

PHASE DIAGRAM OF PALMITIC ACID–TETRADECANOL MIXTURES OBTAINED BY DSC EXPERIMENTS

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A series of PA–TD mixtures were prepared and their thermal properties were studied by DSC and thermal conductivity measurement. The phase diagram of the binary system was constructed, which showed an eutectic behavior for the solid–liquid equilibrium line. The eutectic composition of the binary system was at the mass fraction of TD near 0.7 with an eutectic temperature of about 29°C. At TD side, PA was partially miscible in the TD solid matrix and the solid phase transition of TD had an effect on the solidus line. The eutectic composition mixture could be viewed as a new phase change material with large thermal energy storage capacity.

Keywords: eutectic mixture, phase change materials, phase diagram, thermal conductivity

Introduction

Thermal energy storage [1] can solve the mismatch of thermal energy supplying and utilization and thus is very important in many engineering applications such as solar energy application, waste heat collection [2] and electric power load shifting [3]. Phase change materials (PCMs) are very important for thermal energy storage [4, 5]. Besides, PCMs also have other alluring properties. They can change their phase status in a smaller temperature difference when storing and releasing thermal energy, which makes them greatly attractive in application fields like thermal protection, passive indoor temperature controlling and intelligent buildings.

Fatty acid is a kind of very important organic PCM. It possesses lots of advantages such as high phase change enthalpy (ΔH), chemical and thermal stable and low or none undercooling. Fatty acids are essentially environment friendly since they are obtained from vegetable and animal oils. Sari *et al.* [6–8] studied the phase changing properties, including ΔH , phase changing temperature, melting time and phase changing stability, etc. of myristic acid (MA), palmitic acid (PA) and stearic acid (SA). They found that fatty acids are suitable candidates for PCMs. Their phase changing speed and thermal conductivity can be improved by applying suitable energy storage unit and adding some thermal conductivity promoters. Furthermore, fatty acids can be easily utilized to prepare form-stable PCMs and PCMs microcapsules.

Saturated unitary alcohols have also been widely studied as PCMs. It was reported that the phase change temperature and the ΔH of 1-octadecanol were 57.12°C and 242.85 J g⁻¹, respectively, and the undercooling was only 0.01°C, indicating that it is a perfect PCM candidate [9]. Lauryl alcohol has been employed as core material in microencapsulated PCMs [10]. The results showed that the obtained PCMs exhibit high ΔH and high thermal stability, and can be applied in special coating and temperature-controlling textile. Furthermore, 1-tetradecanol (TD) has also been employed as PCM and the thermal performance of its composite PCMs have been studied [11–13].

Binary and ternary eutectics of organic or inorganic PCMs may be tailored with almost any desired melting point. Lots of fatty acids mixtures [14–18] and few of alkenes mixtures [19] have been reported. However, to the best of our knowledge, no fatty acid-*n*-alcohol mixture has been published from the viewpoint of PCMs. In this paper, we chose the well-investigated PCMs of PA and TD as raw materials, a series of mixtures of PA and TD were prepared. The mixtures were investigated by means of IR, Differential scanning calorimetry (DSC) and thermal conductivity (κ) measurement. DSC has been proved to be a valuable method in binary mixture research [20, 21]. The phase diagram of the binary system was constructed based on the results obtained from the DSC measurement.

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Experimental

Materials

TD was of analytical reagent and was purchased from Bodi Chemical Co., Ltd (Tianjin China). PA was of chemical pure and obtained from China National pharmaceutical Industry Co., Ltd. (Beijing China). The reagents were used without further purification.

Preparation of the mixtures

Certain amounts of TD and PA were mixed in test tubes. The tubes were capped and sealed. The sealed tubes were heated to 70°C to form homogeneous liquid and maintained at this temperature for 10 min. Then the mixtures were cooled to room temperature to become white solids. The solids were grinded for use. The ratios of TD and PA in the mixture were listed in Table 1.

Instrumental methods

IR spectra were recorded on a BRUKER EQUINOX 55 FT-IR spectrometer using KBr pellet (400~4000 cm^{-1}). Phase change properties of the mixtures were obtained by means of Differential scanning calorimeter (DSC, DSC141 Setaram, France) from -10 to 100°C with the heating and cooling rate of 10°C min^{-1} in nitrogen atmosphere. The masses of the composites used for DSC experiments were about 4–9 mg and liquid nitrogen was applied to cool the samples during the cooling run of the DSC experiments. The grinded composites were pressed under 20 MPa to form two cylinders with the diameter of 13 mm. A Hot Disc thermal constant analyzer was used to obtain the κ of the composites at room temperature with a sensor diameter of 2.001 mm. The sensor was sandwiched by two cylinders and fixed by a clamp.

