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INVESTIGATION OF LATENT HEAT-THERMAL ENERGY STORAGE MATERIALS. II. THERMOANALYTICAL EVALUATION OF UREA

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ABSTRACT

Urea is a very suitable material for latent heat-thermal energy storage in the temperature range 100–150°C with respect to the heat of fusion and material cost. Differential scanning calorimetry and thermogravimetry were applied to observe melting and crystallization behavior and to evaluate the thermal stability. Heating and cooling curve methods were also used. It has been revealed that urea has two serious drawbacks; one is a large supercooling tendency and the other is its low thermal stability. By forming a eutectic mixture with potassium chloride or ammonium chloride, the supercooling tendency is remarkably decreased and addition of sebacic acid is also effective for the purpose, but the low thermal stability is not improved by the addition of these compounds. Urea is thus unsuitable for latent heat-thermal energy storage because of its low thermal stability, though the latent heat and the material cost of urea are superior to those of polyethylene which is selected to be a promising material for latent heat-thermal energy storage in the same temperature range.

INTRODUCTION

Thermal energy storage is an essential technique for renewable energy utilization such as solar and wind energy, waste heat recovery, and so on. Thermal energy storage by using the heat of fusion or transition is a very effective scheme because of its high energy density and constant-temperature heat release. In the first step of development of latent heat-thermal energy storage, screening and experimental evaluations of materials are essentially important. As described in previous papers [1–4], screening of the materials of single-component and eutectic mixtures was made in the temperature range 100–500°C with respect to latent heat and material cost, and inexpensive materials which undergo fusion and/or transition with a large latent heat were listed.

In the temperature range 100–150°C, urea and polyethylene were selected. This temperature range is desirable for the purpose of solar thermal energy utilization and waste heat recovery. Some eutectic mixtures of aluminum chloride or ferric chloride are also candidates, since the heat of fusion

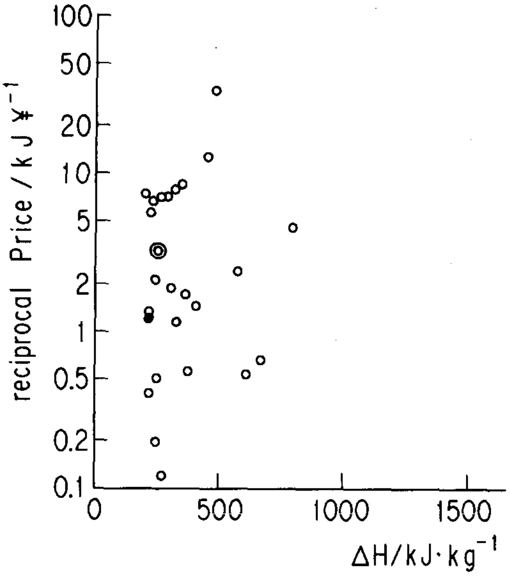

Fig. 1. Plots of reciprocal price of material vs. latent heat. The double circle is urea and the filled circle is polyethylene.

estimated on the assumption of additivity of entropy change on fusion is large enough. However, they were not selected because of their hygroscopic and corrosive nature and complex ion formation which is considered to cause a lower latent heat than the estimated values.

Urea has a very large heat of fusion and it is an inexpensive material because it is produced and used as a fertilizer on a large scale. With respect to the latent heat, ΔH, and material cost, urea is a very promising candidate, as shown in Fig. 1. Also shown are other possible single-component materials in the temperature range 100–1000°C, plotted to illustrate their applicability; from this, it can be seen that urea is preferable to polyethylene. To examine its thermal stability and melting and crystallization behavior, differential scanning calorimetry (DSC) and thermogravimetry (TG) were carried out, and the melting temperature and the heat of fusion were also measured. Heating and cooling curves were also recorded to observe the melting and crystallization behavior for a large amount of the sample. In this report, these thermoanalytical evaluations of urea for the latent heat-thermal energy storage materials are described.

EXPERIMENTAL

A differential scanning calorimeter (Rigaku Denki Co., Ltd.) and a simultaneous measurement apparatus for TG–DTA (Rigaku Denki Co., Ltd.) were used. In both measurements, a shallow pan (5 mm diameter × 2.5 mm depth) made of aluminum was used for the sample container. For DSC, the sample container was sealed with a thin aluminum lid to be durable up to 2 atm internal pressure. TG–DTA was carried out with an open sample container under a nitrogen flow of 70 ml min^{-1}. The heating and cooling curves were obtained with a pyrex glass tube of 22 mm internal diameter × 60 mm depth.

