

Master Curves and Lifetime Prediction for the Epoxy System BADGE n = 0/*m*-XDA by Thermogravimetric Analysis

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ABSTRACT: Master plots were used to corroborate R_n -type mechanisms calculated in a previous study, using the method proposed by Criado et al. (Thermochim Acta 1989, 147, 377). Analysis of experimental data seems to belong to the family of decelerated curves (R_n) in the range of conversion studied. The lifetime of the system diglycidyl ether of bisphenol A (BADGE n = 0)/*m*-xylylenediamine (*m*-XDA) for different decelerated mechanisms was calculated using thermogravimetric analysis. From the experimental data it was found that the optimum temperature range of use for this material is 60–100°C for all R_n -type mechanisms, at which corresponding lifetimes range between 190 years and 1 year. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 461–466, 2001

Key words: epoxy resins; thermogravimetry; lifetime prediction; master curves

INTRODUCTION

Many studies of curing and thermogravimetric kinetic mechanism of thermosets^{1–4} have employed reference theoretical curves known as master curves. These curves are characteristic curves, independent of the conditions of measurements, which are easily obtained from kinetic or thermogravimetric experimental data.

Lifetime prediction is an applied method, which is frequently needed in industry to find out the probable performance of a thermoset, to determine the critical reaction that limits the life of a material, then to measure its kinetic parameters at high temperatures at which the reaction is fast. Finally, using adequate kinetic expressions, the kinetic parameters for reactions at lower temperatures, at which reaction times are longer, can be extrapolated and thus the lifetime of the material can be determined.

The technique used to calculate the lifetime of an epoxy system is to determine the mass loss, despite the fact that the useful life of a material may have ended long before a loss of mass is detected. In this case only determination of the glass-transition temperature by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) could help.

Thermogravimetric analysis experiments are used to identify the lifetime of a material, assuming that we avoid the detailed chemistry and physics of the various failure mechanisms; however, thermogravimetry remains as a convenient technique for lifetime prediction. The lifetime is considered when 5% weight loss⁵ or 5% conversion⁶ is reached from a thermogravimetric analysis (TGA) experiment.

In this study we discuss the applicability of master curves to find out the reaction mechanism for the epoxy system diglycidyl ether of bisphenol A (BADGE n = 0)/*m*-xylylenediamine (*m*-XDA). The method used was proposed by Criado et al.² In addition, we calculate the lifetime for the epoxy

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system with knowledge of the reaction mechanism of the epoxy system.

Combining the Arrhenius law with the general rate equation in terms of the degree of conversion, time, and temperature, we obtain the following relationship for the calculation of the kinetic parameters of a solid-state reaction from dynamic experiments:

$$\frac{d\alpha}{dt} = \frac{A}{\beta} f(\alpha) e^{-(E/RT)} \quad (1)$$

where $f(\alpha)$ is a function depending on the reaction mechanism, A is the preexponential factor, E is the activation energy, T is the absolute temperature, R is the gas constant, and $\beta = dT/dt$ is defined as the heating rate.

By integrating eq. (1) we get

$$g(\alpha) = \int_0^{\alpha_p} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{-(E/RT)} dT \quad (2)$$

where $g(\alpha)$ is the integral function of conversion.^{2,7,8}

In a previous study⁹ the activation energies in nonisothermal conditions using differential and integral methods was calculated. Knowing the activation energy by Flynn–Wall–Ozawa method in the conversion range (5–20%), where it is not necessary to know the reaction mechanism, the kinetic model proposed by Criado et al.² could be defined in the following way:

$$Z(\alpha) = \frac{\left(\frac{d\alpha}{dt}\right)}{\beta} \pi(x)T \quad (3)$$

where $x = E/RT$, and $\pi(x)$ is an approximation of the temperature integral. Considering the general kinetic equation and the integrated form, eq. (3) can be rearranged as

$$Z(\alpha) = f(\alpha)g(\alpha) \quad (4)$$

In this study the fourth rational expression of Senum and Young¹⁰ for $\pi(x)$ was used, which is

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (5)$$

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/eq, as determined by wet analysis.^{11,12} The curing agent was *m*-xylylenediamine (*m*-XDA; Aldrich Chemical Co., Milwaukee, WI).

