THERMAL DECOMPOSITION OF SPONGE BLOWING AGENTS BY PRESSURE THERMAL ANALYSIS*

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Summary

The thermal decomposition of six sponge blowing agents was investigated with a pressure differential scanning calorimeter and a pressure thermobalance to evaluate their thermal hazard. Decomposition heats and kinetic constants in an atmosphere of inert gas or air were obtained using thermal analysis methods. A positive gas pressure was employed in the elucidation of the decomposition behavior of these substances because some of them evaporate during linear heating at atmospheric pressure. The decomposition heats and exothermic onset temperatures of most of the sponge blowing agents tended to increase with a pressure increase in nitrogen or air. The evolution heats, ranging from about 150 to 500 cal/g (in air at 1 atmosphere), were increased to a range of about 250 to 1000 cal/g by a pressurized air atmosphere of 5.3 MPa. Under pressure thermogravimetry conditions the rate of decomposition increased with increasing gas pressure, suggesting a distinction in the decomposition mechanism. The influence of heating rate on the decomposition heat and weight change is also discussed, and kinetic constants such as activation energies at 1 atm are compared with those obtained in pressurized gas atmospheres.

Introduction

Unstable substances such as sponge blowing agents for plastics or rubber and organic peroxides are often transported on land or at sea, and some of them have been reported as being responsible for explosion accidents. An important characteristic of these unstable substances is the fact that the decomposition proceeds by an exothermic reaction in air at relatively low temperature, sometimes resulting in explosion or deflagration. Moreover, most of them exhibit exothermic decomposition even in inert gas atmosphere. For thermal hazard evaluation of these substances it is preferable to determine the ignition temperature, decomposition heat, impact sensitivity and so on. However, difficulty arises occasionally in the evaluation of their thermal properties be-
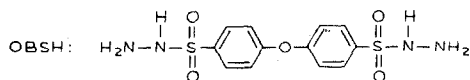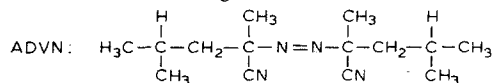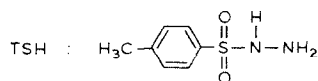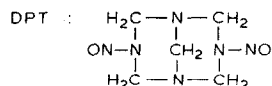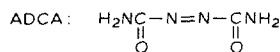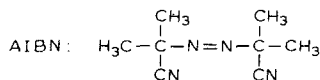
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cause some unstable substances evaporate or sublime during heating at atmospheric pressure. One might be able to elucidate accurately the dangerous properties of these thermally unstable substances by experiments under positive gas pressure*. Consequently, although usual techniques have been applied for the evaluation of sponge blowing agents [1, 6], the authors of this paper tried to investigate the dangerous properties of six sponge blowing agents by measurements of the decomposition heats, weight changes, and kinetic constants, using thermal analysis methods, under positive pressure in atmospheres of air, nitrogen, or helium.

Experimental method

Materials

Sponge blowing agents used in this study were azobisisobutyronitrile (AIBN), azodicarbonamide (ADCA), N,N'-dinitrosopentamethylenetetramine (DPT), p-toluenesulfonyl hydrazide (TSH), 2,2'-azobis(2,4-dimethylvaleronitrile) (ADVN), and 4,4'-oxybis(benzenesulfonyl) hydrazide (OBSH). The structural formulae are shown below. The purities of these compounds were estimated to be more than 97% by elemental analysis.

AIBN :
$$H_3C-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-N=N-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

ADCA :
$$H_2N\underset{\overset{\|}{O}}{C}-N=N-\underset{\overset{\|}{O}}{C}NH_2$$

DPT :
$$\begin{array}{c} H_2C-N-CH_2 \\ ON-N \quad CH_2 \quad N-NO \\ H_2C-N-CH_2 \end{array}$$

TSH :
$$H_3C-\!\!\!\left\langle\bigcirc\right\rangle\!\!\!-\underset{\overset{\|}{O}}{\overset{\overset{O}{\|}}{S}}-\overset{\overset{H}{|}}{N}-NH_2$$

ADVN :
$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-CH_2-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-N=N-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-CH_3$$

OBSH :
$$H_2N-\overset{\overset{H}{|}}{N}-\underset{\overset{\|}{O}}{\overset{\overset{O}{\|}}{S}}-\!\!\!\left\langle\bigcirc\right\rangle\!\!\!-O-\!\!\!\left\langle\bigcirc\right\rangle\!\!\!-\underset{\overset{\|}{O}}{\overset{\overset{O}{\|}}{S}}-\overset{\overset{H}{|}}{N}-NH_2$$

Apparatus and procedures

A pressure differential scanning calorimeter (pressure DSC; Du Pont Co.) was used for the measurements of the decomposition heats of the blowing agents. Nitrogen or air was introduced in the DSC cell at a pressure up to 5.3

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*i.e. pressures in excess of 1 atm.

