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Thermal studies on the solid–liquid phase transition in binary systems of fatty acids

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Abstract

The solid–liquid phase transitions in lauric acid, palmitic acid, stearic acid and their binary systems have been studied by differential scanning calorimetry (DSC) and infrared spectroscopy at various temperatures. The temperatures of the solid–liquid phase transitions in binary systems are $32.84 \pm 0.71^{\circ}C$ with ΔH values of 146.5–195.1 J g^{-1}. The spectra shifts in the temperature range corresponding to the solid–liquid phase transition showed that the solid–liquid phase transition of fatty acids is related to intermolecular hydrogen bonds.

Keywords: Heat storage; DSC method; Binary system; Fatty acids; Solid–liquid phase transition; IR spectra at various temperatures

1. Introduction

Phase change materials (PCMs) for thermal energy storage are typically paraffins and salt hydrates which absorb large amounts of heat as they melt. But these materials have disadvantages of phase segregation during heating–cooling cycles, which makes them unsuitable for applications as heat storage materials [1–4]. Fatty acids are better suited for passive solar applications because they can be obtained at low cost and impregnated into common construction materials, they exhibit no or only minor supercooling and enthalpies are high. A wider range of melting temperatures can be obtained by mixing two compounds together. Differential scanning calorimetry (DSC) was used to determine melting characteristics and enthalpies of these binary systems. Degree of supercooling during heating–cooling cycles and stability of thermal properties after many times of heating–cooling cycles were investigated. IR spectra at various temperatures of these systems declare that the solid–liquid phase transition of fatty acids is related to the intermolecular hydrogen bonds.

2. Experimental

The samples used in this work are lauric acid ($C_{11}H_{23}COOH$) (LA), palmitic acid ($C_{15}H_{31}COOH$) (PA), stearic acid ($C_{17}H_{35}COOH$) (SA).

The binary systems of LA–PA and LA–SA were prepared from liquid mixtures by slow cooling to room temperature. The fusion points and enthalpies in solid–liquid phase transition of single acids and their binary system were measured by DSC-7 instrument (Perkin-Elmer) with the scanning rate $3^{\circ}C\ min^{-1}$ in the temperature range 30–70°C. Samples were

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measured in sealed aluminium pan with the mass of about 2.0 mg.

A Perkin-Elmer M-1730 Fourier transform infrared spectrometer was used to record the infrared spectra of fatty acids and their mixtures by means of E-01-2A HITACHI temperature-controlling apparatus. Samples were grounded with KBr powder and then compressed to transparent pellets. The pellets were heated from room temperature with the heating rate 3°C min^{-1}.

3. Results and discussion

3.1. Thermal analysis

LA, PA and SA are titled as 12-carbon acid, 16-carbon acid and 18-carbon acid, respectively. With the increase of number of carbon atom in molecule of acids, their melting point and fusion enthalpies increase gradually. In this paper, the solid–liquid phase transition of three acids and their binary systems were measured by DSC method. The DSC data of LA–PA were listed in Table 1. It can be seen that the fusion point of binary system is lower than that of single acid. And there's an eutectoid invariant and the eutectoid invariant temperature is about 32.7°C, which makes it possible for solar energy storage. By the method of [5] to seek the composition of eutectoid invariant, namely, by drawing up phase diagram of temperature (T)-composition (x), the composition of eutectoid invariant of LA–PA is obtained as 23% (PA wt.%). The fusion enthalpies of this binary system are so high ($\geq$140 J g^{-1}) that can be comparable with other PCMs, such as salt hydrates and polyalcohols. The thermal properties of LA–SA were measured by the same method and the results show that eutectoid invariant composition and corresponding temperatures are 22% and 39°C, respectively.

