat of the ith component, J/mol; R is the gas constant, which is 8.315 J/(mol·K); T_{mi} is the melting point of the ith component, K; T is the melting point of the mixture, K.

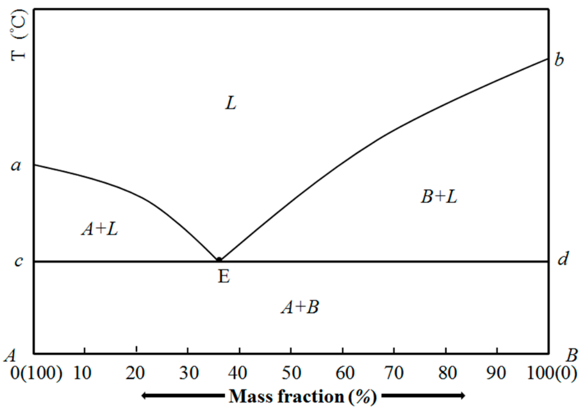

Figure 2. Phase diagram of a binary eutectic mixture system.

For a binary fatty acid eutectic system with components A and B, Formula (1) can be written as the following Formula (2).

$$\begin{cases} -\frac{\Delta H_{mA}}{T_{mA}}(T_m - T_{mA}) - RT_m \ln(1 - x_A) = 0 \\ -\frac{\Delta H_{mB}}{T_{mB}}(T_m - T_{mB}) - RT_m \ln(1 - x_B) = 0 \end{cases}, \quad (2)$$

where: ΔH_{mA} and ΔH_{mB} are the melting latent heat of component A and component B, respectively, J/mol; T_{mA}, T_{mB}, and T_m are the melting temperature of component A and component B and their mixtures, respectively, K; x_A and x_B are the mole fraction of the component A and component B, x_A + x_B =1.

The Formula (3) for calculating the melting point of the eutectic mixture can be obtained by simplifying Formula (2).

$$\begin{cases} T_m = 1/(\frac{1}{T_{mA}} - \frac{R \ln x_A}{\Delta H_{mA}}) \\ T_m = 1/(\frac{1}{T_{mB}} - \frac{R \ln x_B}{\Delta H_{mB}}) \end{cases}, \quad (3)$$

The melting latent heat (ΔH_m, J/mol) of the binary fatty acid eutectic system with components A and B can be obtained according to the phase equilibrium and minimum eutectic theory, as shown in the following Formula (4) [37].

$$\Delta H_m = T_m \sum_{i=1}^{n} \left(\frac{x_i \Delta H_{mi}}{T_{mi}} \right) (i = A, B) \quad (4)$$

According to Formulas (3) and (4), it is possible to build the eutectic phase diagram and identify the eutectic points of binary eutectic mixes of fatty acids. The phase diagrams of ten fatty acid binary eutectic mixtures are shown in Figure 3, and the data are shown in Table 2. The phase change points of these fatty acid binary eutectic mixtures are between 20–60 °C, which is the suitable temperature for the construction environment. Therefore, in the area of building energy conservation, the fatty acid binary eutectic combinations provide a wide range of application possibilities.

The Schrader formula is simply a rough approximation because fatty acids vary in purity and chemical composition. Experiments are needed to verify the mass ratio of two fatty acids in the binary system. A series of fatty acids binary eutectic mixes were created with various mass ratios near the theoretical calculation eutectic point. DSC was used to measure these mixtures' phase transition temperatures, and the mass ratio of the eutectic melting point was determined by comparing these phase transition temperatures.

The results are shown in Table 3. From the comparison between the theoretical values and the experimental values in Table 3, it can be seen that the theoretical values of the mass ratio are very close to the experimental values, and the maximum error is 13.59%, which appears in the CA–SA binary system. This shows that the Schrader formula is indeed applicable to the calculation of the eutectic point of the binary eutectic mixture. Two possible causes of the inaccuracy are that the pure fatty acids include contaminants and that there were experimental errors made throughout the test procedure.