MPa after the cell was flushed three times with the desired gas at 1.8 MPa. The concentration of residual oxygen in pressurized nitrogen in the cell was confirmed to be less than 1 p.p.m. by gas chromatography. These gases were not passed over the sample during linear heating, which was carried out at rates in the range 0.5 to 50°C/min. Samples of about 0.5 to 0.6 mg were weighed to two decimal places and then packed using a non-hermetic pan (6.5 mm ϕ, aluminum) fitted with an aligned cover.

Pressure thermogravimetries (TG) for the sponge blowing agenst were carried out using a high pressure thermobalance (Rigaku Denki Co.) at pressures of 1.0—5.0 MPa. The detailed procedures for the pressure thermobalance have been published elsewhere [2]. An IR ray thermobalance (Rigaku Denki Co.), which is able to raise a sample temperature very quickly at ambient pressure with a flowing gas, was also used with samples of about 10 mg. In the pressure TG experiments, about 5—10 mg of sample was placed in an aluminum cup (5 mm ϕ) and heated at a linear heating rate (2.5—10°C/min) without the gas flowing over the sample.

Results and discussion

Decomposition heats at 5.3 MPa
Figure 1 shows typical DSC traces for the six blowing agents which were decomposed at 5.3 MPa in nitrogen by a heating rate of 5°C/min. The calorific values for the thermal decomposition, which were calibrated with the heat of fusion of In, were evaluated by integrating the areas under the curves.
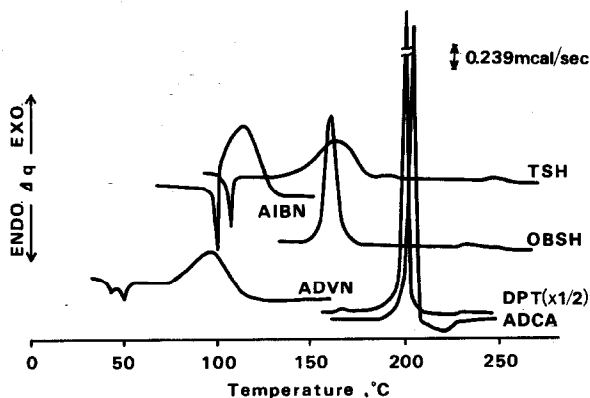

Fig. 1. DSC traces of sponge blowing agents in N_2 at 5.3 MPa. Heating rate: 5°C/min.

All of the blowing agents exhibit exothermic reaction in the temperature range 70 to 210°C. ADVN had the lowest decomposition temperature, but it has a small decomposition heat. ADCA and DPT, which decompose at relatively high temperatures of about 200°C, are assumed to react violently, releasing a large amount of heat. AIBN decomposes with an exotherm as soon

as the sample melts at about 100°C. TSH and OBSH, which have benzene rings in their molecules, tend to liberate light gases such as nitrogen at around 150°C and leave appreciable amounts of heat-stable residue. This was clearly shown in the pressure TG experiments.

When the samples were allowed to decompose in the DSC cell at the same pressure in air, no marked change was observed in the shape of the DSC traces. However, the areas under the curves became much larger than was the case in a nitrogen gas atmosphere. This is possibly because oxidative decomposition may be proceeding at the low temperature ranges with an increase of air pressure, in addition to thermal decomposition. Another distinct aspect in oxidative decomposition is the appearance of a second exothermic peak at high temperatures for ADVN, TSH, and OBSH. These exotherms may be caused by successive oxidation of the residue after the initial decomposition.

The calculated calorific values for the six sponge blowing agents at 5.3 MPa and at ambient pressure in nitrogen or air are summarized with exothermic onset temperatures in Table 1. DPT has the largest decomposition heats,

TABLE 1

Decomposition heats and exothermic onset temperatures of sponge blowing agents in N_2 and air

	Heat in N_2 at 5.3 MPa, (mcal/mg)	Heat in air at 5.3 MPa, (mcal/mg)	Exo. onset temp. in N_2, °C		Exo. onset temp. in air, °C	
			5.3 MPa	1 atm	5.3 MPa	1 atm
AIBN	281.5 ± 22.0 [4]* (219.2)**	741.5 ± 63.9 [8] (356.5)	103	104	102	103
ADCA	368.3 ± 3.3 [3] (155.4)	439.6 ± 12.5 [3] (149.2)	177	178	179	180
DPT	783.5 ± 23.6 [3] (534.4)	1038.6 ± 58.3 [6] (493.4)	163	171	144	166
TSH	278.3 ± 4.3 [3] (227.3)	365.3 1st 298.6 2nd [8] (253.8)	132	127	124	124
ADVN	186.6 ± 27.7 [6] (163.3)	444.3 1st 201.4 2nd [5] (303.1)	66	60	57	63
OBSH	228.7 ± 2.4 [3] (191.9)	269.0 ± 30.0 [8] (202.9)	150	152	133	146

*Number of measurements at 5.3 MPa.
**Heats at 1 atm.

