Lifetime Predictions for the Epoxy System BADGE n=0/m-XDA Using Kinetic Analysis of Thermogravimetry Curves

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ABSTRACT: Lifetime of the epoxy system diglycidil ether of Bisphenol A (BADGE n=0)/m-xylylenediamine (m-XDA) was calculated by thermogravimetric analysis. The Flynn-Wall-Ozawa method is used to determine the activation energy of the reaction. Experimental lifetimes in the range of 60–300°C vary from 1.41 10^9 (2682 years) to 3.35 10^{-4} min. This isoconversional method is not appropiate to calculate lifetime prediction because of high errors. Scaling factors were determined using the ratio of two reaction rates. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1692–1696, 2002

Key words: activation energies; epoxy resin; kinetic analysis

INTRODUCTION

The thermogravimetric analysis is a simple method, in which the change in mass loss is determined as a function of temperature or time under controlled atmosphere. Three modes of thermogravimetry are comonly used: isothermal thermogravimetry, in which the mass loss is recorded as a function of time at constant temperature; quasi-isothermal thermogravimetry, in which the sample is heated to constant mass at each of a series of increasing temperatures; and dynamic thermogravimetry, in which the sample is heated in an environment whose temperature is changing at different heating rates. The last mode is used in this article.

Three modes are used to analyze thermogravimetric data:[1] comparison of isoconversionals from experiments at several heating rates; comparison of derivative curves over wide ranges in heating rate; detailed kinetic analysis of the first 5% weight loss.

The lifetime is considered when 5% weigh loss[2,3] is reached from a dynamic thermogravimetric analysis. Different integral methods are used to study the thermogravimetric kinetic.[4–11] In a previous article[10] the activation energies using differential and integral methods were calculated. In this article we used to the Flynn-Wall-Ozawa method[12, 13] to determine activation energies for different conversions without knowledge of a reaction mechanism. This method involves an approximate integration of the following equation:

$$g(\alpha) = \frac{A}{\beta} \int_0^{T_p} e^{-E_a/RT}\, dT \qquad (1)$$

where A is the preexponential factor, β is the heating rate, E_a is the activation energy, R is the gas constant, T_p is the absolute temperature to reach the conversion, and $g(\alpha)$ is a integral function of conversion.

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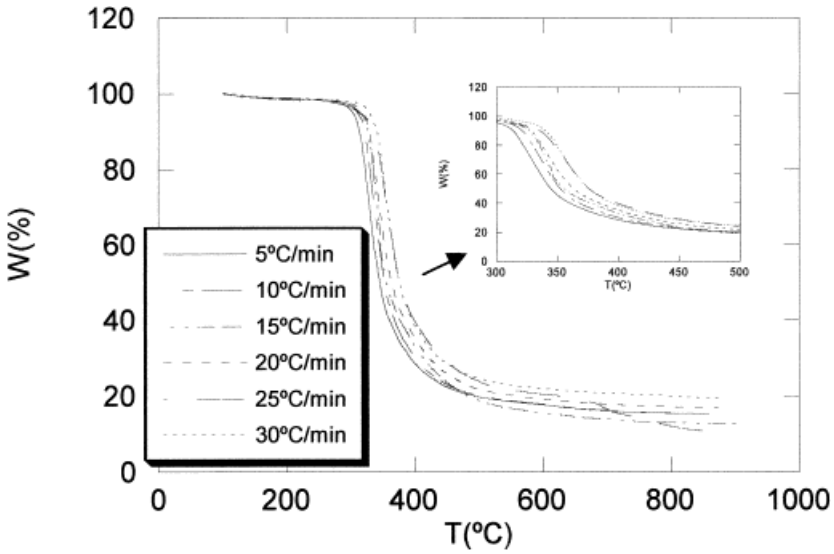

Figure 1 Experimental TG curves at different heating rates.

Equation (1) was integrated using the Doyle approximation,[14] and can be rewritten after taking logarithms as follows:

$$\log \beta = \log\left[\frac{AE_a}{g(\alpha)R}\right] - 2.315 - \frac{0.457E_a}{RT} \qquad (2)$$

In this article, we try to calculate the lifetime of epoxy system BADGE $n=0$/m-XDA without knowledge of reaction mechanism. Using thermogravimetric data the lifetime can be calculated extrapolated from the kinetics for reaction at higher temperatures at which reaction times are small. This extrapolation permits calculation of the kinetic to much longer reaction times expected at the lower temperatures at which the epoxy system will be in use.

EXPERIMENTAL

Materials

The epoxy resin was a commercial BADGE ($n=0$) (Resin 332, Sigma Chemical Co., Saint Louis, MO), with an equivalent molecular weight of 173.6 g/Eq, as determined by wet analysis.[15,16] The curing agent was m-xylylenediamine (m-XDA, Aldrich Chemical Co., Milwaukee, WI), with an equivalente molecular weight of 31.3 g/Eq.