Results and discussion

The thermal energy storage properties of pure TD and pure PA were studied by DSC. There is a single endothermic peak appeared on the heating DSC curve of TD (Fig. 1). The onset temperature is 34.86°C and the ΔH is 220.61 J g^{-1} . On cooling run, there are two exothermic transitions exhibit on the DSC curve. The first is the transition from liquid to hexagonally packed solid phase, while the second corresponding to the transition from hexagonally packed solid phase to an orthorhombically-packed solid phase [22]. For PA, there is only one endothermic or exothermic transition on both heating and cooling DSC curve (Fig. 1), corresponding to the melting and the solidifying of PA. The onset temperature of melting and solidifying is 59.48 and 58.73°C, with ΔH of 200.34 and 201.91 J g^{-1} , respectively. These results agree reasonably with the references [7, 22].

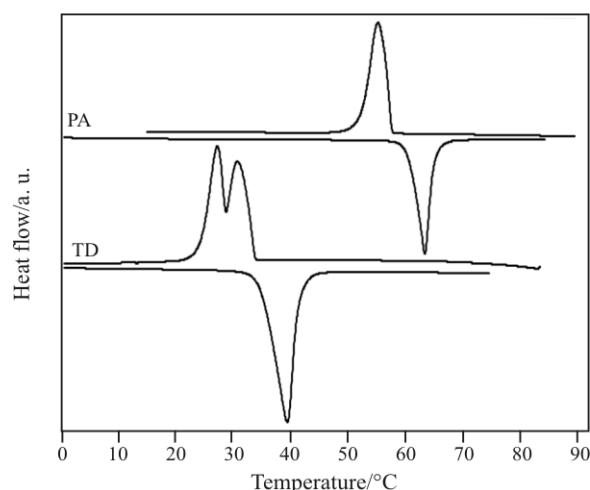


Fig. 1 DSC curves of pure PA and TD

Table 1 Onset temperatures, peak temperatures and ΔH of melting of palmitic acid, tetradecanol and their binary mixtures

| w_{TD} | Higher temperature peak | | | Lower temperature peak | | | $\Delta H_1 + \Delta H_2 / \text{J g}^{-1}$ |
|-----------------|-------------------------|---------|--------------------------------|------------------------|---------|--------------------------------|---|
| | onset/°C | peak/°C | $\Delta H_1 / \text{J g}^{-1}$ | onset/°C | peak/°C | $\Delta H_2 / \text{J g}^{-1}$ | |
| 0.00 | | | | 59.48 | 64.54 | 200.34 | 200.34 |
| 0.10 | 28.02 | 30.67 | 24.03 | 53.9 | 61.08 | 166.54 | 190.57 |
| 0.20 | 28.54 | 31.83 | 47.33 | 49.53 | 59.13 | 135.16 | 182.49 |
| 0.30 | 28.70 | 31.84 | 70.95 | 45.87 | 55.35 | 105.75 | 176.70 |
| 0.40 | 28.73 | 32.11 | 90.23 | 41.98 | 52.06 | 74.53 | 164.76 |
| 0.50 | 28.75 | 33.31 | 117.37 | 36.54 | 49.07 | 39.40 | 156.77 |
| 0.60 | 29.14 | 32.49 | 130.24 | 36.02 | 43.67 | 21.75 | 151.99 |
| 0.70 | | | | 28.71 | 33.12 | 143.05 | 143.05 |
| 0.80 | 21.53 | 25.25 | 0.12 | 29.85 | 34.43 | 136.38 | 136.50 |
| 0.90 | 14.64 | 20.60 | 0.21 | 31.83 | 36.73 | 167.29 | 167.50 |
| 1.00 | | | | 34.05 | 38.89 | 220.61 | 220.61 |

IR spectra of TD, PA and selected mixtures are depicted in Fig. 2. The figure shows that the mixtures show both the characteristic absorption peaks of TD and PA. For the mixture, the absorption intensities of TD become stronger while that of PA become weaker as the mass fraction of TD increased. There is no new absorption band or band shifting appeared in the spectrum of the mixture in which the mole ratio of TD and PA is 1, even the spectrum was collected after the mixture was sealed and heated at 100°C for 24 h. It means that TD and PA are just mixed physically and have not reacted with each other to form ester.