800—1000 mcal/mg, in both gases. It is interesting to note that there is little difference in the evolution heats at ambient pressure in nitrogen and in air except for AIBN and ADVN. The decomposition heats of AIBN and ADVN increase significantly as the pressure in air is increased. The values in air are more than twice those in nitrogen. The decomposition heats of the six blowing agents in air at 5.3 MPa decrease in the order DPT, AIBN, ADVN, ADCA, TSH, and OBSH. At atmospheric pressure in air, the order changes to DPT, AIBN, ADVN, TSH, OBSH, and ADCA. The lowest decomposition heat of ADCA in air at 1 atm may be due to a partial endothermic reaction during heating as discussed later. The exothermic onset temperatures in nitrogen and air are similar in spite of the surrounding gas pressures except in the cases of DPT and OBSH. ADVN has low exothermic onset temperatures but relatively high decomposition heats in air. On the other hand, DPT shows high exothermic onset temperatures with the largest evolution heats in air and nitrogen.

Influence of pressure

Figure 2 shows a variation of weight losses for the blowing agents when decomposed at 4.0 MPa in air at a heating rate of 5°C/min. AIBN, ADCA, and DPT show a violent decomposition at the first stage, as evidenced by a
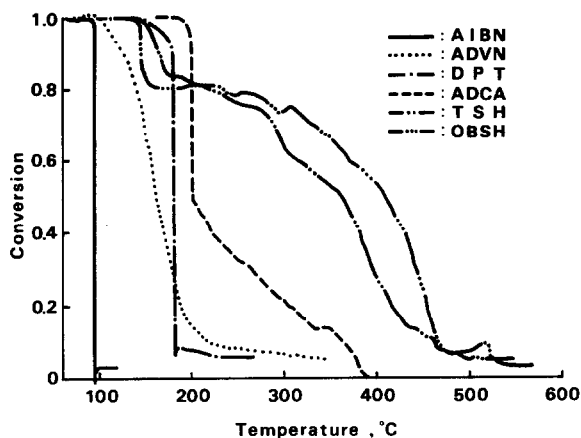

Fig. 2. TG curves of sponge blowing agents in air at 4.0 MPa. Heating rate: 5°C/min.

large weight loss, but ADVN, TSH, and OBSH decompose slowly under these conditions. When the blowing agents were decomposed in the IR thermobalance at ambient pressure in air at a heating rate of 80°C/min (flow rate: 130 ml/min), the violent weight decreases are facilitated for all the materials and the residues from ADCA, TSH, and OBSH decrease as shown in Fig. 3.

As mentioned previously, one of the blowing agents, ADCA, has a tendency to evaporate mostly with an endotherm, even at ambient pressure in air as shown in Fig. 4. It may be natural to consider that an increase of partial
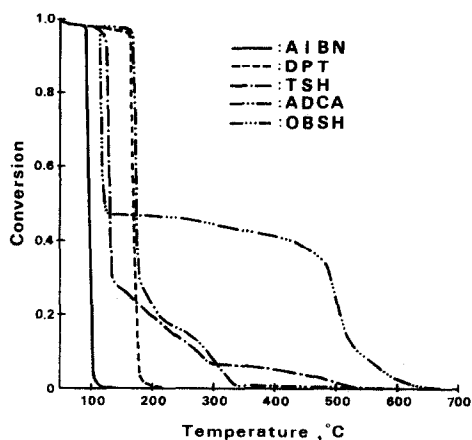
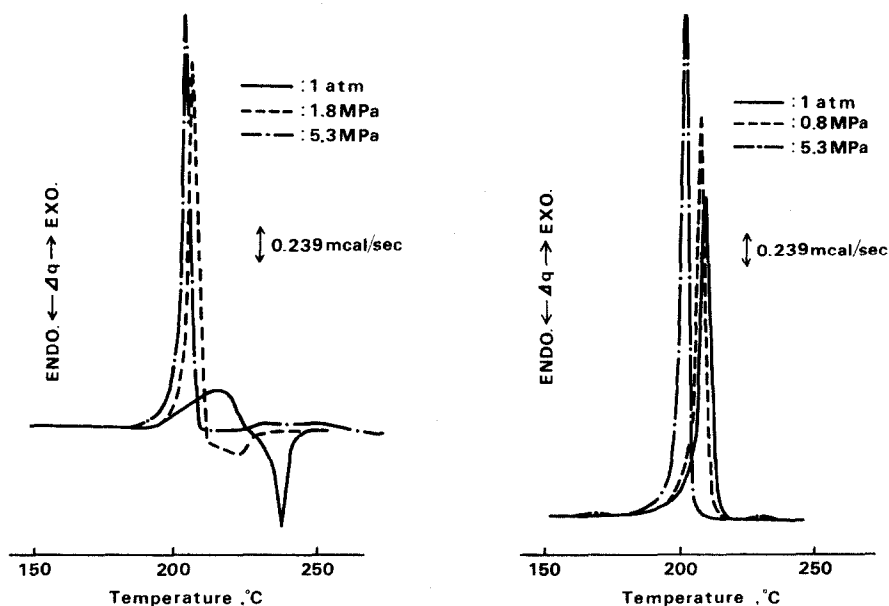Fig. 3. TG curves of sponge blowing agents at ambient pressure of air at 80°C/min. Flow rate: 130 ml/min.