Sample Preparation

The epoxy resin and curing agent were carefully and homogeneously mixed, at a stoichiometric ratio. The mixture is introduced in a cylindrical frame previously waxed to avoid adherence. After 24 h at room temperature, frames are placed for 2 h in a stove at 120°C. Finally, the samples were cut in the form of 6-mm diameter discs weighing 15–25 mg.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed using a Thermogravimetric Analyzer (TGA7) from Perkin-Elmer, controlled by a computer. This microbalance was calibrated making use of the dis-

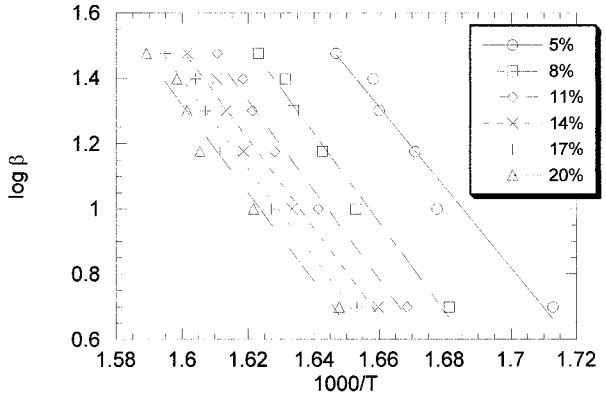

Figure 2 Typical plots of log β vs. 1000/T at several conversion values in the range of 5–20% in steps of 3%.

Table I Lifetimes for Experimental Data and for Different R_n Type Mechanisms[11] at Different Temperatures

		t (min)		
T (°C)	Experimental	R_1	R_2	R_3
60	$1.41\ 10^{9}$	$3.22\ 10^{8}$	$6.86\ 10^{8}$	$6.92\ 10^{8}$
80	$2.76\ 10^{7}$	$6.31\ 10^{6}$	$1.34\ 10^{7}$	$1.36\ 10^{7}$
100	$8.27\ 10^{5}$	$1.89\ 10^{5}$	$4.02\ 10^{5}$	$4.06\ 10^{5}$
120	35339.5	8062.3	17202.0	17370.0
140	2049.8	467.6	997.8	1007.5
160	154.7	35.3	75.3	76.0
180	14.7	3.3	7.1	7.2
200	$16.9\ 10^{-1}$	$3.87\ 10^{-1}$	$8.25\ 10^{-1}$	$8.33\ 10^{-1}$
220	$2.33\ 10^{-1}$	$5.33\ 10^{-2}$	$1.14\ 10^{-1}$	$1.15\ 10^{-1}$
240	$3.76\ 10^{-2}$	$8.57\ 10^{-3}$	$1.82\ 10^{-2}$	$1.85\ 10^{-2}$
260	$6.93\ 10^{-3}$	$1.58\ 10^{-3}$	$3.37\ 10^{-3}$	$3.40\ 10^{-3}$
280	$1.44\ 10^{-3}$	$3.29\ 10^{-4}$	$7.03\ 10^{-4}$	$7.10\ 10^{-4}$
300	$3.35\ 10^{-4}$	$7.66\ 10^{-5}$	$1.63\ 10^{-4}$	$1.65\ 10^{-4}$

continuous change in the magnetic properties of perkalloy and alumel on heating.

The system was operated in the dynamic mode in the temperature range 100–900°C, at different heating rates.

All the experiments were carried out under a dry nitrogen atmosphere. The TGA7 analyzer requires two purge lines: one to purge the balance chamber, and a second one to purge the sample-furnace area. After various experiments, it was found that the optimum gas flow rates were: 25 mL/min for the balance purge gas and 35 mL/min for the sample purge gas.

RESULTS AND DISCUSSION

Dynamic thermogravimetric data at different heating rates (5, 10,15, 20, 25, 30°C/min) were used from kinetic analysis. Figure 1 shows the plot of percent of weight loss vs. temperature at different heating rates. In a previous article[10] we

Table II Scaling Factors and Corrected Lifetimes at Different Temperatures

		t (min)		
T (°C)	Scaling Factor	Corrected Lifetimes	Experimental Lifetimes	Error (%)
60	0.0196	$1.411\ 10^{9}$	$1.408\ 10^{9}$	0.22
80	0.0299	$2.761\ 10^{7}$	$2.763\ 10^{7}$	0.10
100	0.0427	$8.269\ 10^{5}$	$8.267\ 10^{5}$	0.03
120	0.0580	35365.97	35339.48	0.08
140	0.0754	2052.36	2049.82	0.12
160	0.0948	154.65	154.65	0.23
180	0.1157	14.67	14.66	0.04
200	0.1378	1.6949	1.6955	0.04
220	0.1608	$2.3364\ 10^{-1}$	$2.3362\ 10^{-1}$	0.01
240	0.1844	$3.758\ 10^{-2}$	$3.757\ 10^{-2}$	0.02
260	0.2084	$6.930\ 10^{-3}$	$6.929\ 10^{-3}$	0.01
280	0.2325	$1.4444\ 10^{-3}$	$1.4442\ 10^{-3}$	0.01
300	0.2566	$3.3576\ 10^{-4}$	$3.3580\ 10^{-4}$	0.01

Table III Exponential Errors and Confidential Intervals for Lifetimes at Different Temperatures