Urea used was purchased from Wako Pure Chemical Industries, Ltd. (guaranteed grade). Stearic acid (guaranteed grade, > 97% purity), *n*-hexadecane (guaranteed grade, > 99% purity), *n*-hexadecan-1-ol (guaranteed grade, > 99% purity) and sebacic acid (extra pure grade, > 98% purity) were supplied from Tokyo Kasei Kogyo Co., Ltd. Potassium chloride (guaranteed grade) and anhydrous potassium carbonate (guaranteed grade) were purchased from Showa Chemicals Co., Ltd., and ammonium chloride (guaranteed grade) was supplied from Kanto Chemical Co., Inc. Sodium nitrate (guaranteed grade) was purchased from Wako Pure Chemical Industries, Ltd. All were used as received.

RESULTS AND DISCUSSION

A typical DSC curve obtained at a heating rate of 1.25°C min^{-1} is shown in Fig. 2, where T is the temperature. As is clearly seen, urea has a very large supercooling tendency up to 40 K, though the heat of fusion is large; it then rapidly crystallizes, presumably due to nucleation-controlling crystallization. The crystallization peak becomes a trapezoid, possibly because the differential scanning calorimeter may go out of control due to a very rapid exotherm. The heat of crystallization is estimated from the area of the trapezoid and shown in the figure, but it is probably erroneous. In the second run, a similar supercooling tendency was observed. Moreover, the heat of the second fusion is remakably decreased, and the shape of the peak becomes diffuse; these facts suggest the possibility of thermal decomposition. The supercooling tendency is also observed in the heating and cooling curve of a large amount of sample, as shown in Fig. 3, where t is the time.

In order to elucidate the kinetics of thermal decomposition, TG–DTA measurements were carried out at heating rates of 1, 3, 5, 10 and 20°C min^{-1}. Typical results of the residual weight, W, vs. T are reproduced in Fig. 4. The decomposition proceeds in three stages, a phenomenon also observed by Roy and Acharyya [5] by TG. The first stage is analyzed kinetically because the thermal stability is dependent on the kinetic parameters of the first stage of decomposition. The logarithms of heating rates, ϕ, were plotted against the reciprocal absolute temperature, T^{-1}, at a given conversion, C, as shown in Fig. 5 [6,7]. The activation energies, ΔE, were estimated from the slope of the above linear plots by the least-squares method, while the

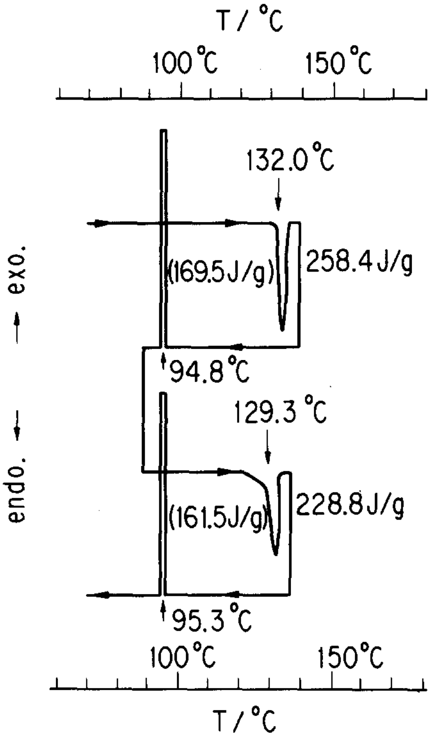

Fig. 2. Typical DSC curve of urea.

reciprocal absolute temperatures at 1°C min^{-1} were also obtained at the intersection of the same linear plots with 1°C min^{-1}.

The estimated activation energies and the reciprocal absolute temperatures at 1°C min^{-1} are listed in Table 1 along with the thermal decomposi-

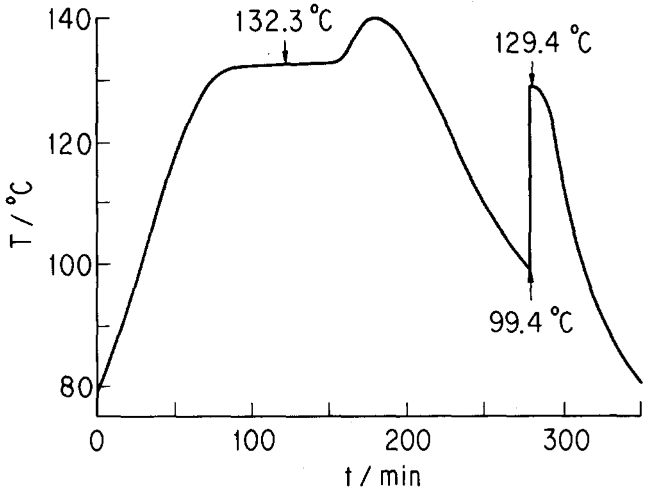

Fig. 3. Heating and cooling curves of urea.

