Phase Change Energy Storage Material Suitable for Solar Heating System

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Abstract. Differential scanning calorimetry (DSC) was used to investigate the thermal properties of palmitic acid, myristic acid, laurel acid and the binary composite of palmitic/laurel acid and palmitic/myristic acid. The results showed that the phase transition temperatures of the three monomers were between 46.9-65.9°C, and the latent heats were above 190 J/g, which could be used as solar energy storage material. When the mass ratio of Palmitic acid and myristic was 1:1, the eutectic mixture could be formed. The latent heat of the eutectic mixture was 186.6 J/g, the melting temperature and the solidification temperature was 50.6°C and 43.8°C respectively. The latent heat of phase change and the melting temperature had not obvious variations after 400 thermal cycles, which proved that the binary composite had good thermal stability and was suitable for solar floor radiant heating system.

1. Introduction
In recent years, with the introduction of air pollution prevention policies and the improvement of solar thermal utilization technology, solar heating system has been gained much more attention and research [1]. Usually, the heat storage material in solar heating system is water, which exists lots of drawbacks. Such as, in the system temperature range, water storage density presents low, water system shows a large space, water temperature presents a wide range, the indoor temperature fluctuations is far more great, and the water temperature is too high will increase the heat loss of pipeline and storage tank, reducing the heat collecting efficiency of the solar collector. To make use of phase change materials for energy storage can not only increase the heat storage capacity, prolong the heating time, but also can reduce the water supply temperature[2], so as to reduce the heat loss of the pipeline, to improve the heat collection efficiency and the heating guarantee rate of the solar collector. Therefore, the phase change energy storage material has great effect in solar heating system, and it can also be used in the rural coal fired electric water tank heat storage system.

The storage and exothermic functions of phase change materials (PCM) are realized by changing the physical state (solid—liquid, liquid—gas, solid—solid), and usually different phase change materials have their own applicable temperature range. In recent years, organic phase change materials have been gained the spotlight study by scholars more and more at home and abroad, as a result of a fact that it presents a smaller undercooling and corrosion resistance than inorganic phase change materials, and it’s thermal performance is much more stable, and phase separation is difficult to occur[3-6]. Around this topic, Chinese scholars such as Liu Cheng[7], etc conducted a theoretical calculation and analysis on the eutectic mixture of three elements in fatty acid. Zhang Nan[8] et al researched and developed a “lauric acid—myristic acid— palmitic acid composite expanded graphite
phase change material” with large latent heat and thermal conductivity. While Fu Lujun[9] et al invented a kind of “form-stable phase change materials” with diatomite as it’s carrier and unflower acid (CA) - myristic acid (MA) is used as it’s energy storage material.

On the research train of thought, palmitic acid [10], lauric acid [11] and myristic acid[12] in organic phase change materials were treated as the research object, and differential scanning calorimetry is used to test the thermal properties of the monomer and the two element composites. Last but not least, the applicability of monomer and composite material in solar heating system were researched and approved.

2. Experiment

2.1. Experimental Materials
Palmitic acid, myristic acid, lauric acid (chemical purity, Sinopharm Chemical Reagent Co., Ltd.)

2.2. Experimental Equipment
Differential scanning calorimetry (200F3), tebau GmbH; electronic balance (CP225D), sartorius Ag; high and low temperature test box (ER-02KA), Guangzhou espec environmental equipment Co. Ltd; electric mixer; insulation sleeve etc..

2.3. Sample Preparation
Utilizing electronic balance to weigh different quality ratio of palmitic acid and lauric acid or palmitic acid / myristic acid, and then through preliminary mixing we poured it into the four bottles with mixers, kept stirring for 1 hours at 80 degrees to cool down to 60~70 degrees and pour into the container, so samples were prepared by cooling at room temperature.

2.4. Performance Testing

2.4.1. Test of phase transition temperature and latent heat of transformation
Utilizing differential scanning calorimetry to measure the phase transition temperature and latent heat of phase change with high purity nitrogen gas as it’s purge gas, whose flow is 20 mg/min, temperature range is 0~90 °C, heating rate is 5 °C /min, cooling rate is 5 °C /min. In the DSC curve diagram, the ordinate value represents heat release, while the negative values represent heat absorption.

