Thermochimica Acta, 77 (1984) 241–249
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

INVESTIGATION OF LATENT HEAT-THERMAL ENERGY STORAGE MATERIALS. III. THERMOANALYTICAL EVALUATION OF PENTAERYTHRITOL

R. SAKAMOTO, M. KAMIMOTO, Y. TAKAHASHI, Y. ABE, K. KANARI
and T. OZAWA

Electrotechnical Laboratory, Sakura-mura, Niihari-gun, Ibaraki 305 (Japan)

(Received 13 January 1984)

ABSTRACT

Differential scanning calorimetry (DSC) and thermogravimetry (TG) are used to evaluate pentaerythritol for latent heat-thermal energy storage materials. Pentaerythritol is a promising material from the viewpoints of latent heat and material cost. Moreover, it is a unique material because of the large heat of crystalline transition which is the property used. The transition behavior was observed by DSC, and the compatibility with some heat transfer fluids, which will be used in direct contact with pentaerythritol as a slurry, was also examined by keeping them in energy-stored state and then observing the heat of transition by DSC. Pentaerythritol is useful in the temperature range 150–200°C, and heat transfer fluids of hydrocarbon are suitable.

INTRODUCTION

Thermal energy storage is essentially important for waste heat recovery, renewable energy utilization, such as solar energy and wind energy, cogeneration, etc. Although conventional sensible heat-thermal energy storage has already been applied to this type of energy utilization, recent research has been directed to advanced thermal energy storage, i.e., latent heat-thermal energy storage, thermal energy storage by reversible chemical reactions, and thermal energy storage by dilution and concentration. The latent heat-thermal energy storage has advantages over the others. For example, it can store thermal energy in a smaller volume than the sensible heat-thermal energy storage, and it can release heat at a relatively constant temperature in comparison with the others, so that the stored heat can be used efficiently. Moreover, it is more technically feasible than the other advanced thermal energy storage methods.

As is described in our previous papers [1–3], the materials, which are not costly and undergo fusion and/or crystalline transition with large latent heat at a desired temperature, were selected from comprehensive screening,

0040-6031/84/$03.00 © 1984 Elsevier Science Publishers B.V.

because the technical feasibility of the latent heat-thermal energy storage is fundamentally dependent on the existence of the applicable storage materials. Pentaerythritol is one of the candidate materials thus selected, and it is a unique material since it has the largest heat of crystalline transition among the practical candidate materials. In order to utilize fully its unique feature of transition, pentaerythritol should be used in direct contact with a heat transfer fluid as modified polyethylene reported previously [4–6]. Therefore, the transition behavior of pentaerythritol and its compatibility with the fluids should be evaluated. Differential scanning calorimetry (DSC) and thermogravimetry (TG) which are suitable for these purposes, were applied to evaluate pentaerythritol for the latent heat-thermal energy storage material. These experimental evaluations are reported in this paper.

EXPERIMENTAL

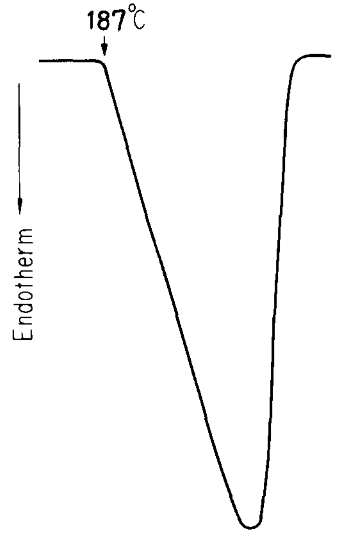
DSC and TG–differential thermal analysis (DTA) simultaneous measurements were carried out with apparatuses made by Rigaku Denki Co., Ltd. Because the sample sublimates above the transition temperature, an aluminum sample container (5 mm in diameter, 2.5 mm deep) which can be sealed and endure an inner pressure of up to 2 atm was used for DSC. For the compatibility test of long duration, the sample was contained with the heat transfer fluids in a sealed glass container which fits into the sample holder of the DSC. The compatibility was examined by observing the change in the transition behavior and the heat of transition with the DSC. For TG–DTA, an open aluminum shallow pan (5 mm in diameter, 2.5 mm deep) was used. The transition temperature was determined by measuring the extrapolated onset temperature.