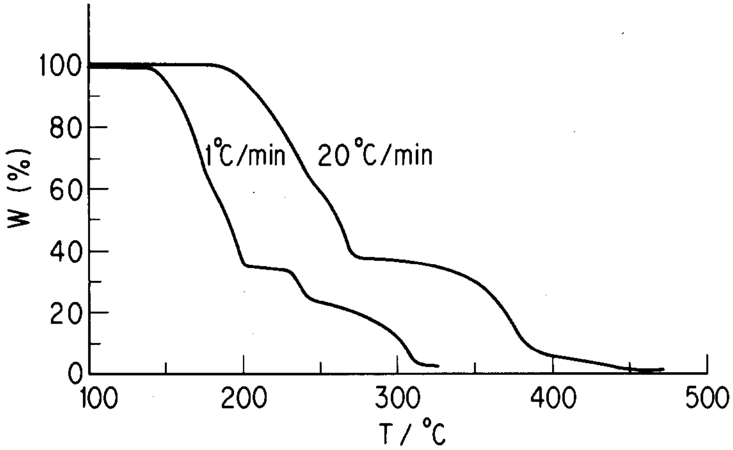

Fig. 4. Typical TG curves of urea.

tion. By using the average activation energy and the reciprocal absolute temperatures, the reduced time, θ, can be calculated, and the TG curves of the first stage, shown in Fig. 4, are converted to the experimental master curve, i.e., the curve of the conversion versus the reduced time which is equal to the real time when the process proceeds at infinite temperature [6,7]. In Fig. 6 the master curve thus obtained is shown. In this figure, logarithms of unconverted fractions are plotted on the ordinate on the assumption that the reaction is first order. As is clearly shown, the first stage of thermal decomposition proceeds predominantly by a first order mechanism.

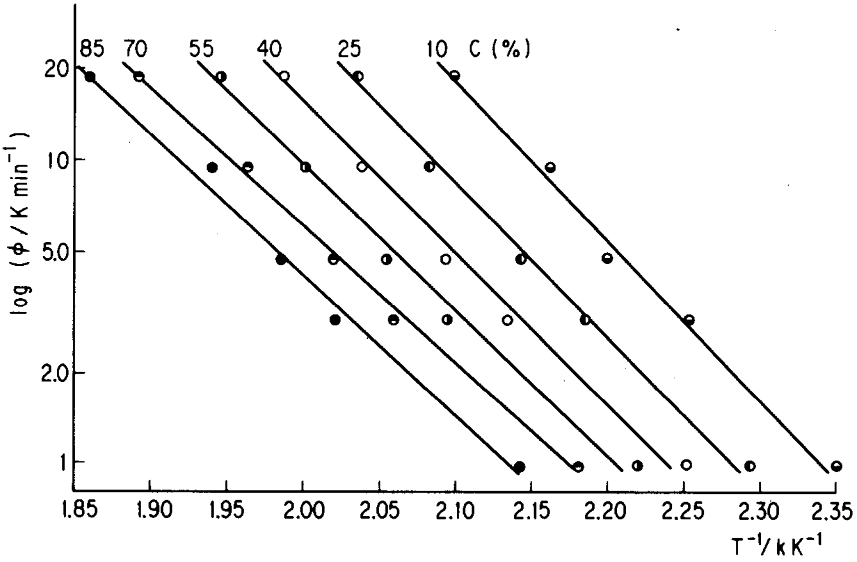

Fig. 5. Plots of logarithm of heating rate vs. reciprocal absolute temperature at indicated conversions.

