Lifetime Prediction of the Epoxy System Badge n = 0/1,2 DCH by Thermogravimetric Analysis

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ABSTRACT: Lifetime of the system diglycidyl ether of bisphenol A (BADGE n = 0)/1,2-diamine cyclohexane (DCH) was predicted by thermogravimetric analysis. Lifetime was considered when either 5% weight loss or 5% conversion was reached. Experimental results were treated using two different methods: The first method was independent of the degradation mechanism and the second was based on the thermodegradation kinetic mechanism. The activation energy of the reaction, determined using the Flynn–Wall–Ozawa method, was 148.51 kJ/mol. This value is in a good agreement with that of 144.01 kJ/mol obtained using Kissinger's method. From the experimental results, it was found that the optimum temperature of service for this material is in the range of 100–140°C, at which the corresponding lifetime range is from 27 to 2633 years. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1239–1244, 2000

Key words: lifetime; thermogravimetric analysis; epoxy resins

INTRODUCTION

Lifetime prediction is an applied technique, which is frequently needed in industry to determine the probable performance of a new material. The philosophy of lifetime prediction is to identify the critical reaction which limits the life of a material, then to measure its kinetics quantitatively at high temperature where the reaction is fast. Finally, using proper kinetic expressions, the kinetics for reactions at lower temperatures, at which reaction times are longer, can be extrapolated and, thus, the time the material will be in service can be predicted. Naturally, the reverse process, extrapolating the kinetics to higher temperatures, could also be carried out to find shorter, predicted, lifetimes. In this article, it is tacitly assumed that the thermogravimetric analysis technique identifies the proper life-determining reaction[1] and that the detailed chemistry and physics of the various failure mechanisms is as assumed, in order to allow us to concentrate on the thermodegradation kinetics and the precision of the chosen extrapolation method.

The materials chosen for the discussion of lifetime determination are thermosets (epoxy resins). The used technique is mass loss, despite the fact that the useful life of a material may have ended long before a loss of mass is detected. Only determination of the glass transition by DSC or DMA could help in such a case. Thermogravimetry remains, however, as a convenient technique for lifetime prediction. The lifetime is considered when 5% weight loss[2] or 5% conversion[3] is reached from a thermogravimetric analysis experiment (TGA).

KINETIC METHODS

Kinetic information can be extracted from a dynamic experiment using various methods. All kinetic methods utilize the basic rate equation that relates the rate of conversion $d\alpha/dt$ at constant

temperature to some function of the reagents $f(\alpha)$ through a rate constant k (ref. 4):

$$\frac{d\alpha}{dt} = kf(\alpha) \qquad (1)$$

where α is the degree of conversion, k is the temperature-dependent rate constant, and $f(\alpha)$ depends on the particular decomposition mechanism.

According to Arrhenius,

$$k = Ae^{-E/RT} \qquad (2)$$

where A is the preexponential factor; E, the activation energy; R, the gas constant; and T, the absolute temperature. A combination of eqs. (1) and (2) gives

$$\frac{d\alpha}{dt} = Af(\alpha)e^{-E/RT} \qquad (3)$$

If the temperature is changed by a controlled and constant heating rate, β, the variation in the degree of conversion can be analyzed as a function of temperature, this temperature being dependent on the time of heating. Therefore, the reaction rate may be written as follows:

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT}\frac{dT}{dt} \qquad (4)$$

where $dT/dt = \beta$ is defined as the heating rate.

A combination of eqs. (3) and (4) leads to

$$\frac{d\alpha}{dT} = \frac{A}{\beta}e^{-E/RT}f(\alpha) \qquad (5)$$

Integration of this equation from an initial temperature, T_0, corresponding to a degree of conversion, α_0, to the peak temperature where $\alpha = \alpha_p$ gives

$$\int_{\alpha_0}^{d_p} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T_p} e^{-E/RT}\,dT \qquad (6)$$

If T_0 is low, it may be reasonably assumed that $\alpha_0 = 0$, and considering that there is no reaction between 0 and T_0 (ref. 5),

$$g(\alpha) = \int_0^{\alpha_p}\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^{T_p} e^{-E/RT}\,dT \qquad (7)$$

where $g(\alpha)$ is the integral function of conversion.

EXPERIMENTAL

Materials

The epoxy resin was a commercial BADGE ($n = 0$; Resin 332 Sigma Chemical Co, St. Louis, MO) with an equivalent molecular weight of 173.6 g/equiv, as determined by wet analysis.[6,7] The amine was 1,2-diamine cyclohexane (DCH; Fluka, Switzerland), with an amine hydrogen equivalent weight of 28.5. Both were used as received.