Fig. 4. DSC traces of ADCA in air at various pressures. Heating rate: 5°C/min.

Fig. 5. DSC traces of DPT in N_2 at various pressures. Heating rate: 5°C/min.

pressure of oxygen will enhance the oxidative decomposition by ease of oxidative cleavage of molecular chains, but in raising the pressures of air or nitrogen, all the blowing agents tend to decompose with exothermic reactions. These situations are shown in Figs. 4 and 5 for the decompositions of ADCA and DPT.

It is interesting to note that the exothermic onset temperatures and the peak temperatures in the DSC curves are shifted to lower temperature, and the decomposition heats are increased with an increase of nitrogen gas pressure. A dependence of pressure on the decomposition heat may be attributed to the differences of molecular structures of the blowing agents. The evolution heats of ADCA and DPT were greatly influenced by the pressure in nitrogen, but those of AIBN were slightly increased when the samples were heated under the same conditions, as shown in Figs. 6 and 7. This may be due to the fact that the decomposition of AIBN is substantially determined by its melting point, for the decomposition begins soon after the melting of the sample.
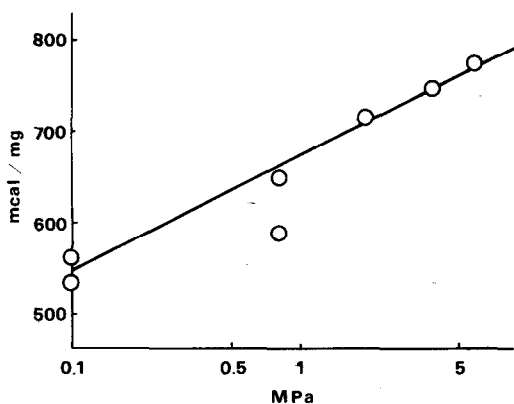
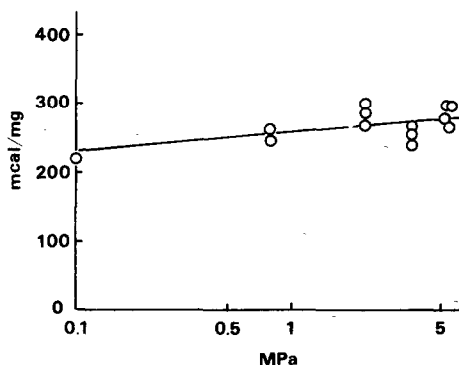Fig. 6. Effect of pressure in N_2 on decomposition heat of DPT.

Fig. 7. Effect of pressure in N_2 on decomposition heat of AIBN.

The decreasing of the decomposition temperatures was also confirmed by the pressure TG experiments. Figures 8 and 9 show the pressure TG curves for ADCA and DPT at various pressures in nitrogen. About 60% of the total weight of ADCA decomposes in the first stage regardless of the increased nitrogen pressure, but the rate of the decomposition seems to become greater as the pressure is increased. The increase of the decomposition heat may depend on a distinction in decomposition products. A more complete decomposition seems to occur at high pressures in nitrogen in the first stage. This tendency is also recognized for DPT with the result that the amount of material that decomposes slowly prior to the violent decomposition decreases with an increase of the pressure as shown in Fig. 9. Thus, the increase of nitrogen gas pressure may cause the sponge blowing agents to decompose completely in such a way that the overall enthalpy change attains a maximum through reaction. Figure 8 also shows that the oxidative decomposition of ADCA at the increased pressure in air readily occurs at lower temperature than in nitrogen.
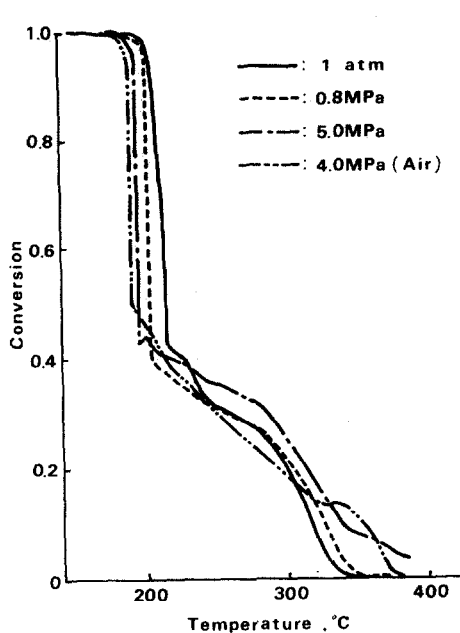
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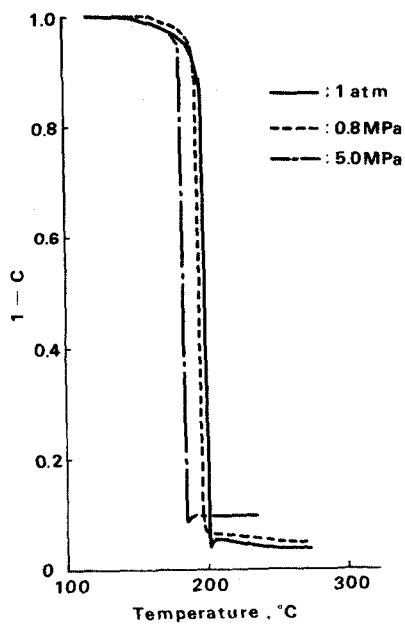Fig. 8. TG curves of ADCA in N_2 at various pressures and in air at 4.0 MPa. Heating rate: 5°C/min.