TABLE 1

Activation energy, reciprocal absolute temperature at 1°C $\min^{-1}$ and reduced time estimated at indicated conversion

$C(\%)$	$E(\mathrm{kJ\ mol^{-1}})$	$T^{-1}\ (\mathrm{kK^{-1}})$	s
10	90.8	2.351	0.037
15	90.2	2.321	0.051
20	89.5	2.303	0.063
25	88.0	2.284	0.077
30	86.6	2.269	0.091
35	85.8	2.254	0.108
40	86.0	2.240	0.126
45	85.0	2.228	0.143
50	84.0	2.217	0.162
55	83.7	2.205	0.184
60	83.7	2.193	0.212
65	81.4	2.181	0.240
70	79.7	2.171	0.269
75	81.0	2.157	0.317
80	82.7	2.143	0.371
85	82.9	2.133	0.412
90	83.4	2.122	0.463
95	85.0	2.111	0.526
Average	85.0 ± 0.7		

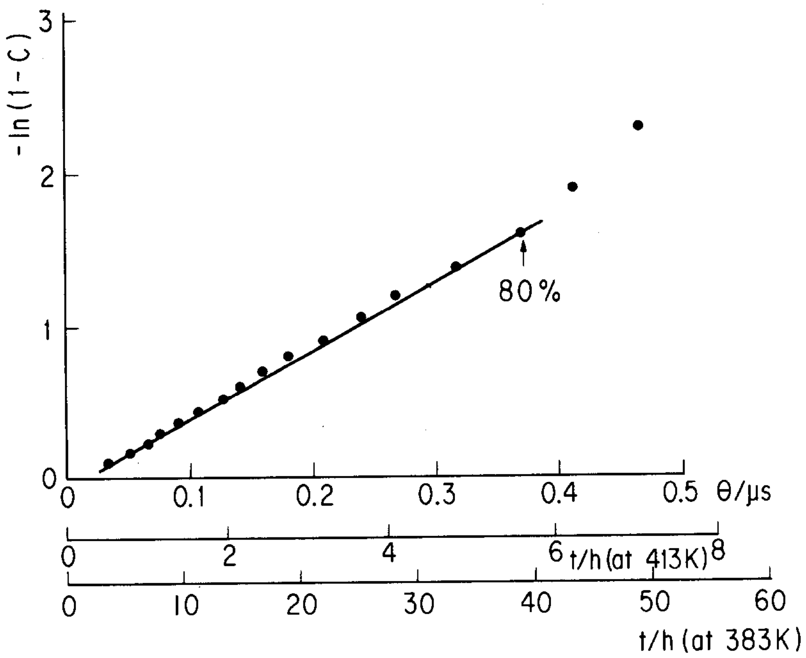

Fig. 6. Experimental master curve of thermal decomposition of urea.

By using the activation energy and the reduced time, it is possible to predict the thermal decomposition under the operating conditions of the materials. The two lower abscissae of Fig. 6 are the real times when the thermal decomposition proceeds at 413 K, which is a little higher than the melting temperature, and at 383 K, which is a little lower than the melting temperature. It is reported [8] that the heat of fusion of urea in a sealed container decreases first and then levels off on repeated heating and cooling by DSC. Therefore, there may be a reversible reaction, and the experimental conditions of the present TG measurements, in which the products could easily volatilize from the open sample container, may be too severe. However, it cannot be denied that the low thermal stability is one of the serious drawbacks of urea, as well as the large supercooling tendency.

To overcome these drawbacks, the effect of formation of eutectic mixtures and clathrate compounds was examined. The addition of clathrate-forming substances, such as *n*-hexadecane, *n*-hexadecan-1-ol and stearic acid [9], does not show any effect on the crystallization behavior. Formation of eutectic mixtures with potassium carbonate and sodium nitrate increases the supercooling tendency; their eutectic mixtures do not crystallize and remain in the

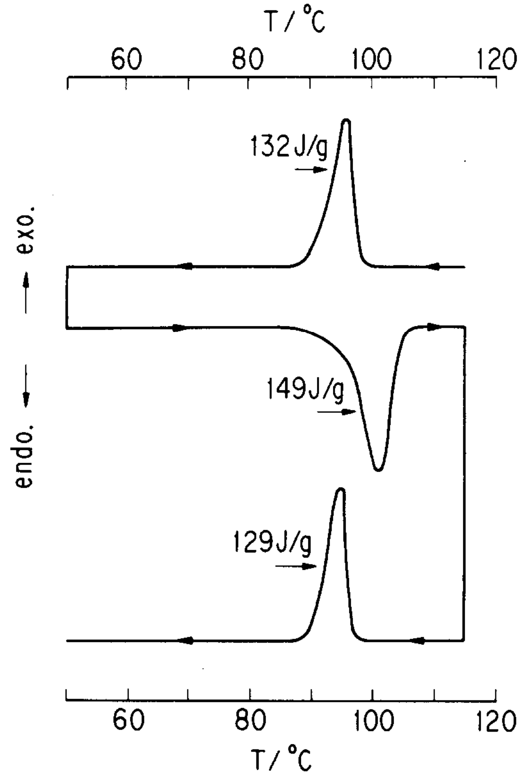

Fig. 7. Typical DSC curve of a eutectic mixture of urea with ammonium chloride.