Sample Preparation

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

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was performed using a thermogravimetric analyzer (TGA7; Perkin–Elmer, Foster City, CA) controlled by a computer. This microbalance was calibrated by making use of the discontinuous change in the magnetic properties of perkalloy and alumel on heating. The Curie point of every metal was calculated by the microbalance, which was calibrated at different heating rates.

The system was operated in the dynamic mode in the temperature range 100–900°C, at different heating rates: 5, 10, 15, 20, 25, and 30°C/min.

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

In a previous study⁹ we calculated activation energies using different integral methods (Coats–Redfern,¹³ Van Krevelen,¹⁴ and Horowitz–Metzger¹⁵). These methods suggest that the solid-state thermodegradation mechanism followed by our system is a decelerated (R_n) type.

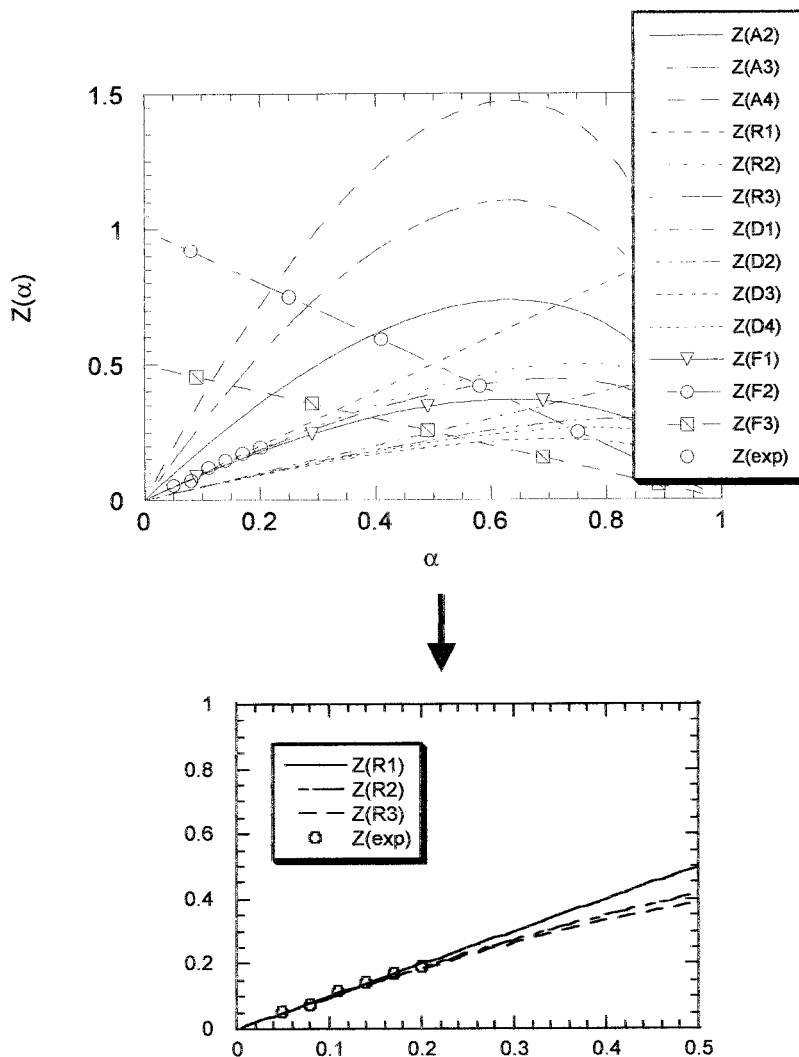


Figure 1 Master curves $Z(\alpha)$ for different solid-state mechanisms.

In this work, we used the method proposed by Criado et al.,² using experimental thermogravimetric data, to corroborate the R_n -type mechanism. This method employed reference theoretical master curves to determine the reaction mechanism.

The master curves of eq. (4) can be seen in Figure 1, where \circ represents the experimental points. These points seem to belong to the family of decelerated curves (R_n) in the range of conversion studied.