Table 1
Thermal properties of LA–PA in solid–liquid phase transition

PA (wt.%)	T_e (°C)	ΔH (J g^{-1})
0	42.44	185.5
10.08	33.54	148.3
19.41	33.55	146.5
22.95	33.09	150.6
28.45	33.08	153.8
39.12	32.44	168.9
43.41	32.35	175.7
49.98	32.37	161.0
59.70	32.48	159.5
69.82	32.25	163.3
80.04	32.13	190.8
90.42	32.27	195.1
100	63.28	202.9

3.2. Supercooling of binary systems

Fig. 1 is the DSC curve in heating–cooling course for 43.41% LA–PA binary system. It can be shown that there's no supercooling in these systems for the reason that the extrapolated onset temperature of two processes approximately coincide. It is due to the character of crystallization and self-nucleation of fatty acids. So, in this sense, fatty acids are more suitable for heat storage than salt hydrates and polyalcohols which have high degree of supercooling of about 15–30°C [6,7].

3.3. Thermal properties after heating–cooling cycles

The DSC curve of 22.95% LA–PA binary system after heating–cooling cycles for n (n = 0, 30, 50, 80, 100) times were showed in Fig. 2 and thermal properties were listed in Table 2. It can be seen that these

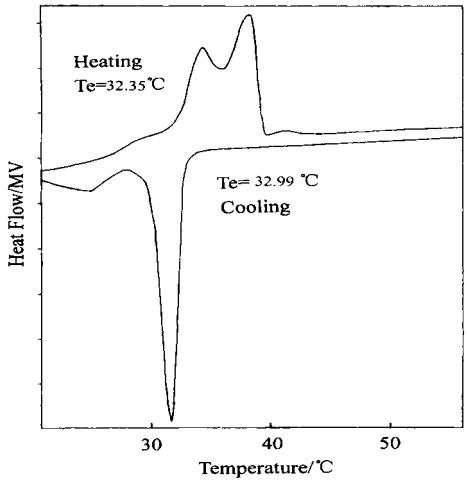

Fig. 1. DSC curve of 43.41% LA–PA binary system in heating–cooling course.

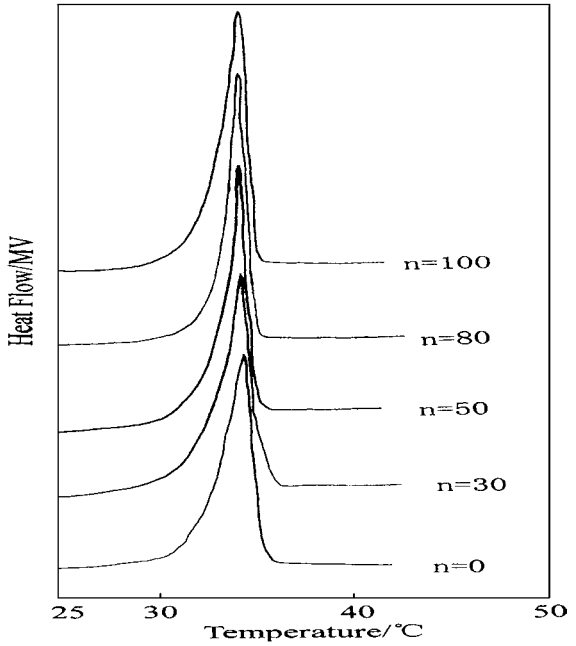

Fig. 2. DSC curves of 22.95% LA–PA binary system after *n* cycles.

curves are completely identical, which showed that the thermal properties of binary system are stable after heating–cooling cycles for many times. It means that those binary systems can be used for a long term.

Table 2
Thermal properties of 22.95% LA–PA binary system after cycles

Cycle times (*n*)	T_e (°C)	ΔH (J g^{-1})
0	33.09	150.64
30	32.91	187.19
50	32.80	174.55
80	33.49	181.33
100	32.92	165.69

3.4. Infrared spectroscopy

Infrared spectroscopy of fatty acids at 20°C show a strong absorption centered at 1720 ± 1 cm^{-1} which is identified with the –C=O stretching band. Since the absorption of unassociated –C=O centered at 1760 cm^{-1} [8], it can be declared that there are intermolecular hydrogen bonds in solid state of fatty acids. The absorption of –OH stretching band in the wide range of 3200–2500 cm^{-1} also indicates the existence of intermolecular hydrogen bonds in solid state.