2.4.2. Evaluation of thermal stability of variable materials [13]. First we need to place the samples into the sealed glass bottles which situated in the high and low temperature cycle test box to make sure the samples melting for a certain number of times (heat preservation 75°C for 2h) and freezing (heat preservation 20°C for 2h) process. And then weighing and DSC testing are needed to evaluate it’s thermal stability.

3. Results and Discussion

3.1. Phase Transition Temperature and Latent Heat of Phase Change of Monomer
From figure 1 we can realize that, the latent heat of fusion of palmitic acid, meristic acid and lauric acid is respectively 218.4, 211.7, 192.2 J/g, which are both above 190 J/g, indicating their latent heat of phase change is larger; their peak temperatures of melting process are respectively 65.9, 56.8, 46.9 °C, whose range of phase transition temperature is lower, indicating it can be used as solar thermal storage material under different temperature requirements. As we all know, in the heating system the ordinary radiator required water temperature is generally 80 degrees, while hot water produced by solar collectors in winter is far more difficult to reach this standard. Thus, the floor radiant heating system can achieve the purpose of heating only with the water temperature of 40-60 degrees that is why the floor radiant heating is generally used in solar heating system. As energy storage materials for solar floor radiant heating system, the phase transition temperature of palmitic acid and myristic acid is higher, so it is difficult to melt it by the hot water produced by solar collectors.
in winter. Although the melting peak temperature of lauric acid is more suitable, but from figure 1 we can find its peak value of the phase transition temperature of the solidification process is 39.0 °C, which is difficult to produce hot water of more than 40 degrees centigrade. That means these three monomers above are not ideal for solar heating.

**Table 1.** Transition temperatures and latent heats of monomers

| Samples       | fusion | freezing       |
|---------------|--------|----------------|
|               | peak value °C | latent heat J·g⁻¹ | peak value °C | latent heat J·g⁻¹ |
| palmitic acid | 65.9   | 218.4          | 59.1          | 222.3           |
| myristic acid | 56.8   | 211.7          | 49.3          | 218.9           |
| lauric acid   | 46.9   | 192.2          | 39.0          | 198.2           |

**Figure 1.** DSC heating curves of monomers

3.2. *Thermal Properties of Composite Phase Change Materials for Energy Storage*

Aiming at adjusting the material phase change temperature, we treat palmitic acid with maximum latent heat as basic material and prepare two phase change energy storage composite material by adding lauric acid and myristic acid, the thermal properties of two element composites were also studied in this experiment.

3.2.1. *Palmitic acid / lauric acid composite.* Samples were prepared by mixed melting of palmitic acid and lauric acid at different mass ratios, and their thermal properties were determined by differential scanning calorimetry; whose relevant experimental results were unveiled by table 2 and figure 2. From table 2 we can find that the latent heat of phase change of three proportional samples is larger which are all above 190 J/g. Meanwhile, with the increase of palmitic acid content, the latent heat of phase change and the phase transition temperature are both increasing. According figure 2, when quality ratio of palmitic acid / lauric acid is 1:1 the melting process reach its peak value at 37.8, 42.9 °C and when quality ratio of palmitic acid / lauric acid is 2:1 the melting process reach its peak value at
36.7, 42.4, 54.2 °C, while when quality ratio of palmitic acid / lauric acid is 3:1 the melting process reach it’s peak value at 36.8, 41.8, 57.3 °C, explaining that the eutectic mixture cannot be formed in three proportional samples, and the range of phase transition temperature is much more wider. From table 2, it ia can be revealed that these three samples appeared two peaks under 40 °C in the solidification process, that is to say the phase transition temperature is too low to meet the application requirements.