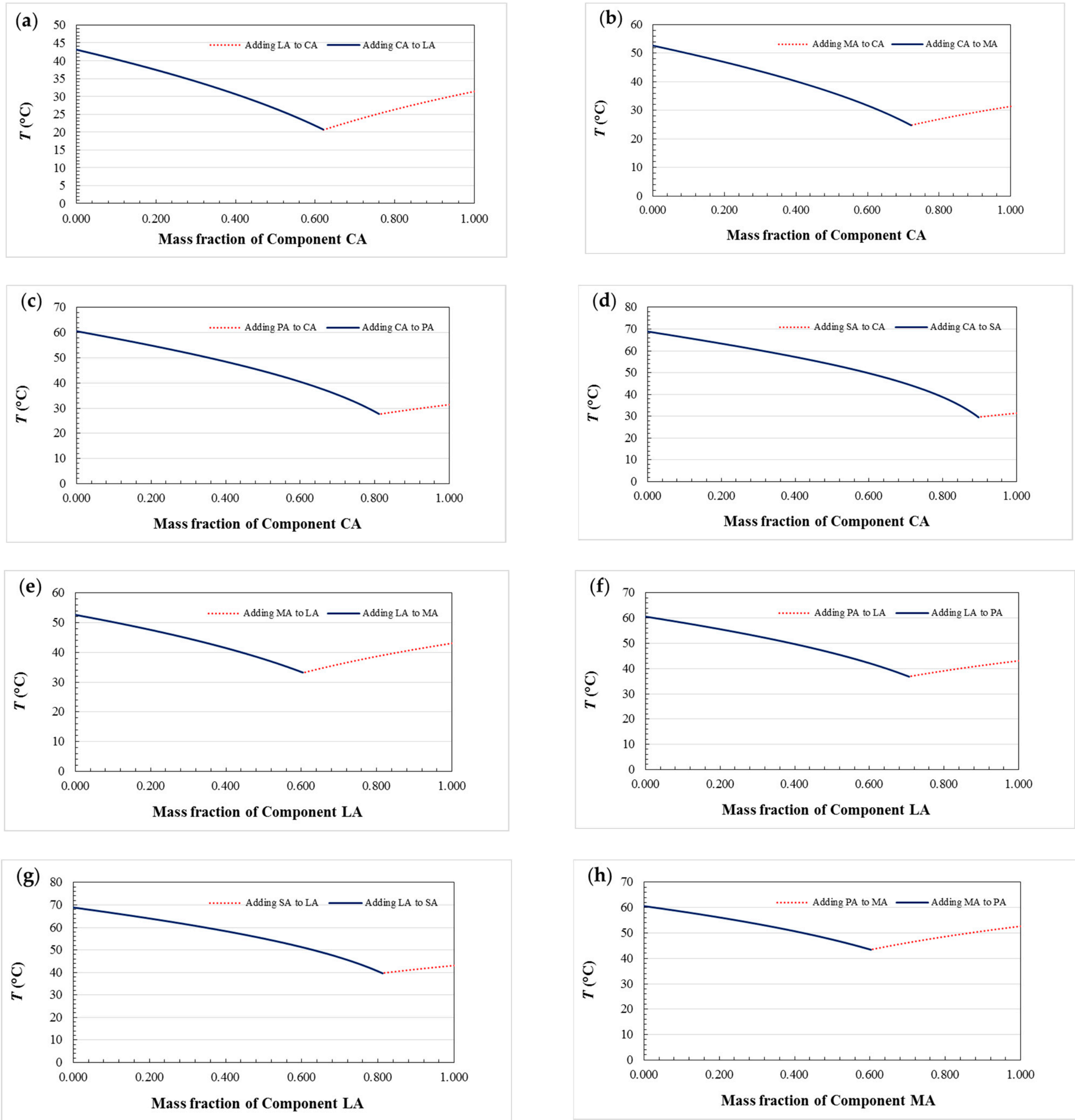

Figure 3. *Cont.*

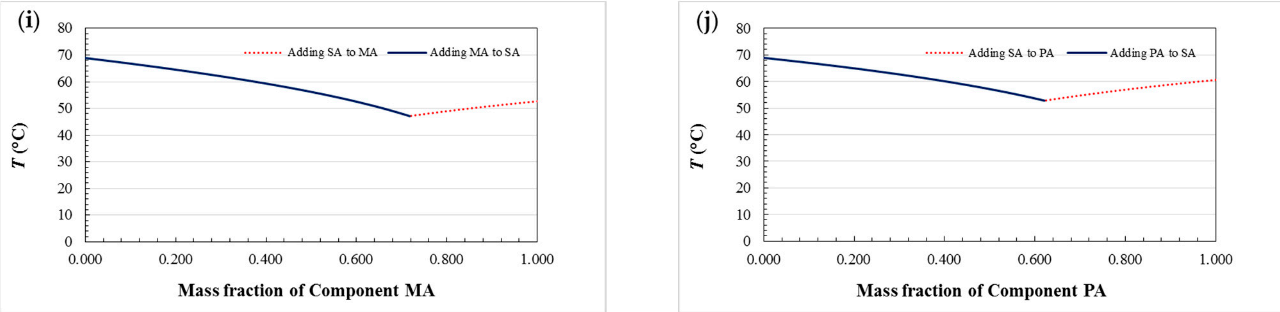

Figure 3. Phase diagram of ten fatty acid binary eutectic mixtures (**a**) CA–LA, (**b**) CA–MA, (**c**) CA–PA, (**d**) CA–SA, (**e**) LA–MA, (**f**) LA–PA, (**g**) LA–SA, (**h**) MA–PA, (**i**) MA–SA, (**j**) PA–SA.

Table 2. Theoretical eutectic point of ten fatty acid binary eutectic mixtures.

Binary Eutectic Mixtures	Theoretical Eutectic Mass Ratio	T_m (°C)	ΔH_m (J/g)
CA–LA	62.0/38.0	20.61	181.0
CA–MA	72.2/27.8	24.81	173.0
CA–PA	81.1/18.9	27.61	175.0
CA–SA	89.7/10.3	29.63	172.0
LA–MA	60.4/39.6	33.16	187.0
LA–PA	70.7/29.3	36.87	191.0
LA–SA	81.2/18.8	39.73	188.0
MA–PA	60.3/39.7	43.48	191.0
MA–SA	71.8/28.2	47.15	192.0