Chemical purpose pentaerythritol (Eastman Kodak, m.p. 260–269°C) was used without further purification for the observation of the transition behavior and the TG–DTA measurements. For the compatibility study, pentaerythritol (Pentarit, Koei Chemical Co.) was used as received. Its purity was 99.8%, and impurities which decrease thermal stability were eliminated from the sample. As heat transfer fluids, alkyldiphenyl (Nippon Steel Chemical Co., Therm S 600), alkyldiphenylethane (Nippon Oil Co., Hitherm PS-5), Caloria HT-43 (Exxon Corp.), ethylene glycol (Kishida Chemical Co.), polydimethylsiloxane (Shin-etsu Chemical Co., KF-96) and polymethylphenylsiloxane (Shin-etsu Chemical Co., KF-54) were used.

RESULTS AND DISCUSSION

The heat of transition of pure pentaerythritol has previously been measured accurately and precisely with an adiabatic calorimeter, along with the effect of moisture on the transition [7]. In the present investigation for practical purposes, however, the heat of transition and the transition behavior were observed without further purification of the reagent as received. A typical example of the DSC curves is shown in Fig. 1. The peak shape is the same as that of a typical melting curve of a pure substance. The temperature and heat of transition are 186–187°C and 287–298 J g^{-1}, respectively. The heat of transition is less than the reported value of 322 J g^{-1} [7]. This discrepancy is presumably due to the moisture and other impurities. When the sample was cooled immediately after completion of the transition, supercooling was observed down to the temperature range 180–170°C, where the sample transformed to the low temperature crystalline phase.

The transition behavior in the cooling mode, i.e., the discharging mode, is very important from a practical viewpoint, therefore, various experiments were carried out. For example, when two or three particles (~ 2 mg) were set in the sample container, DSC curves such as those reproduced in Fig. 2 were obtained; the number of the peaks is likely to correspond to the number of the particles in the sample container. This suggests a nucleation-controlling mechanism. The sharp DSC curves also support this inference. To estimate the kinetic parameters of this transition, the dependence of the DSC curves on the cooling rate was observed for the sample when finely ground with a mortar, as shown in Fig. 3, where T is the temperature. However, as no curve overlaps with another curve at a different cooling rate, the method for the



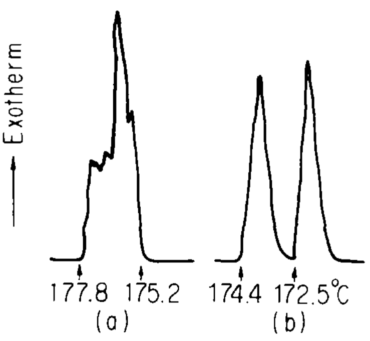


Fig. 1. Typical DSC curve of the crystalline transition of pentaerythritol at a heating rate of 1.25°C $\min^{-1}$.

Fig. 2. Typical DSC curves of the crystalline transition of pentaerythritol on cooling: (a) 0.625°C $\min^{-1}$; (b) 1.25°C $\min^{-1}$.

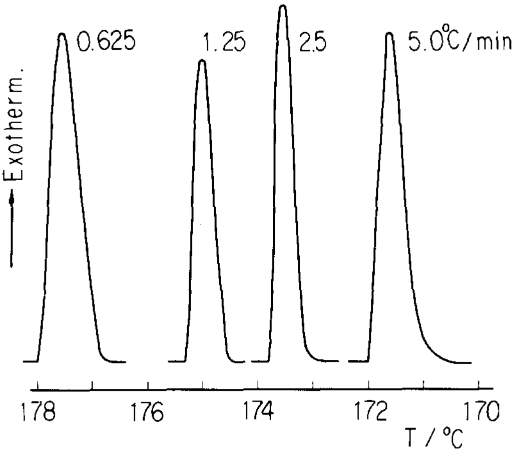


Fig. 3. Dependence of the DSC cooling curves of the crystalline transition of pentaerythritol on the indicated cooling rates.