Figure 3 shows the DSC curves of the TD/PA binary mixtures on heating run. From the curves, the onset temperature and the ΔH of melting could be obtained and the data are listed in Table 1. The heating DSC curves of the binary mixtures show one, two or even three endothermic peaks. Upon crystallization,

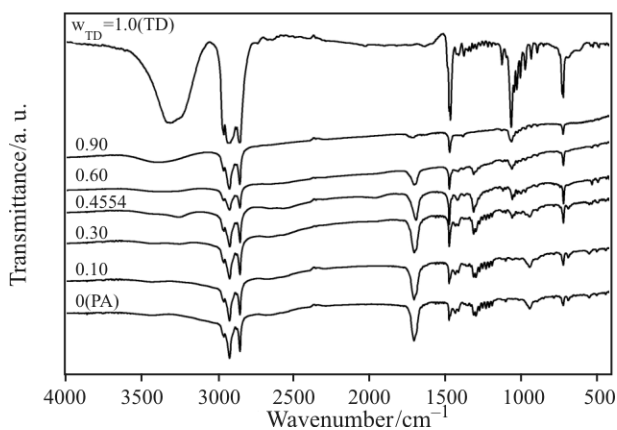


Fig. 2 IR spectra of PA, TD and their binary mixtures

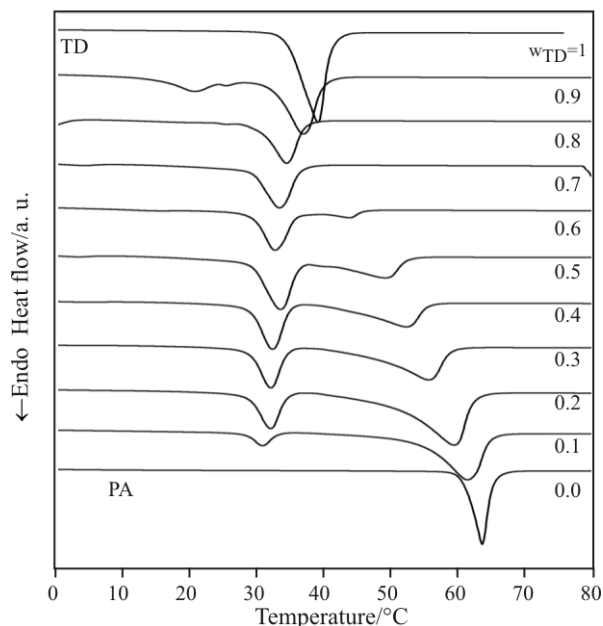


Fig. 3 DSC curves of PA and TD and their binary mixtures on heating run

binary mixtures will form solid solution, intermolecular compound or eutectic system. It can be seen that in the TD/PA binary system, the onset temperature of the thermo-peaks appeared at higher temperature on the DSC curves go through a minimum. Besides, in the mass fraction range of TD between 0.1 and 0.7, there is a thermal peak occurred at a nearly constant temperature on the DSC curves. This is the characteristic of an eutectic system where demixing and segregation occur in the solid phase. In such a case, for none-eutectic composition mixtures, two endothermic peaks will be presented on the DSC curves, with the first peak appearing at lower and constant temperature referred to as eutectic temperature. The second peak appearing at higher but gradually changed temperature referred to as liquidus temperature. For eutectic composition mixture, only one endothermic peak at the eutectic temperature will be appeared on the DSC curve [23]. As a result, it could be concluded from the DSC curves that the eutectic composition of the TD/PA binary mixture is at the mass fraction of TD at 0.7, and that the eutectic temperature of the binary system is 29°C. At the PA mass fraction of 0.2, a small thermo-peak appears at a temperature below the eutectic temperature, implies that PA is partially miscible in the TD solid matrix. At the PA mass fraction of 0.1, there are three thermo-peaks appear on the DSC curve. Obviously, the solid phase transition of TD has an effect on the solidus line (eutectic line) of the phase diagram.

Based on the data obtained from DSC heating run (listed in Table 1), the phase diagram of TD/PA binary system could be obtained (Fig. 4). The solid–liquid equilibrium line can be modeled by using van't Hoff equation [24]:

$$T_{\text{mix}} = T_{\text{d}}^{\text{f}} - w_{\text{p}} \frac{R(T_{\text{d}}^{\text{f}})^2}{\Delta H_{\text{d}}^{\text{f}}}$$

where T_{d}^{f} is the melting point of the major component, w_{p} is the mass fraction of the minor component, $\Delta H_{\text{d}}^{\text{f}}$ is the molar heat of fusion of the major component, R is the universal gas constant and T_{mix} is the temperature along the liquidus line as a function of w_{p} . The equation is applied to each side of TD/PA binary system and the obtained liquidus is also depicted in Fig. 4. It can be seen that the agreement between the results obtained from experiment and calculation is reasonable.