PA–SA	62.1/37.9	52.79	202.0

Table 3. Comparison of the eutectic mass ratios of ten binary eutectic mixes between theoretical and experimental values.

Binary Eutectic Mixtures	Theoretical Eutectic Mass Ratio	Experimental Eutectic Mass Ratio	Absolute Error (%)	Relative Error (%)
CA–LA	62.0/38.0	60.5/39.5	1.5/1.5	2.42/3.95
CA–MA	72.2/27.8	72.0/28.0	0.2/0.2	0.28/0.72
CA–PA	81.1/18.9	82.8/17.2	1.7/1.7	2.10/8.99
CA–SA	89.7/10.3	88.3/11.7	1.4/1.4	1.56/13.59
LA–MA	60.4/39.6	60.0/40.0	0.4/0.4	0.66/1.01
LA–PA	70.7/29.3	69.8/30.2	0.9/0.9	1.27/3.07
LA–SA	81.2/18.8	80.5/19.5	0.7/0.7	0.86/3.72
MA–PA	60.3/39.7	60.8/39.2	0.5/0.5	0.83/1.26
MA–SA	71.8/28.2	71.5/28.5	0.3/0.3	0.42/1.06
PA–SA	62.1/37.9	63.5/36.5	1.4/1.4	2.25/3.69

