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Simultaneous thermal analysis of hexahydrophtalic anhydride

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Abstract

Hexahydrophtalic anhydride is studied by means of a simultaneous thermal analyzer (STA) over a temperature range of 20–400 °C, at the heating rates of 5, 10, 20, and 40 °C/min. All the experiments have been conducted under argon gas environment and then repeated with dried air as the purge gas. All samples show the melting transition followed by the vaporization indicated by the weight loss. The activation energy calculated from the weight loss data has been compared with the enthalpy of vaporization. Although a zero order transition fits well with a reaction order model, the kinetics of vaporization does not follow this model.

Keywords: Simultaneous thermal analyzer; Kinetics; Activation energy; Hexahydrophtalic anhydride

1. Introduction

Hexahydrophtalic anhydride ($C_8H_{10}O_3$) is studied using a thermal analysis simultaneous unit. Its melting point is reported to be 34 °C and its boiling point is reported as 296 °C. Hexahydrophtalic anhydride is used as low toxicity hardener for epoxies. The system composed of an epoxy resin and a hardener of this kind shows a shoulder on the DSC exothermic peak. This shoulder is attributed to the superposition of the endothermic heat from the devolatilization of the hardener, and the exothermic heat from the curing reaction [1]. A method was described to calculate the actual heat of curing by simultaneous thermal analysis [2]. That method implies to take into account the behavior of the single components in an identical experiment. Although the kinetics is different, the behavior is similar to the one described for lauric acid [3].

2. Experimental

All experiments were performed on Rheometric Scientific simultaneous thermal analyzer (STA 1500) with system interface device and a computer workstation. All the samples were placed in aluminum crucibles. The hexahydrophtalic anhydride was supplied by Merck Farma y Química, S.A. (Spain). All the experiments were conducted under argon gas environment followed by the second experiment with dried air as the purge gas. Two replicas were performed with air and three with argon as purge gas. The flow rate of the argon and the dried air was 50 ml/min. The range of temperature studied was from 20 to 400 °C, at the heating rates of 5, 10, 20 and 40 °C/min.

3. Results and discussion

Fig. 1 illustrates the dynamic scanning of the hexahydrophtalic anhydride from 50 to 400 °C at a ramp rate of 20 °C/min under argon flow. The DSC trace

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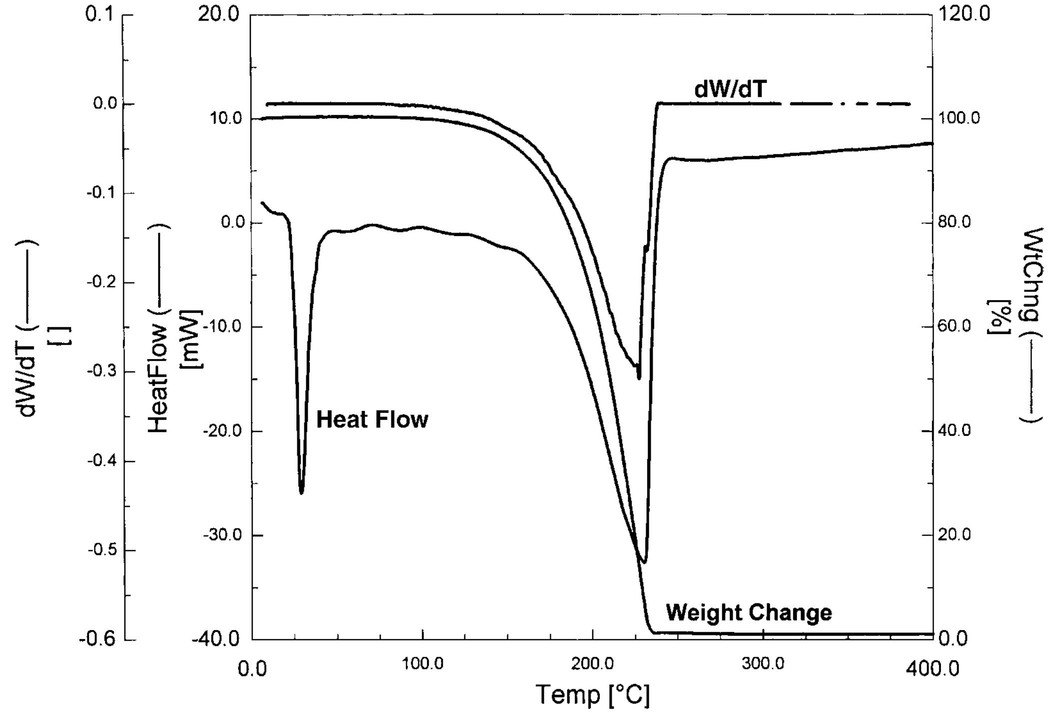