Sample Preparation

Epoxy resin and the cure agent were carefully and homogeneously mixed, at a stoichiometric ratio, before being introduced into a cylindrical frame. The curing reaction was programmed according to a TTT diagram described for this material.[8] It consists of two stages: a first step at 23°C for 24 h and a second one in a stove, at 70°C, for 16 h. After curing, the samples were removed from the frame. For thermogravimetric analysis, the samples were cut into discs of 25–30 mg and 6 mm in diameter.

Technique

Thermogravimetric analyses were performed using a TGA7 from Perkin–Elmer controlled by a 1020 computer. This microbalance was calibrated by using the discontinuous change in the magnetic properties of perkalloy and alumel on heating. The Curie point of every metal can be calculated and the microbalance was calibrated at different heating rates.

The experiments were performed using a dynamic method in the temperature range between 100 and 900°C at heating rates of 5, 15, 25, 35, and 45°C/min. All the experiments were performed under a nitrogen inert atmosphere and the optimum gas flow rates were[9]

Balance purge gas: 25 mL/min.
Sample purge gas: 35 mL/min.

RESULTS AND DICUSSION

Lifetime Determination Without Knowledge of Reaction Mechanism

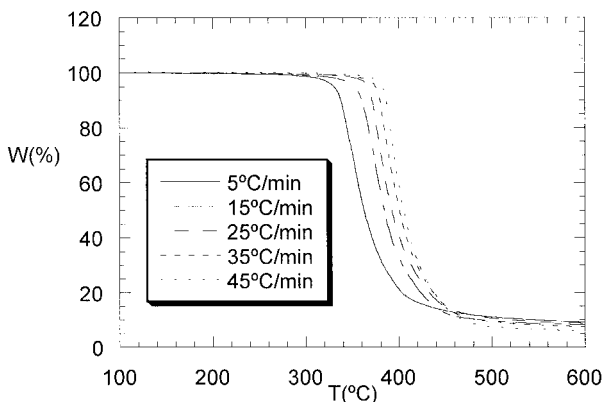One of the methods used for the study of the kinetics of thermodegradation is based on the

Figure 1 Experimental TG curves at the various heating rates used in this study.

mass loss collected in a series of different constant heating rate experiments. Isoconversion occurs at different temperatures for different heating rates.

Kinetic information can be extracted from a dynamic experiment using the Flynn–Wall–Ozawa method.[10,11] This method involves an approximate integration of eq. (7). This equation was integrated using the Doyle[12] approximation and can be rearranged after taking logarithms in the form

$$\log \beta = \log\left[\frac{AE}{g(\alpha)R}\right] - 2.315 - \frac{0.457E}{RT} \quad (8)$$

This is one of the methods that can determine the activation energy without knowledge of the reaction mechanism. Thermal degradation was studied, using the dynamic mode, at different heating rates: 5, 15, 25, 35, and 45°C/min. The curves are shown in Figure 1. This type of curves is the C type,[13] that is, curves with a single-stage decomposition reaction where the starting and ending temperatures of degradation are used to characterize the curve. From these curves, both degradation temperatures, at several isoconversion values, can be experimentally obtained using an intercept method, at each heating rate. To apply the Doyle approximation, conversions of 5, 8, 11, 14, 17, and 20% were used.

From the fit of a plot of log β versus $1/T$ at the various conversions, the activation energy was calculated. The results are illustrated in Figure 2. The parallel lines indicate that the activation energies are essentially the same throughout the reaction and suggest that a single reaction mechanism is operative.[14,15] It must be pointed out that only if parallel lines are obtained is extrapolation to lower temperatures justified. The average value of the activation energy is 148.51 kJ/mol and is close to the corresponding value obtained using Kissinger's method (E_a = 144.01 kJ/mol)[9] that some authors[16] used to checktheir thermodegradation mechanism models. From these data, the lifetime at several temperatures can be predicted, taking into account that the lifetime is assumed to be reached at 5% conversion. Lifetime values corresponding to temperatures between 100 and 360°C are summarized in Table I. From this table, it can be seen that, because of the high lifetime value, 100°C is the
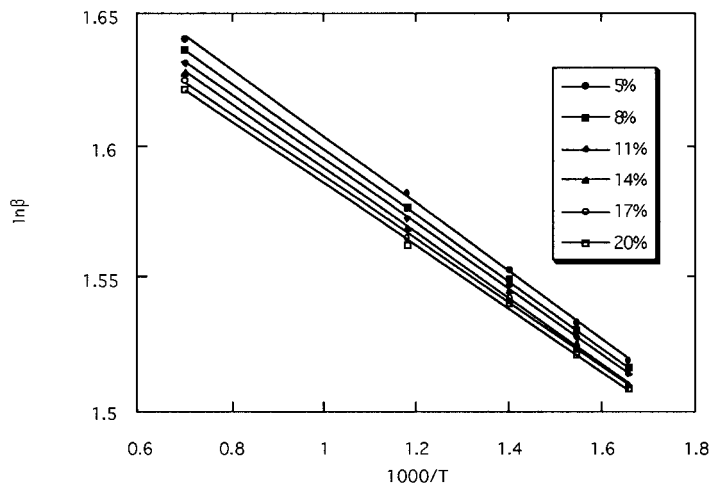