Table I Algebraic Expressions for the R_n Decelerated Mechanisms

Symbol	$g(\alpha)$	Solid-State Processes
R_1	$\alpha = kt$	Phase boundary controlled reaction (one-dimensional movement)
R_2	$(1 - \ln(1 - \alpha)^{1/2}) = kt$	Phase boundary controlled reaction (contracting area)
R_3	$(1 - \ln(1 - \alpha)^{1/3}) = kt$	Phase boundary controlled reaction (contracting volume)

Table II Preexponential Factor Values (A) Calculated Using Flynn–Wall–Ozawa Method for the Different R_n Decelerated Mechanisms

Symbol	A (min ⁻¹)
R_1	2.17×10^{20}
R_2	2.09×10^{21}
R_3	2.05×10^{21}

The equations for the R_n -type mechanisms are shown in Table I. Using the mean activation energy value (192.16 kJ/mol)⁹ calculated by the Flynn–Wall–Ozawa method^{16,17} and the preexponential factor values for different R_n -type mechanisms (Table II), the rate constants (k) can be derived from an Arrhenius equation as a function of temperature. Figure 2 shows k values versus temperature for different R_n -type mechanisms; this figure also shows that k values exponentially increase with increasing temperature for the different decelerated mechanisms. Compared to similar systems (Nuñez et al.¹⁸ and Barral et al.³), our rate constants show that values increase more rapidly. From Table I, the degree of conversion as a function of time can be calculated using the following set of equations:

$$\begin{aligned}\alpha(R_1) &= kt \\ \alpha(R_2) &= 1 - e^{2(1-kt)} \\ \alpha(R_3) &= 1 - e^{3(1-kt)}\end{aligned}\quad (6)$$

Figures 3(a)–(c) show a degree of conversion versus time at temperatures of 190, 200, 210, and 220°C for different R_n -type mechanisms. In these

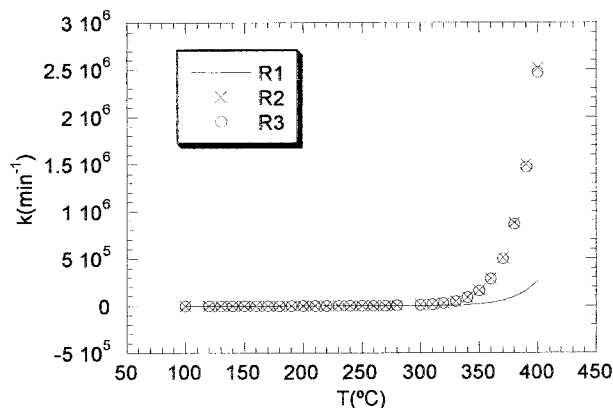
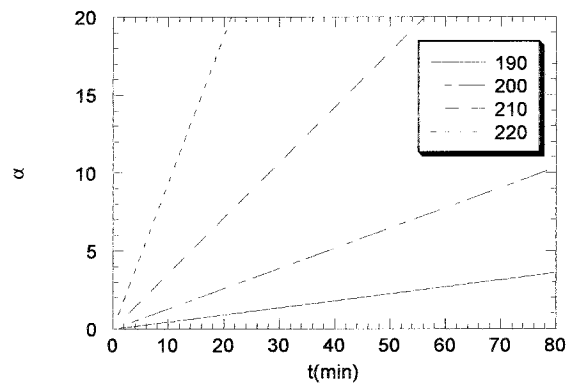
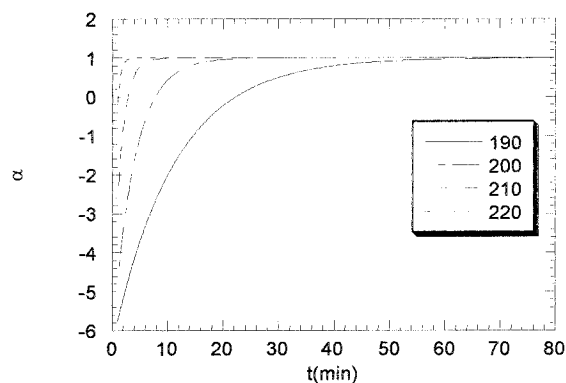