Fig. 1. Hexahydrophtalic anhydride in argon.

shows the melting point of the anhydride followed by evaporation. The TGA trace confirm that the devolatilization process starts at about 100 °C. The DTG shows an increasing rate of loss at the highest temperature of observation. Then, the rate falls quickly to zero when the sample is exhausted. The shape of the DTG plot is typical of a zero order transition due to evaporation.

Kinetic analysis by means of minimum squared and Freeman and Carrol, with and without the modification proposed by Jerez [4–6], have been applied to all the experiments. Although the modification proposed by Jerez shows a slight improvement, the lack of fit obtained in all the experiments reveals that the Freeman and Carrol method is not applicable in this case. Minimum squared fitting has been applied over a range of conversion from $\alpha = 0.2$ to $\alpha = 0.9$, assuming a reaction order model. In accordance with Table 1, a near zero reaction order is obtained with an activation energy around 61 kJ/mol. Table 2 shows the results for the experiments under argon. A near zero reaction order is obtained again and the activation energy is around 60 kJ/mol.

Table 1
Kinetics parameters using minimum squared analysis (air)

Heating rate (°C/min)	$\ln A$	A ($\times 10^4$)	E_a (kJ/mol)	n	r
5	12.24	20.62	60.00	0.083	0.9976
5	11.17	7.13	56.15	0.131	0.9976
10	11.21	7.38	56.07	0.048	0.9976
10	14.8	159.3	67.30	0.167	0.9979
20	12.83	37.38	61.63	0.186	0.9981
20	13.82	100.2	65.40	0.176	0.9976
40	13.20	53.9	63.00	0.124	0.9987
40	14.02	122.4	66.20	0.206	0.9969

Table 2
Results of the analysis by minimum squared of the experiments under argon

Heating rate (°C/min)	E_a (kJ/mol)	n	r
5	54.36	0.10	0.9977
5	62.07	0.14	0.9979
5	61.3	0.15	0.9977
10	64.4	0.17	0.9976
10	59.5	0.16	0.9972
10	58.9	0.14	0.9964
20	56.7	0.12	0.9971
20	63.0	0.14	0.9977
20	57.3	0.12	0.9971
40	59.5	0.13	0.9981
40	62.9	0.22	0.9923
40	59.2	0.12	0.9976

Isoconversional methods of Friedman [7] and Ozawa [8] have been applied on TGA data. The Friedman method starts from the supposition that

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E_a}{RT}\right)f(\alpha) \quad (1)$$

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha=\alpha_i} = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln(Af(\alpha_i)) \quad (2)$$

where α is the degree of reaction.

Plots of $\ln(d\alpha/dt)$ against $1/T$ should fit to a straight line with a slope of $-E_a/R$. Figs. 2 and 3 contain the results of the analysis for α range from 0.05 to 0.9. The activation energy obtained with air and argon purge was 69.8 and 67.8 kJ/mol, respectively. These values are close with the activation energy obtained by minimum squared method. Fig. 4 displays the comparison of activation energy obtained by Friedman's method for both air and argon.