3.2. DSC Analysis of Fatty Acids Binary Eutectic Mixture

Figure 4 shows the DSC curves of ten fatty acids binary eutectic mixtures prepared, Table 4 shows the thermal performance characteristics, and the comparison with the theoretical values is shown in Table 5. The figure and table above show that the phase transition temperature range of these fatty acid binary eutectic mixtures is 17.7–57.1 °C, and the minimum and maximum melting enthalpy values are 145.2 J/g and 193.0 J/kg, respectively. These findings demonstrate that these fatty acid binary eutectic mixtures considerably expand the temperature range of fatty acid PCMs, and can be employed for low-temperature TES applications. It can also be seen from the comparison of theoretical calculation results with experimental data in Table 5, the maximum difference of the phase transition temperature is 6.23 °C, which appears in the CA–SA binary system, and the maximum difference in latent heat is 28.1 J/g, which appears in the LA–MA binary system.

The reason as mentioned above lies in that there may be impurities in the pure fatty acid and experimental errors.

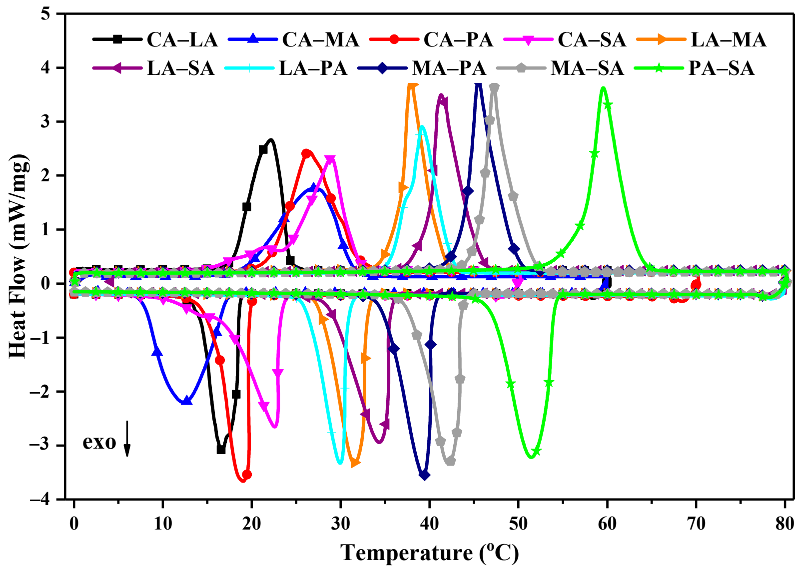

Figure 4. DSC curves of ten fatty acid binary eutectic mixtures.

Table 4. Experimental thermal performance parameters of ten fatty acid binary eutectic mixtures.

Binary Eutectic Mixtures	Melting		Freezing	
	T_m (°C)	ΔH_m (J/g)	T_f (°C)	ΔH_f (J/g)
CA–LA	17.70	155.2	18.60	142.2
CA–MA	19.43	150.9	18.35	149.2
CA–PA	22.10	165.6	20.00	159.7
CA–SA	23.40	150.5	23.40	148.0
LA–MA	36.10	158.9	32.80	149.7
LA–PA	37.80	164.0	34.60	154.8
LA–SA	39.90	167.1	35.60	158.3
MA–PA	44.10	182.2	40.40	171.9
MA–SA	44.80	186.9	43.70	184.4
PA–SA	57.10	193.0	53.70	188.6

Standard uncertainties provided with a 95% confidence interval for our measurements are u(T_m) = 0.5 °C, u(ΔH_m) = 4%, u(T_f) = 0.5 °C, u(ΔH_f) = 4%.

Table 5. Comparison of the theoretical and experimental values of thermal performance parameters of ten binary eutectic mixtures.