In order to verify that the TD/PA mixtures are eutectic system, the ΔH of each thermo-peak was calculated and the results are shown in Fig. 5. We presume the thermo-peaks appearing at higher temperature on the DSC curves as liquidus transition and the thermo-peaks appearing at lower and constant temperature on the DSC curves as eutectic transition.

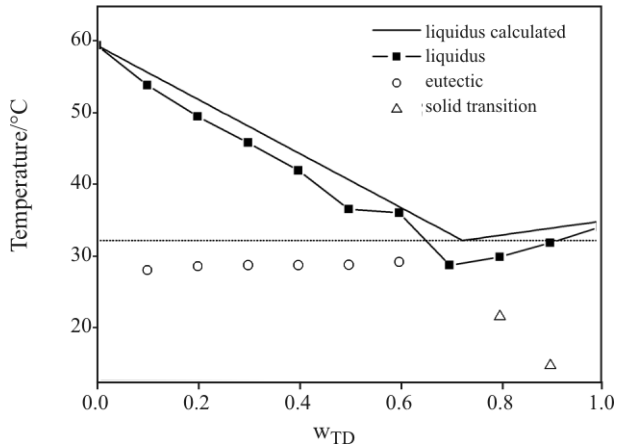


Fig. 4 Phase diagram of PA/TD binary system

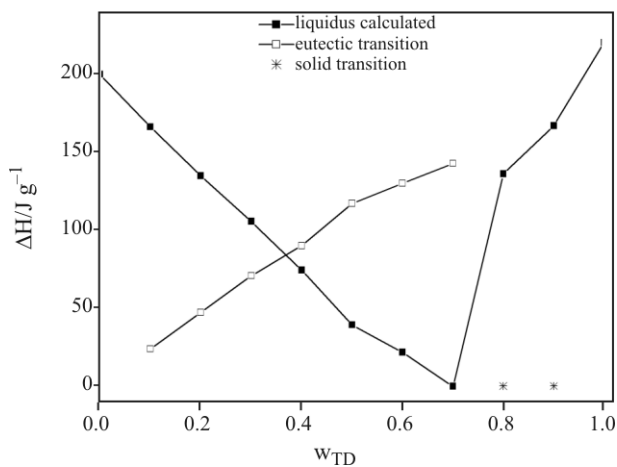


Fig. 5 Relationships between the ΔH of liquidus transition, eutectic transition and the TD mass fraction

It can be seen that, from the pure components to the eutectic composition, the ΔH of liquidus transition decrease linearly as the mass fraction of pure components decreased. Two approximate lines could be obtained by plotting the ΔH of liquidus transition. These two lines intersect at the eutectic composition. At the TD side, the ΔH of the eutectic transition is difficult to obtain due to the existence of solid–solid transition. However, the ΔH of the eutectic transition at the PA side is increased linearly as the mass fraction of TD increased and achieves a maximum at the eutectic composition. Obviously the TD/PA mixtures are eutectic system. Furthermore, we can extract from the figure that the ΔH of the eutectic composition mixture is 143 J g^{-1} . This means that a new PCM candidate which melting at 29°C with high phase changing enthalpy is obtained.

We have also measured the κ of the binary mixture and the results are shown in Fig. 6. At PA side, the κ of the mixture increases as the mass fraction of TD increased. However, at TD side and the eutectic composition, the κ shows no relationship with the composition of the mixture and is close to the κ of

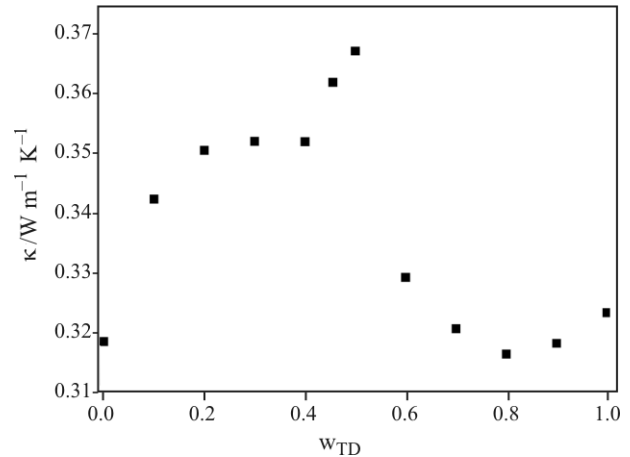


Fig. 6 Thermal conductivity κ of PA, TD and their binary mixtures

pure TD and PA. This result indicates that thermal conductivity enhancement is needed for the eutectic composition mixture to be utilized as PCM.