T (°C)	$e^{+2\sigma\Delta T/RT_1T_2}$	$e^{-2\sigma\Delta T/RT_1T_2}$	$+t$ (min)	$-t$ (min)
60	3.50	0.29	$4.94\ 10^{9}$	$4.03\ 10^{8}$
80	3.06	0.33	$8.44\ 10^{7}$	$9.03\ 10^{6}$
100	2.73	0.37	$2.25\ 10^{6}$	$3.02\ 10^{5}$
120	2.47	0.40	87288.5	14241.8
140	2.28	0.44	4673.6	899.9
160	2.11	0.47	326.31	72.69
180	1.99	0.50	29.16	7.37
200	1.87	0.53	3.17	0.90
220	1.79	0.56	$4.23\ 10^{-1}$	$1.32\ 10^{-1}$
240	1.71	0.58	$6.42\ 10^{-2}$	$1.22\ 10^{-2}$
260	1.65	0.61	$1.14\ 10^{-2}$	$4.21\ 10^{-3}$
280	1.59	0.63	$2.29\ 10^{-3}$	$9.04\ 10^{-4}$
300	1.54	0.65	$5.16\ 10^{-4}$	$2.17\ 10^{-4}$

calculated the activation energies for different conversions using the Flynn-Wall-Ozawa method. These data was obtained from a linear fitting of the plot of log β vs. $1/T$. This plot is shown in Figure 2. As can be seen, the lines are parallel for all conversions. This indicate identical activation energies throughout the reaction. Then we can use a single activation energy for the reaction that can be calculated from the average value for the different conversions. This value is 192.2 $\pm$ 30.6 kJ/mol. Using dynamic thermogravimetry data the lifetime can be calculated taking into account that the assumed lifetime is 5% weight loss. Table I show experimental lifetimes in the temperature range of 60–300°C. From this table the deep fall of the lifetime with temperature can be observed. The lifetime bewteen 60–300°C differ by 2679 years. This results is in good agreement with data for similar epoxy system.[7,11] Comparison of these values with those obtained using different Rn type mechanisms[11] present errors higher than 50% for R_2 and R_3 and higher than 75% for R_1.

It is interesting to judge how precisely one can predict from these data the determination of lifetime at each temperature. The ratio of two reaction rates is given by the following equation:

$$\frac{k_2}{k_1} = e^{-E_a\Delta T/RT_1T_2} \tag{3}$$

This ratio is known as the scaling factor, and led the calculation of the lifetime. Table II shows the scaling factor and the lifetimes in the temperature range of 60–300°C. From this data we can conclude that the percentage errror between the lifetime obtained with the scaling factor and the experimental lifetime was less than 0.5%.

Introduccing an error of two standard deviations, $\pm 2\sigma$, in the activation energy, the error shows a multiplicative exponential propagation as can be seen in following equation:

$$\text{error} = e^{\pm 2\sigma\Delta T/RT_1T_2} \tag{4}$$

Table III show the error calculated using eq. (4). The error introduced by two standard deviations gives an error of about 92% at all temperatures. These sharp differences are produced with a small error in activation energy.

CONCLUSIONS

Based on the experimental lifetime and the higher errors, it can be concluded that the thermogravimetric analysis using isoconversionals from different heating rates is not a useful method to determine the lifetime of this epoxy system.

REFERENCES

1. Wunderlich, B. Thermal Analysis; Academic Press Inc.: New York, 1990.
2. Flynn, J. H. J Therm Anal 1995, 44, 499.
3. Liaw, D. J.; Shen, W. C. Polym Eng Sci 1994, 34, 1297.

4. Flynn, J. H. Polym Eng Sci 1980, 20, 675.
5. Jiménez A.; Berenger V.; López J., Sánchez A. J Appl Polym Sci 1993, 50, 1565.
6. Ma, S.; Hill, J. O.; Heng, S. J Therm Anal 1991, 37, 1161.
7. Barral, L.; Cano, J.; López, J.; López-Bueno, I.; Nogueira, P.; Ramírez, C.; Abad, M. J. Calorim J Therm Anal 1999, 55, 37.
8. Núñez, L.; Fraga, F.; Núñez. M. R.; Villanueva, M. Polymer 2000, 41, 4635.
9. Núñez, L. ; Fraga, F.; Núñez, M. R.; Villanueva, M. J Appl Polym Sci 2000, 78, 1239.
10. Fraga, F.; Rodríguez Núñez, E. J Appl Polym Sci, to appear.
11. Fraga, F.; Rodriguez Núñez, E. J Appl Polym Sci, to appear.
12. Flynn, J. H.; Wall, L. A. J Res Nat Bur Standards A Phys Chem 1996, 70A, 487.
13. Ozawa, T. Bull Chem Soc Jpn 1965, 38, 1881.
14. Doyle, C. D. Nature 1965, 207, 240.
15. Lee, H.; Neville, K. Handbook of Epoxy Resin; McGraw-Hill: New York, 1967.
16. May C. A. Epoxy Resins: Chemistry and Technology; Marcel Dekker, New York: 1988.