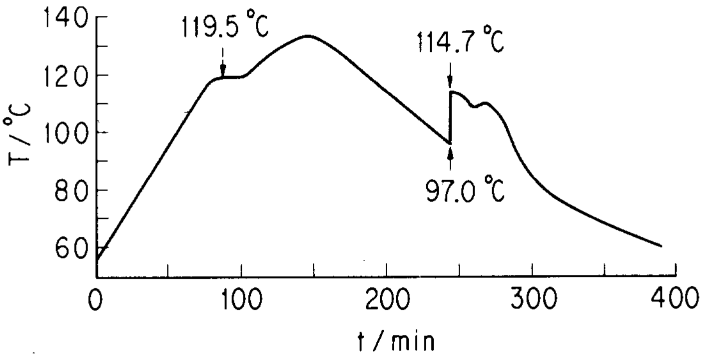

Fig. 8. Typical heating and cooling curves of a eutectic mixture of urea with potassium chloride.

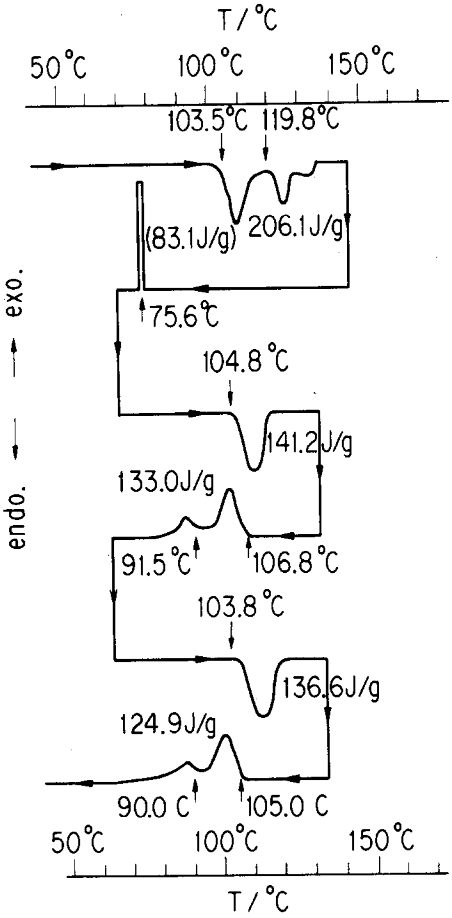

Fig. 9. Typical DSC curve of a mixture of urea with sebacic acid.

liquid state even at room temperature. A decrease in the supercooling tendency is found in eutectic mixtures with ammonium chloride (17 mol%) and potassium chloride (9 mol%). A DSC curve is shown in Fig. 7, and heating and cooling curves are reproduced in Fig. 8. The mixture with sebacic acid (36 wt.%) also shows little supercooling, as shown in Fig. 9. However, their heats of fusion are not as large as that of urea. TG–DTA measurements were also carried out for these mixtures, but constant activation energy cannot be obtained; this suggests complicated thermal decomposition mechanisms, and the kinetic prediction cannot be made. However, the TG curves of the mixtures shift to a lower temperature range, and the thermal stability is not improved. Roy and Acharyya [5] observed the thermal decomposition of a mixture of urea and ammonium chloride by TG; they also found decomposition in a similar temperature range.

CONCLUSION

Urea has two serious drawbacks; one is its large supercooling tendency and the other is its low thermal stability. The supercooling tendency can be overcome by the formation of eutectic mixtures with ammonium chloride and potassium chloride and the addition of sebacic acid is also effective. However, the mixture formation does not improve the thermal stability, and it remarkably decreases the heat of fusion. The melting temperatures are also decreased. Taking account of the low thermal stability, urea is not considered to be a suitable material for thermal energy storage. Instead of urea, modified polyethylene was finally selected for the materials in the temperature range from 100 to 150°C, as is described in our previous papers [1,10]. This conclusion is only for urea and for the mixtures containing urea as a main component. However, a mixture of salt hydrate and urea is a candidate material for solar heating in the lower temperature range [11].

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