Figure 2 Plots of log b versus 1000/T at different conversion values in the range 5–20% in steps of 3%.

Table I   Experimental Lifetimes for the System BADGE n = 0/1, 2 DCH at Several Temperatures

T (°C)	t_{exp} (min)
100	1.38×10^9
120	1.25×10^8
140	1.42×10^7
160	1.98×10^6
180	3.28×10^5
200	6.32×10^4
220	1.39×10^4
240	3.45×10^3
260	9.51×10^2
280	2.88×10^2
300	9.45×10^1
320	3.35×10^1
340	1.24×10^1
360	5.10×10^0

Table II   Scaling Factor and Lifetimes Corrections at Several Temperatures

T (°C)	Scaling Factor	t (min)	Error (%)
100	0.09013	1.39×10^9	0.11
120	0.11377	1.25×10^8	0.11
140	0.13906	1.42×10^7	0.09
160	0.16551	1.98×10^6	0.11
180	0.19270	3.28×10^5	0.05
200	0.22023	6.33×10^4	0.07
220	0.24780	1.40×10^4	0.09
240	0.27514	3.46×10^3	0.03
260	0.30205	9.52×10^2	0.08
280	0.32837	2.88×10^2	0.05
300	0.35398	9.45×10^1	0.07
320	0.37879	3.35×10^1	0.03
340	0.40275	1.27×10^1	0.08
360	0.42582	5.10×10^0	0

optimum working temperature for this material. This value coincides with the value, 100°C, obtained through the curing kinetic study[17] and the construction of a TTT diagram.[8] From the same table, the sharp fall of the lifetime with increasing temperature can be observed, as the lifetime corresponding to 360°C is only 5.10 minutes. As can be seen, the optimal temperature range is 100–140°C, at which the corresponding lifetime range is of 27–2633 years.

The ratio of two reaction-rate constants is known as the scaling factor[1]:

$$\frac{k_2}{k_1} = e^{-E\Delta T/RT_1T_2} \qquad (9)$$

Use of eq. (9) led to the calculation of the scaling factor which allows a correction (or adjustment) of the time data. Table II shows values of the scaling factor and lifetime corrections at various temperatures. As shown, the lifetime calculated through the scaling factor does not essentially differ from the experimental values. The percentage error was less than 1%. In this way, the use of the scaling factor minimizes the scattering with respect to the previously determined lifetime.

Assuming for the scaling factor an error equal to twice the standard deviation, to get a 95% confidence,

$$error = e^{+2\sigma\Delta T/RT_1T_2} \qquad (10)$$

This equation shows a multiplicative exponential propagation for the error.

From eq. (10), the maximum and minimum values of the lifetime can be calculated. These values are listed in Table III. As can be seen, the experimental data shown in Table I are inside the confidence interval listed in Table III. Based on these assumptions and the data presented here, it can be argued that thermogravimetric analysis is an useful method to determine the lifetime of epoxy materials.

Calculation of Lifetime Using Thermodegradation Mechanism

Study of the thermodegradation kinetics[9] of the system BADGE n = 0/1,2 DCH confirms that this