It can be seen from Fig. 3 that with the increase of temperature the absorption of $\gamma_{-C=O}$ and γ_{-OH} shifts to high frequency while the absorption of out-of-plane vibration of –OH shifts to lower frequency. That declares the hydrogen bonds between molecules are broken and rotational and vibrational disorder is introduced. Comparing Table 3 with Table 1, it is

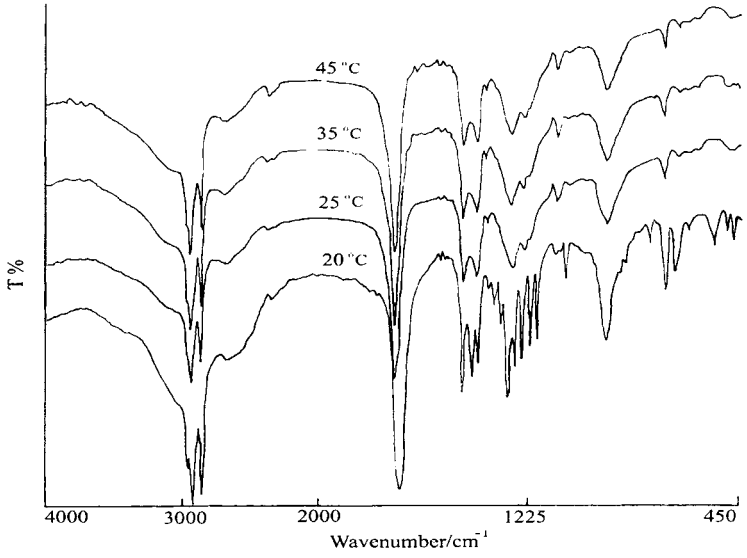

Fig. 3. Infrared spectra of lauric acid at various temperatures.

Table 3
Spectra shifts to higher frequency and corresponding temperature range

Sample	$\Delta\sigma$ (cm^{-1})			
	$\gamma_{-C=O}$	γ_{-OH}	δ_{-OH}	ΔT (°C)
Lauric acid	11	10	−4	20–50
Palmitic acid	10	8	−6	35–65
49.98% LA–PA	6	6	−6	20–40

clear that the temperature range related to the absorption shifts is corresponding to the transition temperature by DSC, which also prove that the intermolecular hydrogen bonds are involved in the solid–liquid phase transition of fatty acids. When the temperature is increased above the fusion point, there is no shift for those absorption, which declares that the intermolecular hydrogen bonds have been broken completely and the solid–liquid phase transitions have finished after the fusion point.

4. Conclusion

As an organic solid–liquid PCMs with so many advantages, e.g. large amounts of heat, low fusion point, no supercooling and stable thermal properties after heating–cooling cycles for many times, binary systems of fatty acids have potential for heat storage and can be used widely in solar energy storage. The solid–liquid phase transition of fatty acids is related to intermolecular hydrogen bonds.

References

[1] M.W. Babich, S.W. Hwang, R.D. Mounts, Thermochim. Acta 226 (1993) 163.
[2] M.W. Babich, S.W. Hwang, R.D. Mounts, Thermochim. Acta 210 (1992) 83.
[3] M.W. Babich, S.W. Hwang, R.D. Mounts, Thermochim. Acta 210 (1992) 77.
[4] D. Feldman, D. Banu, Thermochim. Acta 272 (1996) 243.
[5] K.P.K. Peippok, P.D. Lund, Solar Energy 46 (5) (1991) 275.
[6] D.S. Ruan, T.P. Zhang, D.S. Zhang, Acta Energine Solar Sinica 15 (1) (1994) 19.
[7] Y.P. Zhang, H.P. Hu, X.D. Kong, Heat Storage in Phase Transition, China University of Science and Technology Press, Hefei, 1996, p. 10.
[8] Y.K. Chen, Technique and Application of Infrared Spectroscopy, Shanghai Jiaotong University Press, Shanghai, 1993, p. 13.