If a reaction order is assumed, then

$$f(\alpha) = (1-\alpha)^n \quad (3)$$

$$\ln(Af(\alpha)) = \ln(A) + n\ln(1-\alpha) \quad (4)$$

Plots of $\ln(Af(\alpha))$ against $\ln(1-\alpha)$ should give a straight line with slope of the reaction order n. Although the reaction order found by this method was close to zero in both cases, with air and argon as purge gases, the very low correlation index ($r = 0.4$

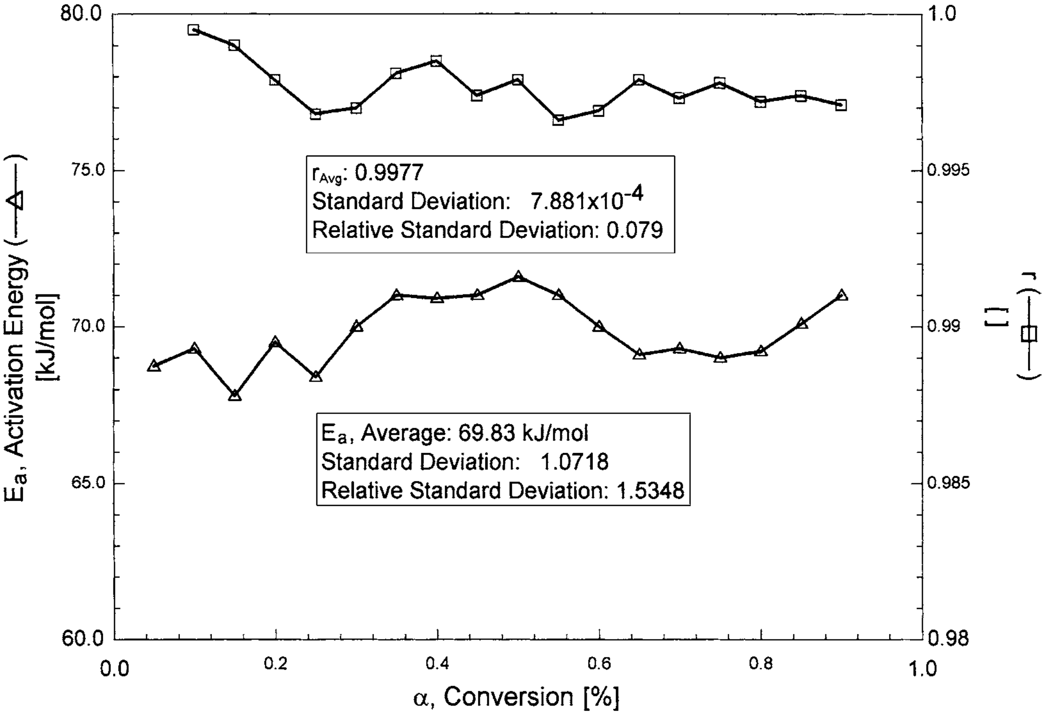

Fig. 2. Activation energy from Friedman's method (air).

