【論文】 HEAT CAPACITY, HEAT OF TRANSITION, AND THERMAL CONDUCTIVITY OF PENTAERYTHRITOL AND ITS SLURRY

Yoshio TAKAHASHI, Masayuki KAMIMOTO, Yoshiyuki ABE
Electrotechnical Laboratory
1-1-4 Umezono, Tsukuba, Ibaraki 305
Yuji NAGASAKA, Akira NAGASHIMA
Department of Mechanical Engineering, Keio University
3-14-1 Hiyoshi, Yokohama 223

Pentaerythritol is a promising latent thermal storage material with transition temperature 188°C. Use of slurry of pentaerythritol and heat transfer oil (Hitherm PS-5) can enhance heat conduction in the storage material. In the present study, heat capacity and heat of transition were measured by differential scanning calorimetry on pentaerythritol and Hitherm PS-5. Thermal conductivities of Hitherm PS-5 and the slurry with 70 weight % of pentaerythritol were measured by the transient hot-wire method. The data of heat capacities and thermal conductivities were correlated by linear equations. The thermal conductivity of the slurry showed a discontinuity at the transition temperature due to a change in crystal structure.

1. INTRODUCTION

The latent heat of pentaerythritol ($C(CH_2OH)_4$) at the transition point of 188 °C is as large as the heat of fusion of ice. The heat of transition is about 300 kJ/kg [1-4], although it is different from sample to sample depending on the purity of the material. The temperature range around 188 °C is quite important for process heat utilization because of the possibility of steam generation.

From thermoanalytical evaluations, Sakamoto et al.[2] concluded that pentaerythritol is a promising latent thermal storage material in the temperature range between 150 and 200 °C.

In order to make effective use of pentaerythritol as a latent thermal storage material, the authors et al. proposed a few active-heat-exchange thermal storage devices [5,6] and an encapsulated-type (passive) storage device [6]. For both the active and passive heat exchange devices, use of pentaerythritol slurry with heat transfer oil (for example, Hitherm PS-5) is recommended to enhance the heat conduction in the storage materials.

Heat capacity, latent heat, and thermal conductivity are fundamental thermophysical properties for thermal storage materials. They are strongly related to energy density, power density, temperature efficiency, and so on. Data of such thermophysical properties are therefore needed in various stages of R&D of storage systems.

Heat capacity and latent heat of the slurry are usually the sum of those properties of the component materials. On the other hand, it is difficult to

estimate thermal conductivity of the slurry accurately from the values of the components. In the present study, measurements of heat capacity and heat of transition were made on the components : pentaerythritol and Hitherm PS-5, and thermal conductivity was measured on the slurry and Hitherm PS-5.

2. EXPERIMENTAL

2.1 Samples

Pentaerythritol was supplied by Koei Chemical Co., Ltd. Its purity was determined to be 99.7 % by the standardized method (Japan Industrial Standard). The diameter of the crystal was around 0.3 to 0.8 μm. Pentaerythritol was dried at 110 °C for 24 h before measurements. For Hitherm PS-5 (Nippon Oil Co., Ltd., alkylidiphenyl ethane), measurements were made on a fresh sample as was received.

2.2 Apparatus and Procedure

2.2.1 Heat capacity and heat of transition
A Perkin-Elmer DSC-2 was used. Data acquisition and processing were made with a data logger (Hewlett Packard HP 3497A) and a personal computer (Hewlett Packard HP 9816S).

An aluminum sample pan for a volatile specimen was used because of high vapor pressure of pentaerythritol and the Hitherm PS-5. Mass of the specimen was measured after each DSC measurement to check the vaporization of the specimen due to a possible break of the sealed sample pan.

Heat capacity measurements were made in a usual way by observing DSC base lines for an empty pan, a reference material (sapphire), and a sample. An example of the measured signals is

shown in Fig. 1. Correction was made for weight difference between the pan for the reference and the pan for the sample by using the specific heat capacity data of aluminum. Specific heat capacity of a sample c_S was calculated by the following equation:

$$c_S = \frac{W_R \left[\left(\frac{c_P \Delta W_P (Y_R - Y_B)}{c_R W_R} \right) - Y_B \right] c_R}{W_S (Y_R - Y_B)}, \quad (1)$$

where W_R and W_S are weights of the reference and the sample, and ΔW_P is the weight difference between the pan for the reference and that for the sample. In this study, the weights of the samples were 12.73 mg and 8.91 mg for pentaerythritol and Hitherm PS-5, respectively. c_R and c_P are the specific heat capacities of the reference and the blank (empty pan), respectively. Y_S , Y_R , and Y_B are the DSC signals for the sample, reference, and the blank, respectively. The accuracy of our DSC measurements is estimated within $\pm 2\%$.