Fig. 9. TG curves of DPT in N_2 at various pressures. Heating rate: 5°C/min.
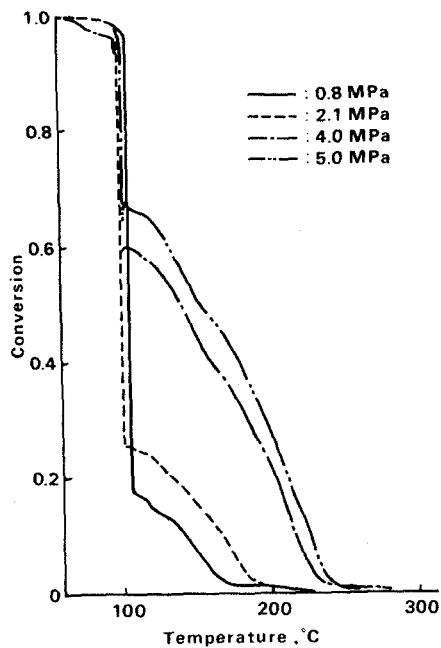

Fig. 10. TG curves of AIBN in N_2 at various pressures. Heating rate: 5°C/min.

Figure 10 shows the pressure TG curves of AIBN in nitrogen, where large quantities of residues are observed after first stage decomposition. The amount of first stage decomposition clearly increases with a decrease of pressure in nitrogen without significant differences in the decomposition rate. When the DSC curves shown in Fig. 11 are compared with the TG curves, it is found
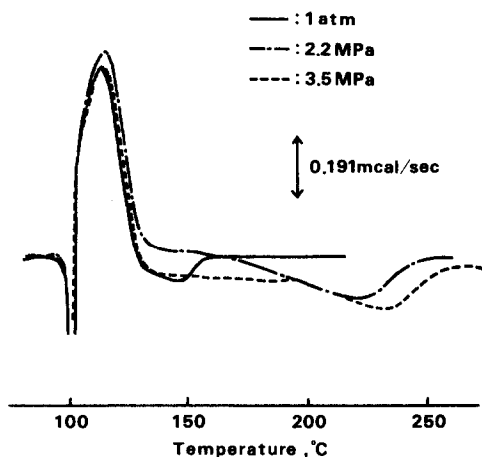

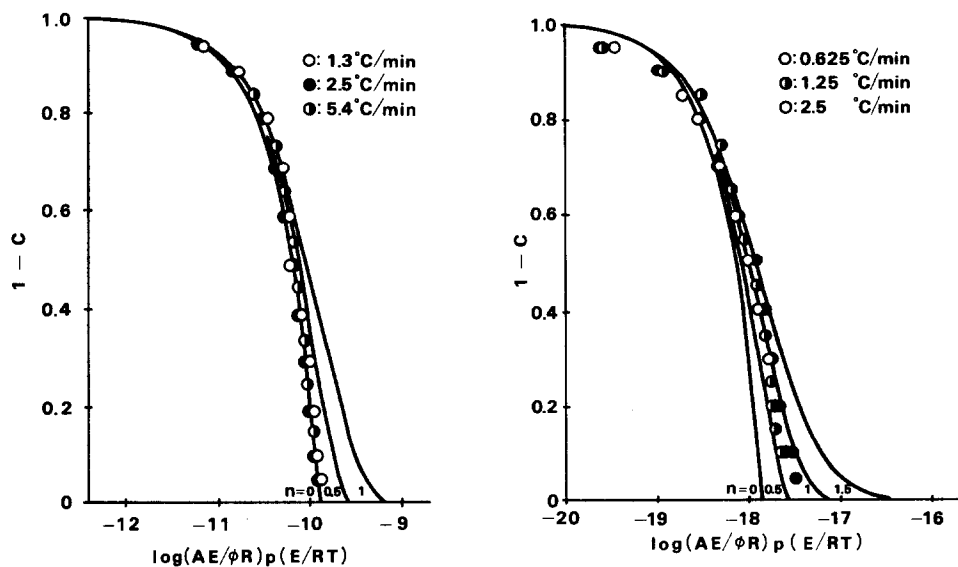Fig. 11. DSC traces of AIBN in N_2 at various pressures. Heating rate: 5°C/min.