Binary Eutectic Mixtures	Experimental Value		Theoretical Value		Error	
	T_m (°C)	ΔH_m (J/g)	T_f (°C)	ΔH_f (J/g)	T_m (°C)	ΔH_m (J/g)
CA–LA	17.70	155.2	20.61	181.0	2.91	25.8
CA–MA	19.43	150.9	24.81	173.0	5.38	22.1
CA–PA	22.10	165.6	27.61	175.0	5.51	9.4
CA–SA	23.40	150.5	29.63	172.0	6.23	21.5
LA–MA	36.10	158.9	33.16	187.0	−2.94	28.1
LA–PA	37.80	164.0	36.87	191.0	−0.93	27.0
LA–SA	39.90	167.1	39.73	188.0	−0.17	20.9
MA–PA	44.10	182.2	43.48	191.0	−0.62	8.8
MA–SA	44.80	186.9	47.15	192.0	2.35	5.1
PA–SA	57.10	193.0	52.79	202.0	−4.31	9.0

Standard uncertainties provided with a 95% confidence interval for our measurements are u(T_m) = 0.5 °C, u(ΔH_m) = 4%, u(T_f) = 0.5 °C, u(ΔH_f) = 4%.

3.3. Thermal Stability Analysis of Fatty Acids Binary Eutectic Mixture

Thermal stability includes thermal decomposition stability and thermal cycle reliability.

3.3.1. Thermal Decomposition Stability

Thermal decomposition stability refers to the high temperature resistance of PCMs, which can decide whether or not there is an obvious mass loss in the temperature range at which PCMs are employed. The thermal decomposition stability of fatty acid PCMs is usually studied by thermogravimetric analysis. Table 6 shows the TGA test results of these eutectic mixtures. Taking LA–MA eutectic mixture as an example, the TGA curves of the LA–MA are shown in Figure 5, and it can be seen that the LA-MA eutectic mixture starts to evaporate slowly at a temperature of about 140.1 °C, and epitaxial initiation temperature is about 198.1 °C, and the predominant weight loss zone is between 140 and 250 °C. The volatilization of samples is what causes the weight loss. When the temperature is 232.2 °C, the weight loss rate is maximum. The temperature is 259.2 °C when the weight loss rate is close to 99.5%. According to the above analysis, although LA–MA phase change material can be used for low-temperature TES systems such as building energy conservation, it cannot be used for medium-high temperature phase change TES systems.

Table 6. Thermal stability parameters of ten fatty acid binary eutectic mixtures.

Binary Eutectic Mixtures	Initial Weight Loss Temperature (°C)	Epitaxial Initiation Temperature (°C)	Maximum Temperature of Weight Loss Rate (°C)
CA–LA	110.8	169.5	199.3
CA–MA	110.7	164.2	202.4
CA–PA	110.1	161.1	198.4
CA–SA	107.5	158.3	186.6
LA–MA	140.1	198.1	232.2
LA–PA	134.4	187.7	225.4
LA–SA	134.8	191.3	222.6
MA–PA	157.4	210.6	245.2
MA–SA	157.9	214.9	247.3
PA–SA	165.7	225.5	258.5

Standard uncertainties provided with a 95% confidence interval for our measurements are u(T_m) = 0.5 °C.

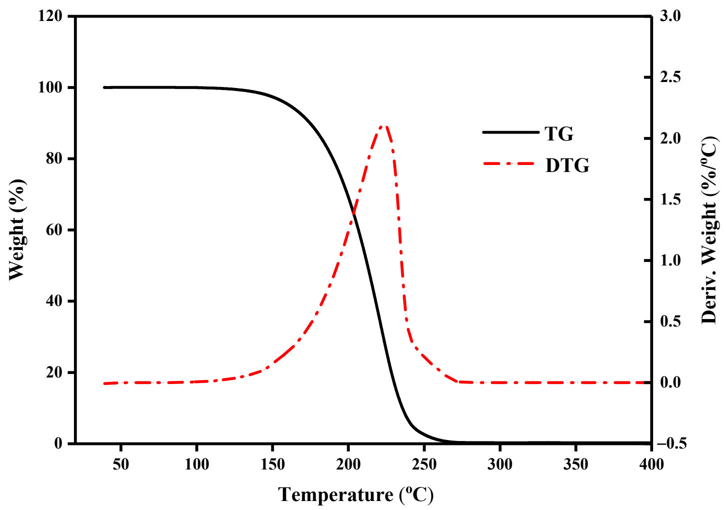

Figure 5. TGA curves of the binary eutectic mixtures LA-MA.