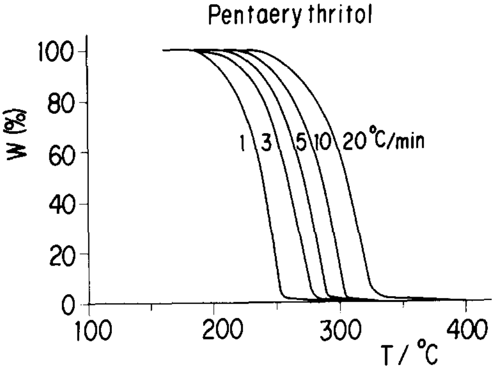


Fig. 4. Typical TG curves of pentaerythritol at indicated heating rates.

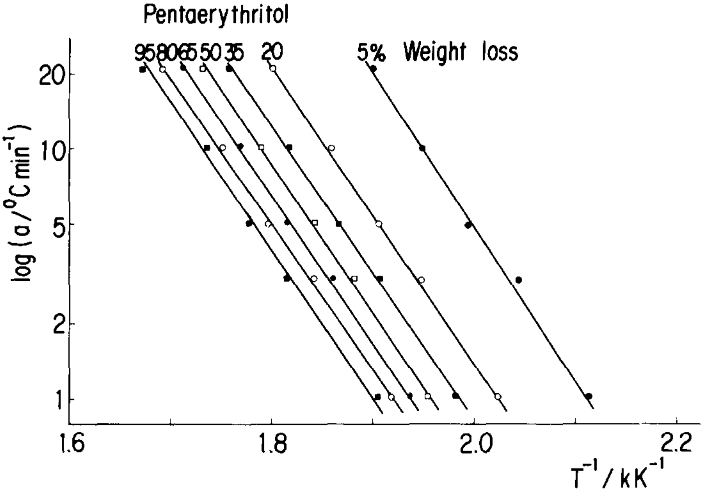


Fig. 5. Plots of the logarithm of heating rate vs. reciprocal absolute temperature at indicated conversions.

kinetic analysis of thermoanalytical data of a nucleation-and-growth process proposed by Ozawa [8] cannot be applied. This suggests a nucleation-controlling process with high growth rate. The extent of supercooling is less than 10°C in the practical discharging mode, therefore, this tendency is not considered to be a serious drawback.

To evaluate the thermal stability, TG was carried out in the flow of nitrogen with an open sample container. The results at different heating rates are shown in Fig. 4, where W is the residual weight. It is interesting to note that weight loss begins below the melting temperature and no change is observed at the melting temperature, 261°C, in the TG curves. By applying the method for kinetic analysis of thermoanalytical data of chemical reactions proposed by Ozawa [9], the kinetic parameters were estimated. First, the activation energy, ΔE, was estimated by plotting the logarithm of the heating rate, a, against the reciprocal absolute temperature, T^{-1}, at a given weight loss, as is shown in Fig. 5. The activation energies are estimated at every 5% conversion, C, as listed in Table 1. Although a little scattering of the plots is observed in the low conversion range and the activation energies estimated in the same range are somewhat larger than in the rest of the range, the variation of the estimated activation energy is negligibly small. It can be concluded, therefore, that the weight loss proceeds by a single unit

TABLE 1

Activation energy, reciprocal absolute temperature at 1°C min^{-1} and reduced time of thermal decomposition

C (%)	ΔE (kJ mol^{-1})	T^{-1} (kK^{-1})	θ (ns)	t at 185.6°C (h)
5	108.7	2.116	3.84	0.62
10	107.1	2.074	6.73	1.08
15	107.7	2.043	10.19	1.63
20	105.8	2.025	12.94	2.07
25	104.6	2.011	15.63	2.50
30	104.0	1.997	18.84	3.02
35	104.0	1.986	21.83	3.50
40	103.9	1.976	24.95	4.00
45	103.4	1.968	27.80	4.45
50	104.1	1.959	31.33	5.02
55	103.1	1.952	34.43	5.52
60	103.4	1.945	37.84	6.06
65	103.0	1.939	41.02	6.57
70	103.4	1.932	44.98	7.21
75	102.4	1.927	48.19	7.72
80	102.6	1.921	52.24	8.37
85	102.5	1.915	56.62	9.07
90	102.8	1.909	61.37	9.83
95	101.3	1.903	66.52	10.66
Average	104.1 ± 0.4			