Fig. 12. Comparison of theoretical and experimental TG curves of AIBN in He at 1 atm for nth order reaction; where $\log p(E/RT) \cong -2.315 - 0.457(E/RT)$.

Fig. 13. Comparison of theoretical and experimental TG curves of DPT in He at 1 atm for nth order reaction.

that there are only slight differences in the energy release at the various pressures, in spite of significant distinctions in the TG curves. This result appears to be inconsistent with the proposal that the decomposition heat may be proportional to the amount of material decomposed. Figure 12 shows TG curves of AIBN in helium at 1 atm with slow heating rates; from thermal analysis theory [3], the weight decrease of AIBN under these conditions may mostly be due to evaporation or sublimation, because the order of the reaction approximates zero. The phenomenon mentioned above is attributed to the partial evaporation or sublimation of AIBN. On the other hand, the reaction order of DPT is around 0.7 to 1.0, as shown in Fig. 13.

Influence of heating rate
    Particular attention should be given to heating rate when thermal data are obtained by thermal analysis, because decomposition of a sample varies with the heating rate. Figure 14 shows a variation of the decomposition heats of
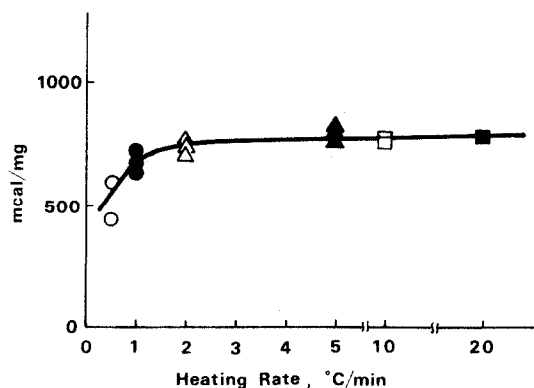

Fig. 14. Variation of decomposition heats of DPT with heating rates in N_2 at 5.3 MPa.

DPT at 5.3 MPa in nitrogen with heating rates from 0.5 to 20°C/min. It can be seen from the figure that the evolution heats may be only slightly influenced by the heating rate when the rate exceeds 3°C/min. In the present DSC experiments, a heating rate of 5°C/min was adopted in most cases for this reason. The decrease of evolution heats at the low heating rates may be dependent on a difference in the decomposition mechanism compared with that at the high heating rates.
    Figure 15 shows the pressure TG curves of DPT at 4.0 MPa in air at heating rates of 2.5—10°C/min. As is shown in the figure, the decomposition temperatures tend to increase and the amounts of decomposing material in the slow decomposition region tend to decrease as the heating rate is increased. Thus, the change of heating rate affects decomposition temperature and weight change as well as evolution heat.
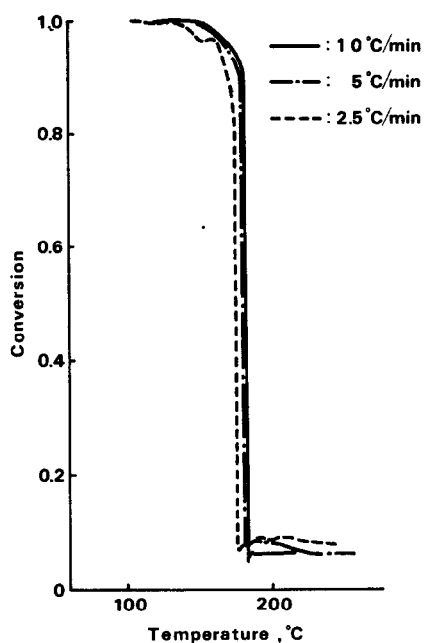   An extrapolated exothermic onset temperature in DSC traces mostly

Fig. 15. TG curves of DPT in air at 4.0 MPa with various heating rates.