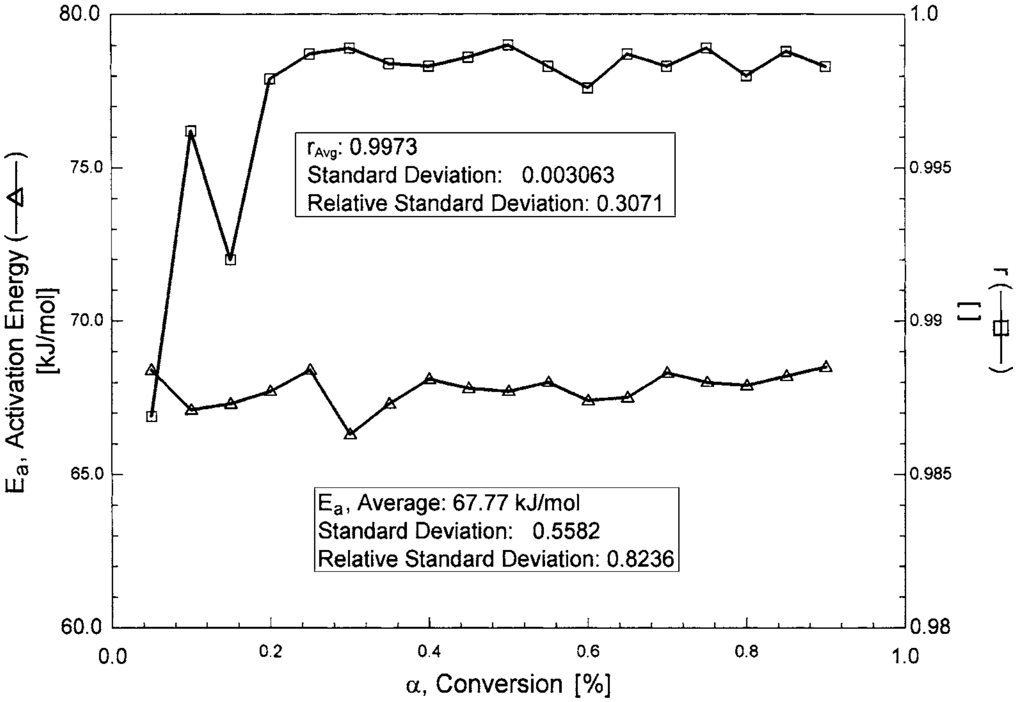

Fig. 3. Activation energy from Friedman's method (argon).

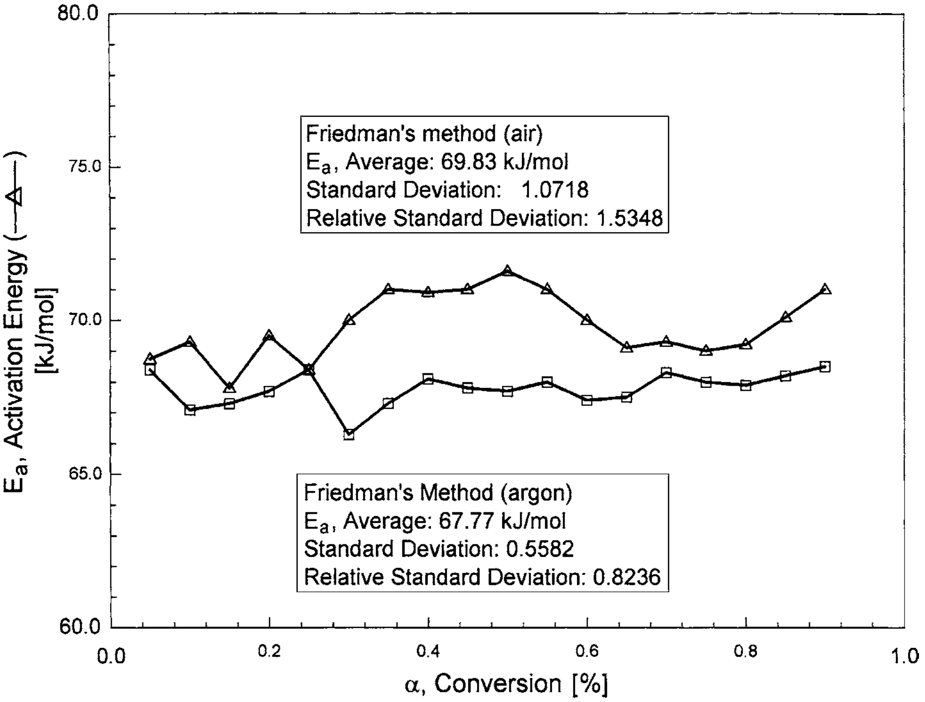

Fig. 4. Activation energy from Friedman's method.