3.3.2. Thermal Cycle Reliability

The ability of PCMs to store energy after multiple heat storage and release procedures is referred to as thermal cycle reliability. It is a crucial element for determining the service life of PCMs, and an accelerated thermal cycling test is frequently used to verify the thermal cycle reliability of PCMs. Table 7 shows the T_m and $\triangle H_m$ values of these eutectic mixtures before and after 1000 thermal cycling. Taking LA–MA PCMs as an example, the LA-MA PCMs DSC curves before and after cycling as well as the variations in thermal performance characteristics with the number of thermal cycles are shown in Figure 6. Based on Figure 6, T_m values changed by −0.70 °C and −0.70 °C after 500 and 1000 thermal cycles, respectively, while T_f values changed by −1.50 °C and −0.70 °C, respectively. The value of T_m and T_f changes very little as the heat cycling number rises. After 200 and 1000 thermal cycling, ΔH_m values changed by −7.4% and −4.7%, and ΔH_f values changed by −8.9% and −7.2%, respectively, this is acceptable.

Table 7. T_m and ΔH_m values of ten binary eutectic mixtures before and after 1000 thermal cycling.

Binary Eutectic Mixtures	Before Thermal Cycling		After Thermal Cycling		Difference	
	T_m (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_m (%)
CA–LA	17.70	155.2	17.90	150.2	0.20	−3.2
CA–MA	19.43	150.9	20.51	145.3	1.08	−3.7
CA–PA	22.10	165.6	21.10	160.3	−1.00	−3.2
CA–SA	23.40	150.5	24.50	145.3	1.10	−3.5
LA–MA	36.10	158.9	35.40	151.4	−0.70	−4.7
LA–PA	37.80	164.0	35.20	152.3	−2.60	−7.1
LA–SA	39.90	167.1	38.50	162.3	−1.40	−2.9
MA–PA	44.10	182.2	44.30	176.2	0.20	−3.3
MA–SA	44.80	186.9	43.10	180.2	−1.70	−3.6
PA–SA	57.10	193.0	55.60	186.5	−1.50	−3.4

Standard uncertainties provided with a 95% confidence interval for our measurements are u(T_m) = 0.5 °C, u(ΔH_m) = 4%, u(T_f) = 0.5 °C, u(ΔH_f) = 4%.

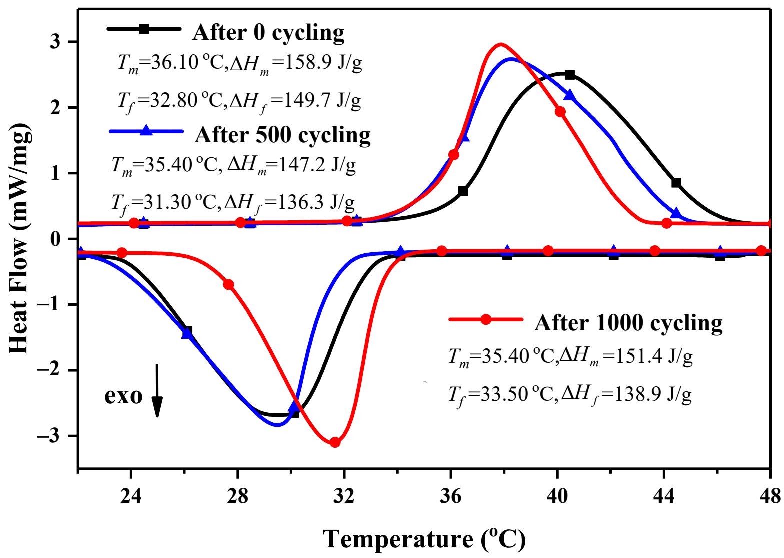

Figure 6. LA–MA PCMs DSC curves before and after thermal cycling.