corresponds closely to DTA peak temperature, and the peak temperatures usually are lowered as heating rate is decreased. An activation energy for the decomposing material can be calculated from the relation
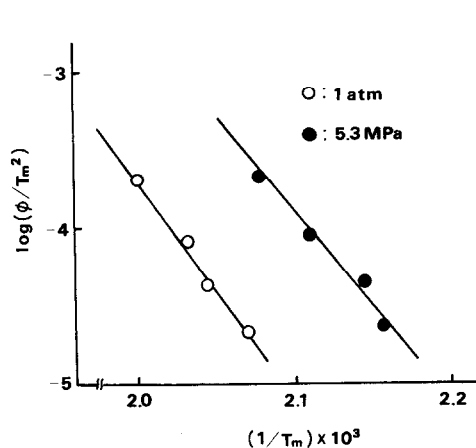
$$d(\ln \phi/T_m{}^2)/d(1/T_m) = - E/R,$$

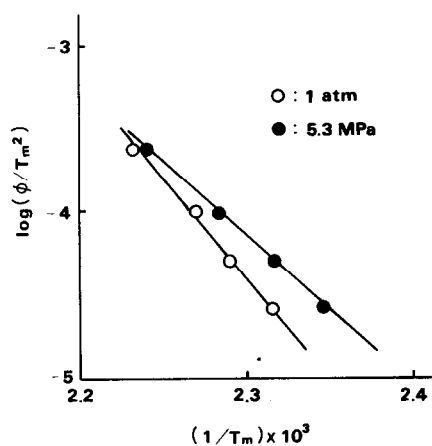Fig. 16. Kissinger plots for the decomposition of DPT in air at 1 atm and 5.3 MPa.

Fig. 17. Kissinger plots for the decomposition of OBSH in air at 1 atm and 5.3 MPa.

where ϕ is the heating rate, T_m the peak temperature in DTA, R the gas constant, and E the activation energy [4, 7]. Figures 16 and 17 show the relations between $\log(\phi/T_m{}^2)$ and $(1/T_m)$ for DPT and OBSH which were allowed to decompose at atmospheric pressure and at 5.3 MPa in air with various heating rates. The activation energies are calculated from the slopes.

The apparent activation energies thus calculated for the six blowing agents in air and nitrogen are summarized in Table 2. The activation energies in air

TABLE 2

Activation energies of sponge blowing agents in air and N_2; obtained from DSC traces

	Pressure	AIBN	ADCA	DPT	TSH	ADVN	OBSH	(kcal/mole)
Air	1 atm	82.3	41.5	66.4	27.4	21.2	53.2	
	5.3 MPa	74.9	41.5	52.3	23.8	26.9	41.2	
N_2	1 atm	44.8	62.8	60.1	25.7	19.8	60.2	
	5.3 MPa	34.3	39.1	64.7	25.2	20.6	61.0	

are decreased with an increase of pressure except for ADVN. AIBN has the greatest activation energies in air, 75—82 kcal/mole, and the values for the other blowing agents decrease in the order of DPT, OBSH, ADCA, TSH, and ADVN. The large activation energies for AIBN are due to an appearance of sharp slopes in the exotherms of the DSC curves which suggests that AIBN violently decomposes in air under certain conditions.

In nitrogen gas atmospheres, the activation energies for the six blowing agents are not as greatly influenced by pressure, except for ADCA and AIBN, whose activation energies at 5.3 MPa are less than those at ambient pressure. DPT and OBSH have large activation energies among them. By assuming the reaction order of DPT is 1 and frequency factor is represented by

$$A = \phi E \exp(E/RT_m)/RT_m^2, \quad [4]$$

the reaction rate of DPT in nitrogen is found to be $k = 9.1 \times 10^{29} \exp(-6640($ $RT)$ (min^{-1}) at 1 atm, and $k = 2.8 \times 10^{24} \exp(-52300/RT)$ (min^{-1}) at 5.3 MPa

On the other hand, not all the sponge blowing agents exhibited violent decompositions when these materials were allowed to decompose at ambient pressure in air at very low heating rates. Figure 18 shows the TG curves of AIBN, ADCA, DPT, TSH, and ADVN which were linearly heated at 0.625°C/ min at atmospheric pressure in air at a flow rate of 130 ml/min. All the blowing agents initiate reaction at lower temperatures, compared with the pressure TG curves. AIBN and ADVN, for example, begin to reduce their weights at around 50°C, whilst DPT and TSH begin at around 100°C. From these results there may be a possibility of spontaneous ignition or decomposition when a large amount of these blowing agents are stored in a warm place.

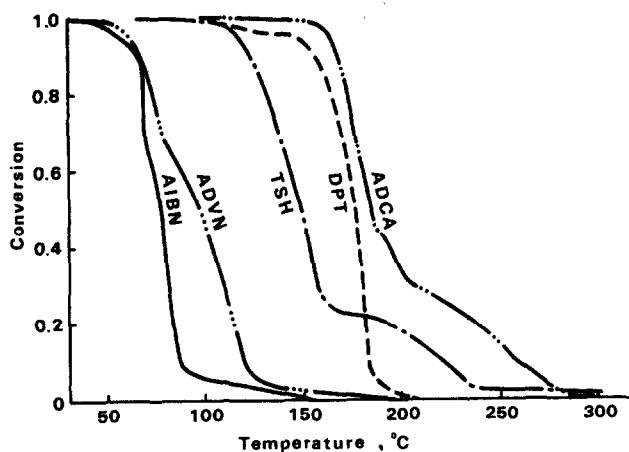Figure 19 shows a variation of TG curves of DPT which were linearly