Conclusions

In this paper, a series of PA-TD mixtures were prepared and their thermal properties were studied by DSC and thermal conductivity measurement. According to the DSC experimental results, the phase diagram was constructed, which shows a eutectic behavior for the solid–liquid equilibrium line. The eutectic composition of the binary system is at the mass fraction of TD near 0.7. On the PA side, the eutectic line with an eutectic temperature of about 29°C is stable on the heating phase diagram. On the TD side, PA is partially miscible in the TD solid matrix. At the TD mole fraction of 0.9, there are three endothermal peaks appearing on the heating DSC curve which is caused by the solid phase transition of TD. The eutectic composition mixture can be viewed as a new phase change material with high thermal energy storage capability. However, its thermal conductivity should be enhanced.

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References

- 1 S. M. Hasnain, *Energy Convers. Manage.*, 39 (1998) 1127.
- 2 N. Maruoka and T. Akiyama, *Energy*, 31 (2006) 1632.

- 3 C. K. Halford and R. F. Boehm, *Energy Buildings*, 39 (2007) 298.
- 4 B. Zalb, J. M. Marín, L. F. Cabeza and H. Mehling, *Appl. Therm. Eng.*, 23 (2003) 251.
- 5 M. M. Farid, A. M. Khudhair, S. A. K. Razack and S. Al-Hallaj, *Energy Convers. Manage.*, 45 (2004) 1597.
- 6 A. Sari and K. Kaygusuz, *Renew. Energy*, 24 (2001) 303.
- 7 A. Sari and K. Kaygusuz, *Energy Convers. Manage.*, 43 (2002) 863.
- 8 A. Karaipekli, A. Sari and K. Kaygusu, *Renew. Energy*, 32 (2007) 2201.
- 9 J. H. Fu and D. X. Zheng, *J. Beijing Univ. Chem. Techn. (Natural Science Edition)*, 31 (2004) 18, in Chinese.
- 10 G. Lu, C. Y. Miao, Y. W. Yao, G. Y. Tang and D. Weng, *New Chem. Mater.*, 34 (2006) 26, in Chinese.
- 11 J. L. Zeng, J. Zhang, Y. Y. Liu, Z. X. Cao, Z. H. Zhang, F. Xu and L. X. Sun, *J. Therm. Anal. Cal.*, 91 (2008) 455.
- 12 J. L. Zeng, Y. Y. Liu, Z. X. Cao, J. Zhang, Z. H. Zhang, L. X. Sun and F. Xu, *J. Therm. Anal. Cal.*, 91 (2008) 443.
- 13 J. L. Zeng, L. X. Sun, F. Xu, Z. C. Tan, Z. H. Zhang, J. Zhang and T. Zhang, *J. Therm. Anal. Cal.*, 87 (2007) 369.
- 14 A. Sari and A. Karaipekli, *Mater. Lett.*, 62 (2008) 903.
- 15 A. Sari, H. Sari and A. Önal, *Energy Convers. Manage.*, 45 (2004) 365.
- 16 S. Lv, N. Zhu and G. Feng, *Energy Buildings*, 38 (2006) 708.
- 17 F. O. Cedenño, M. M. Prieto, A. Espina and J. R. García, *Thermochim. Acta*, 369 (2001) 39.
- 18 M. C. Costa, M. P. Rolemberg, L. A. D. Boros, M. A. Krähenbühl, M. G. de Oliveira and A. J. A. Meirelles, *J. Chem. Eng. Data*, 52 (2007) 30.
- 19 B. He, V. Martin and F. Setterwall, *Fluid Phase Equilib.*, 212 (2003) 97.
- 20 S. L. Hafsaoui and R. Mahmoud, *J. Therm. Anal. Cal.*, 88 (2007) 565.
- 21 K. Khimeche and A. Dahmani, *J. Therm. Anal. Cal.*, 84 (2006) 47.
- 22 L. Carreto, A. R. Almeida, A. C. Fernandes and W. L. C. Vaz, *Biophys. J.*, 82 (2002) 530.
- 23 F. G. Gandolfo, A. Bot and E. Flöter, *Thermochim. Acta*, 404 (2003) 9.
- 24 L. M. Oberoi, K. S. Alexander and A. T. Riga, *J. Therm. Anal. Cal.*, 78 (2004) 83.

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