### Table 2. Thermal properties of palmitic/lauaric acid composites

| mass ratio | fusion | | freezing |
|------------|--------|---|----------|
| | peak value /°C | latent heat /J·g⁻¹ | peak value /°C | latent heat /J·g⁻¹ |
| 1:1 | 37.8/42.9 | 193.5 | 32.9/36.9 | 191.2 |
| 2:1 | 36.7/42.4 | 206.5 | 31.5/36.8 | 206.6 |
| 3:1 | 36.8/41.8 | 209.5 | 31.4/37.1 | 202.2 |

3.2.2. Palmitic acid / myristic acid composite. Samples were prepared by mixed melting of palmitic acid and myristic acid composite at different mass ratios, and their thermal properties were determined by differential scanning calorimetry, whose relevant experimental results were unveiled by table 3 and figure 3, figure 4. During figure 3, the latent heat of mixed sample of palmitic acid and myristic acid is about 190 J/g, showing the latent heat of phase change is larger. Similarly, from figure 3, figure 4 we can conclude that when quality ratio of palmitic acid and myristic acid is 3:1, the melting process reach its peak value at 49.5, 58.3 °C, while the solidification process reach its peak value at 45.2, 50.4 °C, illustrating eutectic mixture cannot be formed. When quality ratio of palmitic acid and myristic acid is 2:1, the melting process reach its peak value at 50.8 °C, while the solidification process reach its peak value at 44.9, 47.7 °C, But the two are far more closer with 2.8°C difference. When quality ratio of palmitic acid and myristic acid is 1:1, the melting process reach its peak value at 50.6 °C, while the solidification process reach it’s temperature at 43.8°C without peak value, showing that the eutectic mixture has been formed. Thus, when quality ratio of palmitic acid and myristic acid is 1:1, it is suitable to be used as energy storage material for solar radiant floor heating system, in which hot water...
over 40 degrees can be produced during the exothermic process.

| mass ratio | fusion | freezing |
|------------|--------|----------|
|            | peak value /°C | latent heat /J·g⁻¹ | peak value /°C | latent heat /J·g⁻¹ |
| 1:1        | 50.6    | 186.6    | 43.8    | 193.3    |
| 2:1        | 50.8    | 191.1    | 44.9/47.7 | 197.6    |
| 3:1        | 49.5/58.3 | 205.7    | 45.2/50.4 | 212.8    |

**Table 3.** Thermal properties of palmitic/myristic acid composites

![Figure 3. DSC heating curves of palmitic/myristic acid composites](image)

![Figure 4. DSC cooling curves of palmitic/myristic acid composites](image)

3.3. *Thermal Stability of Phase Change Materials for Energy Storage*

To measure the thermal stability of the monomer and two element composites with palmitic acid/myristic acid mass ratio of 1:1, we can reach the relevant results showed in table 4. It is unveiled that after 400 cycles of thermal cycling, the weight and latent heat of the monomer and the composite both
have experienced a little change, the latent heat variation is less than 1.3 J/g, and the weight change is less than 0.106 g, fully demonstrating that the monomer and the two element composite presents good thermal stability and long service life.

### Table 4. Masses and latent heats after 400 thermal cycles

| samples                | Mass before cycles/g | Mass after cycles /g | latent heat before cycles /J·g⁻¹ | latent heat after cycles /J·g⁻¹ |
|------------------------|-----------------------|----------------------|----------------------------------|-------------------------------|
| palmitic acid          | 47.568                | 47.557               | 218.4                            | 218.0                         |
| lauric acid            | 50.125                | 50.019               | 211.7                            | 210.6                         |
| myristic acid          | 45.362                | 45.355               | 192.2                            | 190.9                         |
| 1:1 palmitic acid / myristic acid | 44.285  | 44.273               | 186.6                            | 185.7                         |

4. Conclusion

The latent heat of palmitic acid, myristic acid and lauric acid are respectively, 218.4, 211.7 and 192.2 J/g, whose latent heat of phase change is larger; the phase transition temperatures are respectively 65.9, 56.8 and 46.9°C and they can be used as solar phase change energy storage materials under different temperature requirements. In 40-60 degrees water temperature which is required by the solar floor radiant heating system, the eutectic mixture cannot be formed in the mass ratio of palmitic acid and lauric acid in the range of 1:1-1:3, the range of phase transition temperature is not suitable.

When the mass ratio of palmitic acid and myristic acid is 1:1, the eutectic mixture is formed, the relevant latent heat of the phase change is 186.6 J/g, the melting point is 50.6, and the freezing point is 43.8°C. It can be used as the energy storage material of solar radiant floor heating system.

5. References

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