Fig. 18. Variation of weight decreases of sponge blowing agents at ambient pressure of air. Heating rate: 0.625°C/min.
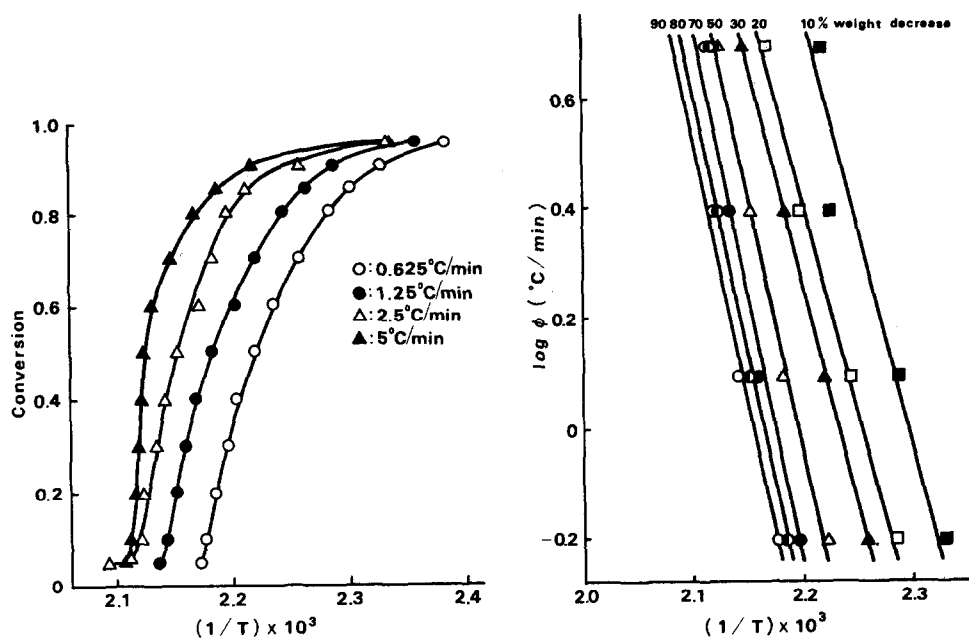

Fig. 19. TG curves of DPT at ambient pressure of He with various heating rates, plotted against reciprocal absolute temperature.

Fig. 20. Plots of logarithm of heating rate versus reciprocal absolute temperature for DPT in He at 1 atm.

heated at 0.625—5.0°C/min in helium at a flow rate of 140 ml/min. The TG curves are shifted to a lower temperature range and remain mostly parallel to each other as the heating rate is decreased. Thermal analysis theory suggests that the reaction may mostly occur by a single simple mechanism through the temperature range [5, 7]. However, the reaction of DPT at ambient pressure in air does not show a single simple mechanism, and the TG curves cannot be superposed upon each other by a lateral shift. This suggests that the decomposition of DPT in air at 1 atm consists of two reactions, oxidative decomposition and thermal decomposition.

Kinetic parameters can be calculated using the TG curves. Figure 20 shows plots of the logarithm of heating rate versus the reciprocal absolute temperature for DPT in helium. The activation energy of DPT, about 39.4 kcal/mole, was estimated from the slopes. The frequency factor for the decomposition of DPT was calculated to be 4.0×10^{17} (min^{-1}) from Fig. 13. Thus, the activation energies of the blowing agents which were heated very slowly at ambient pressure in helium were appreciably small, 13—40 kcal/mole, as compared with those obtained for the materials that decomposed violently, suggesting a great distinction in the decomposition mechanism between them.

Conclusion

Pressure thermal analyses on DSC and TG were applied for the hazard evaluation for six sponge blowing agents. An endothermic reaction, due to evaporation or sublimation, sometimes takes place in the measurement of decomposition heats of unstable substances in air at atmospheric pressure. It is, therefore, desirable to carry out the experiments under excess pressure. The increase of the decomposition heats of the blowing agents in the increased nitrogen or air pressure is particularly interesting in this study. It suggests that the decomposition of the blowing agents in a sealed vessel may result in a serious explosion, even in an oxygen deficient atmosphere. In the TG experiments, it is easy to recognize a weight decreasing mode such as quantity of residue or decomposition rate, and an estimation of kinetic constants is also possible from the TG curves. Though we can not conclude that the blowing agents which have large decomposition heats or low exothermic decomposition temperatures are more hazardous, pressure thermal analysis may be a useful tool for the evaluation of thermal hazard. Hence, it is preferable to obtain some correlations between the thermal analysis method and the usual testing method.

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