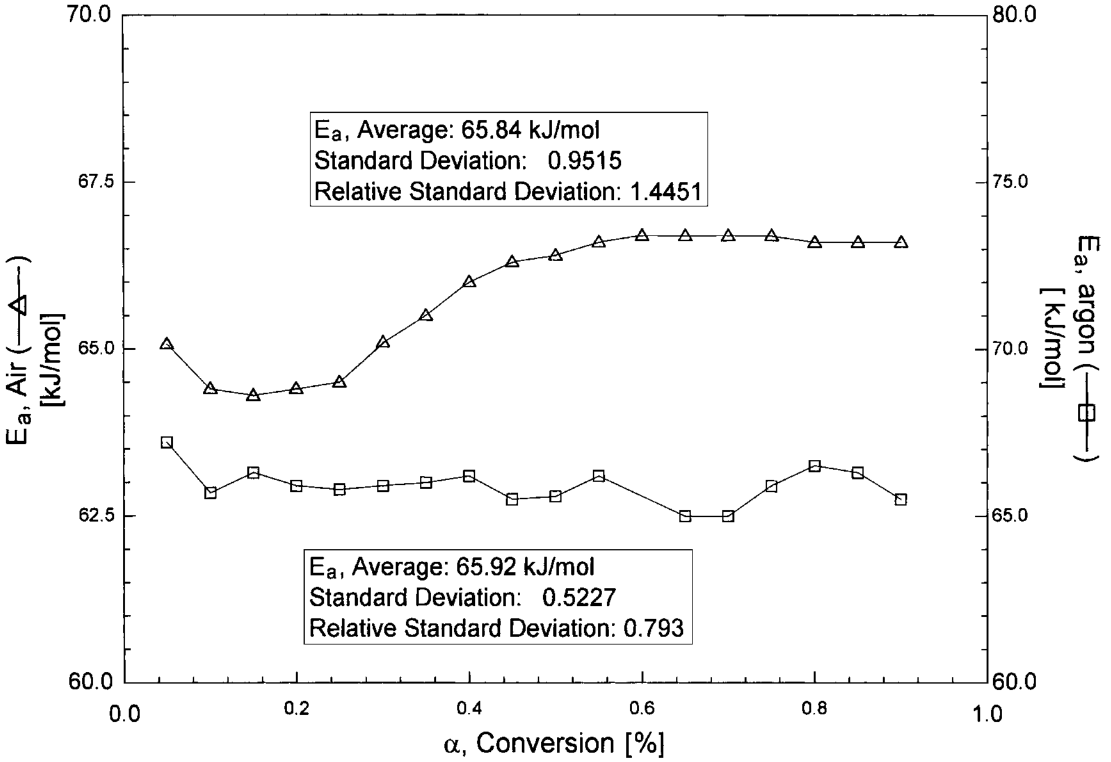

Fig. 5. Activation energy from Ozawa's method.

and $r = 0.6$) suggests that this process does not follow a reaction order model.

The method proposed by Ozawa states that

$$\log \beta = \text{constant} - 0.4567 \frac{E_a}{RT} \tag{6}$$

where β is the heating rate (°C/min).

The plot of $\log \beta$ against $1/T$ should fit to a straight line and E_a can be determined from the slope. The results of the analysis by this method are shown in Fig. 5. Similar mean values were obtained for E_a when air and argon were used, 65.8 and 65.9 kJ, respectively. These values are not far from the other obtained by the other methods.

As a comparison, the activation energy had been also calculated from the thermal data by the methods of Duswalt [9] and Kissinger [10], using ASTM E 698-79 test procedure for a non-weight loss experiment.

The enthalpy of vaporization, calculated by direct integration of the DSC traces, found to be 50–60 kJ/mol. The values obtained from argon experiments are lower than the values from air experiments.

4. Conclusions

Hexahydrophtalic anhydride has been investigated by simultaneous thermal analysis at different heating rates in different gas environments. The samples show the melting transition followed by the vaporization. The values obtained for the kinetic parameters by different methods are similar in the most part of the cases. The activation energy calculated from the weight loss data has been compared with the calculated from thermal data and with the enthalpy of vaporization.

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