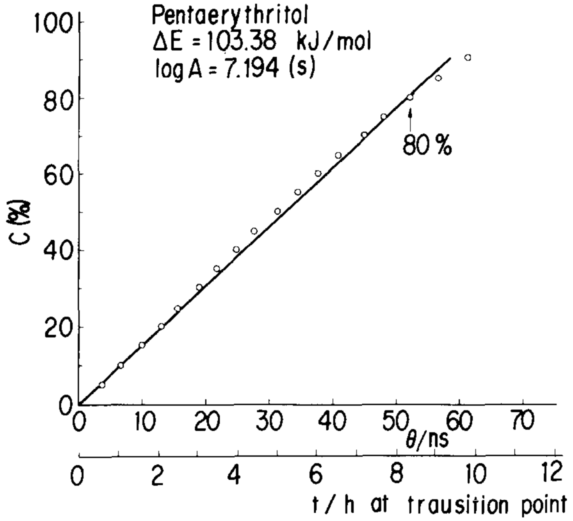


Fig. 6. Isothermal experimental master curve of weight loss of pentaerythritol.

process. By omitting the activation energies estimated at 5, 10 and 15% conversions, because apparent weight change causes error in determining the conversion especially in the low conversion range, the average activation energy of 103.4 ± 0.3 kJ mol^{-1} was obtained.

Using this average activation energy and the reciprocal absolute temperature at 1°C min^{-1} obtained at the intersection of 1°C min^{-1} with the above linear plots (Fig. 5), the reduced times, θ, at every 5% conversion are calculated [9]. The real times, t, are also predicted at every 5% conversion on the assumption that the process proceeds isothermally at the reported transition temperature. These values are both listed in Table 1. By using the reduced times thus calculated, TG curves were converted to an isothermal experimental master curve as shown in Fig. 6. Because a linear line can be drawn up to the point of 80% conversion, the process can be concluded to be of zero order and it is inferred to be the sublimation. The logarithm of the pre-exponential factor is estimated to be 7.194 (s). The process of zero order is also supported with the predicted real time in Table 1, in which the real time is approximately proportional to the conversion.

A TG curve was synthesized by using the reciprocal absolute temperatures in Table 1, and this experimental master TG curve is compared with the theoretical TG curve calculated by using the estimated kinetic parameters in Fig. 7; as seen from this figure, the agreement is very good. Therefore, the thermal decomposition does not occur in the temperature range observed by TG, and pentaerythritol should be used in a sealed container for thermal energy storage to prevent the material from sublimating away.

For evaluating the thermal stability and the compatibility with the heat transfer fluids, the powder of pentaerythritol (Koei Chemical Co.) was

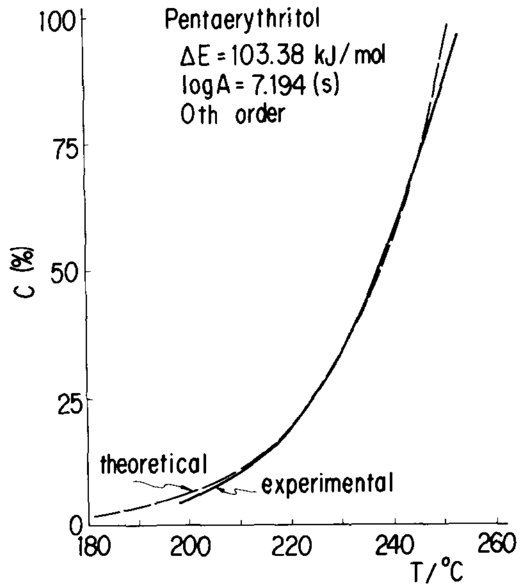


Fig. 7. Experimental master TG curve of weight loss of pentaerythritol (———) in comparison with theoretical TG curve of indicated kinetic parameters (- - - - - -).