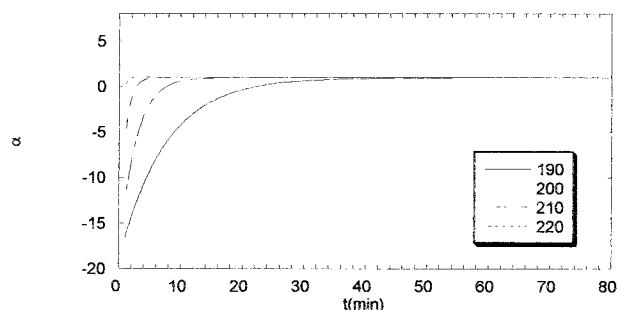
Figure 2 Rate constant as a function of temperature.



(a)



(b)



(c)

Figure 3 Plots of conversion versus time for (a) R_1 ; (b) R_2 ; and (c) R_3 at 190, 200, 210, and 220°C.

figures can be observed a decelerated behavior where the degree of conversion shows slight increases at low temperatures, increasing sharply with increasing temperature for all R_n -type mechanisms. At all temperatures analyzed, the degree of conversion did not show autoacceleration in the initial stages. For similar systems^{3,4,18} the mechanism reaction is sigmoidal and the degree of conversion showed autoacceleration, indicated by a slight positive curvature in the initial stages.

Table III Lifetimes at Different Temperatures for Different R_n Type Mechanisms

Temperature (°C)	t (min)		
	R_1	R_2	R_3
60	3.22×10^8	6.86×10^8	6.92×10^8
80	6.31×10^6	1.34×10^7	1.36×10^7
100	1.89×10^5	4.02×10^5	4.06×10^5
120	8062.3	17,202.0	17,370.0
140	467.6	997.8	1007.5
160	35.3	75.3	76.0
180	3.3	7.1	7.2
200	3.87×10^{-1}	8.25×10^{-1}	8.33×10^{-1}
220	5.33×10^{-2}	1.14×10^{-1}	1.15×10^{-1}
240	8.57×10^{-3}	1.82×10^{-2}	1.85×10^{-2}
260	1.58×10^{-3}	3.37×10^{-3}	3.40×10^{-3}
280	3.29×10^{-4}	7.03×10^{-4}	7.10×10^{-4}
300	7.66×10^{-5}	1.63×10^{-4}	1.65×10^{-4}

Taking into account that lifetime is defined as the time necessary for a 5% conversion,⁶ eq. (6) leads to

$$\begin{aligned}
 t(R_1) &= \frac{0.05}{k} \\
 t(R_2) &= \frac{1.026}{k} \\
 t(R_3) &= \frac{1.017}{k} \quad (7)
 \end{aligned}$$

These equations allow the calculation of lifetime as a function of temperature. Table III shows the lifetimes at different temperatures for different R_n -type mechanisms. Comparison of lifetime values obtained using an R_1 -type mechanism with those using R_2 - and R_3 -type mechanisms reveals important differences. The lifetime values for an R_1 -type mechanism are smaller than those calculated using R_2 - and R_3 -type mechanisms. Table III also shows the sharp fall of lifetime with increasing temperature for all R_n -type mechanisms, as the lifetime corresponding to 200°C for the R_2 -type mechanism is only 0.82 min. As can be seen the optimum temperature range is 60–100°C for all R_n -type mechanisms, at which the corresponding lifetimes are in the range 190 years to 1 year. Similar systems⁴ show higher lifetimes for similar temperatures. This indicates that our epoxy system is less stable at higher temperatures (around 200°C) than this epoxy system.

CONCLUSIONS

Master curves confirm that the epoxy system studied here follows a decelerated R_n thermodegradation mechanism in the conversion range considered.

It is difficult to calculate the lifetime of this epoxy system with good accuracy because of the difficulty of determining the type of decelerated mechanism; however, we think that the R_1 -type mechanism [i.e., phase boundary controlled reaction (one-dimensional movement)] is less probable because our epoxy system has a branching structure with a three-dimensional movement of crosslinks.

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