The temperature increment in each scan was 40 K for Hitherm PS-5 and 40, 50, or 60 K for pentaerythritol depending on the temperature range. The heating rate was 5 K/min. The DSC data was recorded at every 12 seconds in the steady state and at every 3 seconds in the transition region; therefore, specific heat capacities were determined at every 1 K in the steady state and at every 1/4 K in the transition region.

Heat of fusion was determined from the integration of the specific heat capacity curve thus obtained. This method using the sapphire as a reference material was proposed by one of the authors (YT)[7]; the latent heat can be determined more accurately than the conventional latent heat measurement by DSC using reference metals with a known latent heat such as indium.

2.2.2 Thermal conductivity The principle of the thermal conductivity measurement is based upon the transient hot-wire method. This method is well known and the comprehensive paper on the theory and the error analysis is available [8], then only the principle of the measurement and the present experimental apparatus are described here.

In the idealized model, the transient hot-wire apparatus consists of a vertical thin metallic wire immersed in a liquid sample where the wire acts both as an electric heating element and a resistance thermometer. Initially at temperature T_0 , a step voltage is ap-

plied at time $t = 0$ across the wire. Then the transient temperature rise of the wire can be written as follows;

$$\Delta T(t) = T(t) - T_0 = (q/4\pi\lambda) \ln(4\kappa t/a^2 C), \quad (2)$$

here λ : thermal conductivity, κ : thermal diffusivity, a : a radius of the wire, q : heat generation per unit length of the wire and $C = \exp \gamma = 1.781...$ where γ : Euler's constant. According to Eq.(2), the thermal conductivity can be measured by a straight line for a plot of $\Delta T(t)$ against $\ln t$ and q given by

$$\lambda = (q/4\pi)/(d\Delta T/d \ln t). \quad (3)$$

When natural convection occurs during the measurement, it can be detected as a convex curvature off the straight line. Therefore this method has the advantage to eliminate the error due to onset of natural convection.

Figure 2 shows a block diagram of the present fully automated transient hot-wire apparatus [9]. The apparatus consists mainly of six components: microcomputer, a heater power controller, a digital voltmeter (DVM), a bridge with selection switches for sequence control, a power supply and a hot-wire cell with thermostatic bath.

We have featured the following functions for the present apparatus. (1) The time of onset of natural convection can be detected for an individual run, then the thermal conductivity is calculated using the temperature rise between appropriate time intervals. (2) All sequential switchings and resistor adjustment procedures can be performed. (3) Temperature of the thermostatic bath can be controlled, and after filling a liquid sample in a cell, the

Fig. 1 An example of DSC signals for an empty pan (blank), a pan with a reference (sapphire), and a pan with a sample (pentaerythritol).

apparatus can start to take measurement. In other words, the apparatus can measure the thermal conductivity of dielectric liquids without any manual procedures except for the sample preparation.

A cross-sectional view of the hot-wire cell together with a vessel is shown in Fig. 3. The main frame of the hot-wire cell consists of SUS rods 11 on whose ends alumina discs 6 are fastened. The platinum wire (99.99 %) of 30 μm in diameter 10 and of about 100 mm in length is soldered between two platinum hooks 4 with an axial stress of predetermined magnitude. Two potential leads 5 of the same wire are spot welded at positions 15 mm from each end of the wire in order to eliminate the end effects.

The relation of the temperature-resistance of the wire is calibrated

in situ in the temperature range from 0 to 200 °C in advance. The temperature was measured with the aid of a standard resistance thermometer which was calibrated on IPTS-68. In order to confirm that the apparatus operates in accordance with the theory, the thermal conductivity of toluene was measured repeatedly and compared with the values recommended by the present authors [10].

In the course of filling the slurry of pentaerythritol and Hitherm PS-5 in the cell, a considerable care was taken because the cell was originally designed only for liquid. The hot-wire itself is so fragile that the cell cannot be inserted directly into the slurry contained in the vessel. Therefore the cell was fixed in the vessel first and then small crystal of pentaerythritol was filled very slowly through the sample inlet 1 in Fig. 3. After filling the maximum possible amount of pentaerythritol without giving any detectable stress on the wire, Hitherm PS-5 was poured from the inlet in almost like a drop by drop process to prevent mixing of air in the slurry.