Table III   Confidence Interval for the Lifetimes at Several Temperatures

T (°C)	Maximum Lifetime (min)	Minimum Lifetime (min)
100	1.59×10^9	1.20×10^9
120	1.42×10^8	1.10×10^8
140	1.60×10^7	1.27×10^7
160	2.20×10^6	1.78×10^6
180	3.61×10^5	2.98×10^5
200	6.91×10^4	5.78×10^4
220	1.51×10^4	1.28×10^4
240	3.73×10^3	3.20×10^3
260	1.02×10^3	8.87×10^3
280	3.07×10^2	2.69×10^2
300	1.00×10^2	8.89×10^1
320	3.54×10^1	3.16×10^1
340	1.34×10^1	1.00×10^1
360	5.36×10^0	4.85×10^0
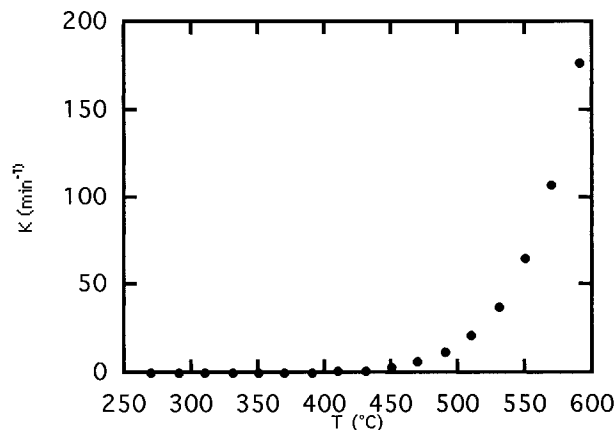
Figure 3   Rate constant as a function of temperature.

Figure 4   Plot of conversion versus time at 330, 350, and 370°C.

epoxy system follows a sigmoidal A_4 mechanism, that is, a nucleation and growth solid-state process (Avrami equation). The corresponding equation is

$$[-\ln(1 - \alpha)]^{\frac{1}{4}} = kt \qquad (11)$$

Using the mean activation energy value calculated by the Flynn–Wall–Ozawa method, 148.53 kJ/mol, and the preexponential factor value, $A = 1.72 \times 10^{11}$ min^{-1}, the rate constant can be derived from the Arrhenius equation as a function of temperature. Figure 3 shows that k values exponentially increase with increasing temperature. Equation (11) allows the calculation of the conversion degree as a function of time:

$$\alpha = 1 - e^{-k^4 t^4} \qquad (12)$$

Figure 4 is a degree of conversion versus time plot at temperatures 330, 350, and 370°C, corresponding to the main period temperatures of the thermodegradation curves (Fig. 1). This figure shows that the degree of conversion sharply increases at low temperatures and then decreases with the temperature.

Taking into account that the lifetime was defined as the time necessary for a 5% conversion, eq. (12) leads to

$$t = \frac{0.476}{k} \qquad (13)$$

This equation allows the calculation of the lifetime as a function of temperature through the constant rate k. Figure 5 shows lifetime values as
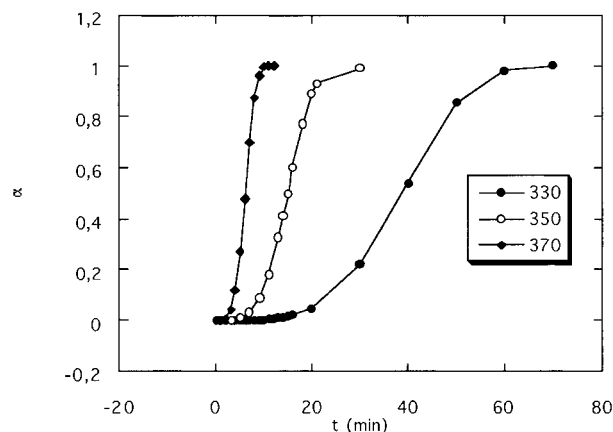
a function of temperature. Comparison of lifetime values obtained using this method with those calculated without the knowledge of the reaction mechanism shows important differences. This may be due to that the sigmoidal A_4 mechanism can only be used to 15% conversion, that is, inside the Doyle approximation range.

CONCLUSIONS

It may be concluded that the lifetimes predicted by this last method are less reliable than are those obtained using experimental data. That may be due to that the thermodegradation kinetics does not fit to any of the solid-state mechanisms used for comparison. We are trying to develop a mechanism design, a combination of known mechanisms, able to fit experimental results in the whole range of conversions.
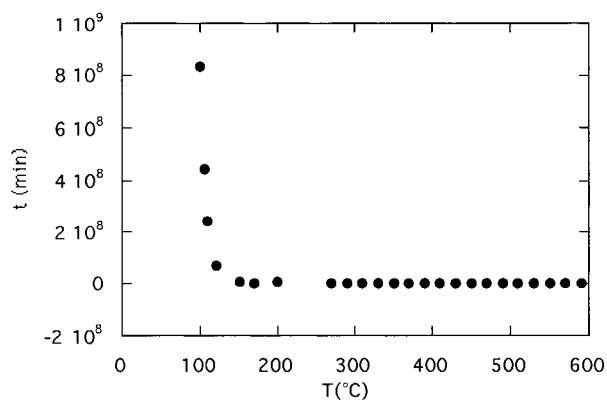

Figure 5   Lifetime as a function of temperature.

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