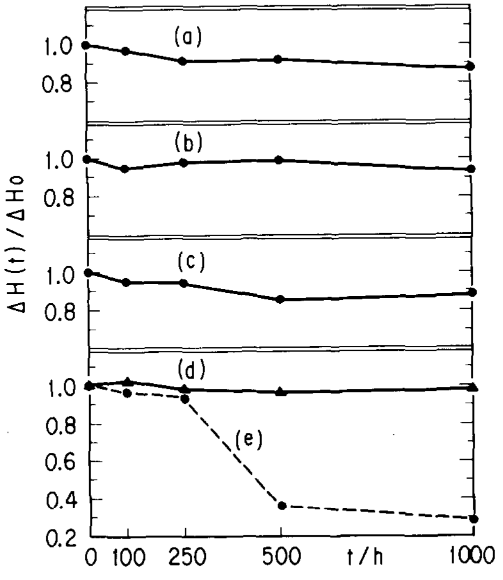


Fig. 8. Compatibility test of pentaerythritol with heat transfer fluids: (a) pentaerythritol; (b) pentaerythritol with Caloria HT-43; (c) pentaerythritol with alkyldiphenylethane; (d) pentaerythritol with polydimethylsiloxane; (e) pentacrythritol with polymethylphenylsiloxane.

placed in a sealed glass container, which can be used for the DSC measurement, with and without the heat transfer fluids in nitrogen atmosphere in which oxygen was exclusively purged. The glass container was maintained in the temperature range 195–200°C, i.e., in the charging state, for long durations up to 1000 h. The DSC measurements were made intermittently for these samples. With the exception of the sample with polymethylphenylsiloxane, little change in the DSC curve and the extrapolated onset temperature was observed, and the ratios of the heat of transition, $\Delta H(t)$, to the initial heat of transition, ΔH_0, are shown in Fig. 8. From these results, it can be concluded that pentaerythritol can be used for thermal energy storage in direct contact with the heat transfer fluids of hydrocarbon, such as alkyldiphenylethane, alkyldiphenyl and Caloria HT, in a sealed container, and their compatibility is also concluded to be very good. However, polydimethylsiloxane is not as suitable as the hydrocarbon fluid because of its high viscosity, though it has good compatibility. Ethylene glycol is not good because of its interaction with pentaerythritol, since both are polyhydric alcohols.

CONCLUSIONS

From the experimental evaluation described above, the following conclusions can be deduced. Pentaerythritol is a very promising material for the latent heat-thermal energy storage in the temperature range 150–200°C, and it can be used in direct contact with the heat transfer fluids of hydrocarbon in a sealed container for long duration; the direct contact in a slurry would be very effective for the heat transfer both in charging and discharging modes. A bench-scale shell-and-coil type thermal energy storage apparatus for using the slurry of pentaerythritol and alkyldiphenylethane was manufactured, and observations of its characteristics and performance are now under way in our laboratory. The results of the observation will be reported in the near future.

REFERENCES

1 T. Ozawa, M. Kamimoto, R. Sakamoto, Y. Takahashi and K. Kanari, Denshi Gijutsu Sogo Kenkyujo Iho, 43 (1979) 289.

2 T. Ozawa, M. Kamimoto, R. Sakamoto, Y. Takahashi and K. Kanari, Denshi Gijutsu Sogo Kenkyujo Iho, 44 (1980) 707.

3 T. Ozawa, K. Kamimoto, R. Sakamoto, Y. Takahashi and K. Kanari, Proc. 7th Int. CODATA Conf., Kyoto, 1980.

4 Y. Takahashi, R. Sakamoto, M. Kamimoto, K. Kanari and T. Ozawa, Thermochim. Acta, 50 (1981) 31.

5 Y. Abe, Y. Takahashi, R. Sakamoto, K. Kanari, M. Kamimoto and T. Ozawa, ASME/JSME Therm. Eng. Joint Conf. Proc., 2 (1983) 365.

6 M. Kamimoto, Y. Abe, S. Sawata, T. Tani and T. Ozawa, Proc. 18th Intersoc. Energy Conv. Eng. Conf., Orlando, FL, 1983, p. 1790.
7 I. Nitta, S. Seki and M. Momotani, Proc. Jpn. Acad., 26(9) (1950) 25; I. Nitta, S. Seki, M. Momotani and S. Nakagawa, Proc. Jpn. Acad., 26(10) (1950) 11; I. Nitta, T. Watanabe, S. Seki and M. Momotani, Proc. Jpn. Acad., 26(10) (1950) 19; I. Nitta, S. Seki and K. Suzuki, Bull. Chem. Soc. Jpn., 24 (1951) 63.
8 T. Ozawa, Polymer, 12 (1971) 150.
9 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881; J. Therm. Anal., 2 (1970) 301; 9 (1976) 369.