The apparent final weight fraction of pentaerythritol was approximately 70 %, which is close to the value needed for encapsulated type storage devices. Even with this procedure for the sample preparation, small amount of residual air near the wire could not be avoided. Then the measurement was repeated on heating and cooling processes for several times. The final results were obtained on cooling after through the crystalline transition of pentaerythritol at 188 °C. The reason for this is that small crystals of pentaerythritol stick together after the phase transition and this condition might resemble that in actual thermal storage systems.

3. RESULTS AND DISCUSSION

3.1 Heat Capacity and Heat of Transition

3.1.1 Pentaerythritol Figure 4 shows the specific heat capacity data on pentaerythritol and the integrated enthalpy change curve; a part of the data are listed in Table 1 with 5 K intervals. The data points are plotted on an enlarged scale in Fig. 5 together with the results by Nitta et al. [1]. Note that the specific heat capacities in the transition temperature range are apparent values since the temperature on the abscissa is not corrected. From the extrapolated onset temperature T_t , the transition temperature was determined to be 185.6 °C. The heat of transition was determined to be 285 J/g from the difference in the extrapolated

Fig. 2 Experimental apparatus for thermal conductivity measurements.

Fig. 3 Hot-wire cell with vessel.

3.1.2 Hitherm PS-5 The measured specific heat capacity data are shown in Fig. 6 together with the catalogue values [11]; the data are also listed in Table 2 with 5 K intervals.

The catalogue values show a large discrepancy from the measured ones. Such discrepancies are also reported on many kinds of heat transfer oils [12,13]. The specific heat capacity data measured in this study were fitted to the following linear expressions. The standard deviation from the smoothed values is less than 0.3 %;

$$c_p/Jg^{-1}K^{-1} = 0.7293+0.00321\times(T/K) \qquad 334\;K<T<513\;K. \quad (4)$$

3.2 Thermal Conductivity

3.2.1 Hitherm PS-5 The results of the measurements are listed in Table 3. The temperature rise of the platinum wire was about 1 K at 3 s after the initiation of heating. The accuracy of the present data is estimated to be $\pm 1.5\%$. The results were correlated by the following equation within the estimated accuracy.

Table 3 Experimental thermal Conductivities of Hitherm PS-5.

T		λ	
K		$Wm^{-1}K^{-1}$	
300.50	0.1230	410.65	0.1126
300.54	0.1228	410.67	0.1121
300.58	0.1233	451.58	0.1094
350.12	0.1186	451.70	0.1085
350.17	0.1178	451.70	0.1083
350.16	0.1187	493.00	0.1058
410.74	0.1118	493.31	0.1053

Fig. 7 Thermal conductivity of Hitherm PS-5.

$$\lambda/Wm^{-1}K^{-1} = 0.1508-9.27\times10^{-5}\times(T/K) \qquad 300\;K<T<493\;K. \quad (5)$$

In Fig. 7, the present thermal conductivity results on Hitherm PS-5 are compared with those taken from its catalogue [11]. Although the discrepancy amounts to more than 5 % at low temperature range, this seems to be reasonable taking into account rather rough estimation method which might be used for the catalogue values.

3.2.2 Slurry of pentaerythritol and Hitherm PS-5 The correlated equation on the thermal conductivity of pentaerythritol slurry is as follows;

$$\lambda/Wm^{-1}K^{-1}=0.6631-8.272\times10^{-4}\times(T/K) \qquad 296\;K<T<461\;K, \quad (6)$$

$$\lambda/Wm^{-1}K^{-1}=0.9086-1.463\times10^{-3}\times(T/K) \qquad 461\;K<T<513\;K. \quad (7)$$

Table 4 Experimental thermal conductivities of pentaerythritol slurry.

T		λ	
K		$Wm^{-1}K^{-1}$	
296.15	0.4141	409.11	0.3246
296.48	0.4150	409.10	0.3242
296.74	0.4146	450.20	0.2887
296.86	0.4150	450.24	0.2894
332.73	0.3905	450.04	0.2890
332.49	0.3902	450.07	0.2901
332.09	0.3895	492.90	0.1898
358.89	0.3679	492.91	0.1889
358.94	0.3706	492.78	0.1838
358.93	0.3711	513.33	0.1568
358.81	0.3699	513.70	0.1577
409.50	0.3231

Fig. 8 Thermal conductivity of pentaerythritol slurry.

Fig. 4 Specific heat capacity data and the enthalpy change calculated from the data on pentaerythritol.

Fig. 5 Specific heat capacity of pentaerythritol on an enlarged scale.

Table 1 Experimental specific heat capacities of pentaerythritol.