The samples of LA–MA PCMs eutectic mixtures were measured by FTIR to judge whether the composition of the mixture has changed before and after thermal cycling, and the infrared spectrum is shown in Figure 7. Compare the spectra in Figure 7a,b, it is found that the peaks of the two spectra are in the same frequency band and match each other, and the characteristic peaks have not changed, indicating that there is no change in the composition of LA–MA PCMs eutectic mixtures before and after thermal cycling. As a result, after thermal cycling, the mixtures do not experience any chemical deterioration.

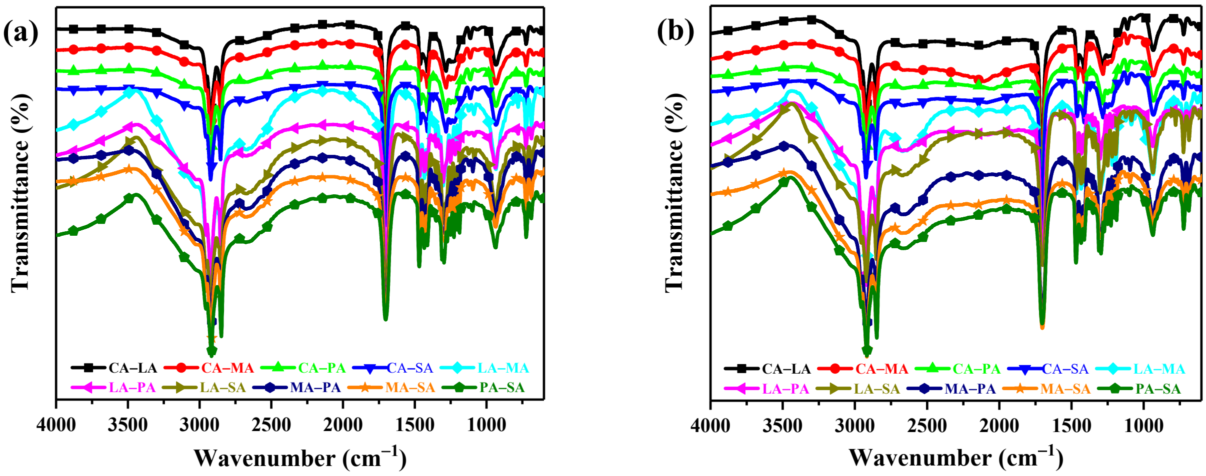

Figure 7. FT–IR spectra of ten fatty acid binary eutectic mixtures before and after 1000 thermal cycling (**a**) before thermal cycling, (**b**) after thermal cycling.

4. Conclusions

Ten fatty acid binary eutectic mixtures were prepared by using five pure fatty acids as raw materials, and the phase diagrams and the thermal properties of the binary eutectic mixtures were systematically studied.

(1) The theoretical eutectic points of ten fatty acid binary eutectic mixtures are calculated, and the phase diagrams of ten fatty acids binary eutectic compounds are drawn. There are some differences compared with the experimental values, which may be caused by impurities in the pure fatty acid used and experimental errors.
(2) The phase change temperature of these fatty acid binary eutectic mixtures is between 17.7 °C and 57.1 °C, and the phase change latent heat is between 145.2 J/g and 193.0 J/g, which has the suitable temperature and larger phase change latent heat.
(3) The fatty acid binary eutectic mixtures have good thermal stability in the temperature range below 100 °C, the change of phase transition temperature and latent heat with the number of thermal cycles is small, and they have good long-term cycle thermal reliability.

These fatty acid binary eutectic mixtures can be used in low-temperature TES systems such as building energy conservation, solar energy storage, and waste heat recovery.

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