T	c_p	T	c_p
K	$\text{JK}^{-1}\text{g}^{-1}$	K	$\text{JK}^{-1}\text{g}^{-1}$
334	1.55	415	1.99
335	1.56	420	2.04
340	1.59	425	2.08
345	1.61	430	2.12
350	1.64	435	2.17
355	1.66	440	2.24
360	1.69	445	2.32
365	1.71	450	2.44
370	1.74	455	2.57
375	1.75	460	6.82
380	1.79	465	31.3
385	1.82	470	25.4
390	1.84	475	3.19
395	1.86	480	2.77
400	1.90	485	2.77
405	1.92	490	2.77
410	1.95	493	2.77

lines of the enthalpy change at the extrapolated onset temperature.

Several values of heat of transition have been reported; they are between 269 and 322 J/g [1-4]. Nitta et al.[1] pointed out that the residual water in the sample might have a strong effect on the value of heat of transition. In the present study, it was measured for the dried sample and for the sample being kept for 8400 h under saturated vapor of water at room temperature. They did not show any difference. The scattering of the values reported by several investigators is therefore considered due to the difference in purity of the samples. From a scientific view point, the heat of transition of pentaerythritol has to be re-examined using an extra pure sample.

Fig. 6 Specific heat capacity of Hitherm PS-5.

Table 2 Experimental specific heat capacities of Hitherm PS-5.

T	c_p	T	c_p
K	$\text{JK}^{-1}\text{g}^{-1}$	K	$\text{JK}^{-1}\text{g}^{-1}$
334	1.80	425	2.13
335	1.81	430	2.14
340	1.85	435	2.15
345	1.85	440	2.16
350	1.87	445	2.20
355	1.88	450	2.18
360	1.88	455	2.21
365	1.92	460	2.22
370	1.93	465	2.24
375	1.94	470	2.26
380	1.95	475	2.27
385	1.96	480	2.28
390	1.98	485	2.29
395	2.02	490	2.32
400	2.03	495	2.34
405	2.05	500	2.36
410	2.07	505	2.37
415	2.07	510	2.38
420	2.10	513	2.38

Figure 8 shows the results on the slurry of pentaerythritol and Hitherm PS-5. As seen from this figure, the thermal conductivity shows discontinuity at the phase transition temperature of pentaerythritol. The discontinuity, i.e. a decrease above the transition point, seems reasonable since the high temperature phase of pentaerythritol is a plastic crystal with disordered lattices, which causes an increase in phonon scattering.

4. CONCLUDING REMARKS

Heat capacity and heat of transition were measured by differential scanning calorimetry on pentaerythritol, which is a promising latent thermal storage material with transition temperature 188 °C. Also measured was heat capacity and thermal conductivity of Hitherm PS-5, which is used to make slurry of pentaerythritol. The thermal conductivity was measured by the transient hot-wire method. It was applied to measure the thermal conductivity of the slurry of pentaerythritol and Hitherm PS-5.

Both the heat capacity and thermal conductivity data were correlated by linear equations. The thermal conductivity of the slurry showed a discontinuity at the transition temperature due to a change in crystal structure.

The present data has been used to analyze the results of heat transfer experiments and to design latent thermal storage units using pentaerythritol slurry. The following R&D are going on: (1) development of ways of stabilizing the slurry to prevent its adhesion to the containers etc. and (2) development of inexpensive encapsulation using materials which do not cause a degradation of pentaerythritol [6].

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ペンタエリトリールとそのスラリーの 熱容量、転移熱、および熱伝導率

高橋義夫、神本正行、阿部宜之
電子技術総合研究所
〒305 茨城県つくば市梅園1-1-4
長坂雄次、長島 昭
慶応義塾大学理工学部機械工学科
〒223 横浜市港北区日吉3-14-1

ペンタエリトリールは188℃に転移点を有する有望な潜熱蓄熱材料である。筆者らは、蓄熱材料側の伝熱を促進するために、これを熱媒体油とスラリー化して用いる方法をいくつか提案している。本研究では、ペンタエリトリールおよび熱媒体油ハイサームPS-5（アルキルジフェニルエタン）の熱容量および転移熱を示差走査熱量測定（DSC）により測定した。また、ハイサームPS-5、ならびにペンタエリトリールとハイサームPS-5のスラリーの熱伝導率を、非常細線法により測定した。熱容量と熱伝導率の測定値の温度依存性は、ペンタエリトリールの熱容量を除き、直線よく近似できた。スラリーの熱伝導率は、ペンタエリトリールの相転移に伴う結晶構造の変化のために転移点で不連続となり、転移点以上で小さな値となることがわかった。

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