

Lifetime Prediction of the Epoxy System DGEBA ($n = 0$)/1,2-DCH Modified with an Epoxy Reactive Diluent by Thermogravimetric Analysis

Lisardo Núñez, M. Villanueva, M. R. Núñez, B. Rial

Research Group TERBIPROMAT, Departamento Física Aplicada, Universidad de Santiago, 15782, Santiago, Spain

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ABSTRACT: Thermogravimetric analysis was used to predict the lifetime of two three-component systems of diglycidyl ether of bisphenol A ($n = 0$)/1,2-diamine cyclohexane [DGEBA ($n = 0$)/1,2-DCH] modified with different concentrations of an epoxy reactive diluent, vinylcyclohexene dioxide (VCHD). Experimental results were treated using two methods. The first method was independent of the degradation mechanism, and the second was based on the thermodegradation kinetic mechanism. The activation energies of the reaction were determined using the Flynn–Wall–

Ozawa method. These values were compared with those obtained using Kissinger's method. From experimental results it was found that the optimum temperature of service for these materials were different, so one or the other must be selected, depending on the application temperature considered. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3835–3839, 2003

Key words: lifetime; thermogravimetric analysis; epoxy resins; reactive diluent

INTRODUCTION

Lifetime prediction is an applied technique that is frequently needed in industry to find out the probable performance of a new material. The philosophy of lifetime prediction is to identify the critical reaction that limits the life of a material; then to measure its kinetics quantitatively at high temperature, when the reaction is fast; and, finally, to extrapolate, using proper kinetic expressions, the kinetics for reactions at lower temperatures, when reaction times are longer. Thus, the time the material is in service will be predicted. Naturally, the reverse process, extrapolating the kinetics to higher temperatures, could also be carried out to find shorter predicted lifetimes. In this study it was tacitly assumed that the thermogravimetric analysis technique identified the proper life-determining reaction¹ and that the detailed chemistry and physics of the various failure mechanisms was as assumed. These assumptions were made to allow us to concentrate on the thermodegradation kinetics and the precision of the selected extrapolation method.

The materials chosen for the discussion of lifetime determination are thermosets (epoxy resins). In epoxy resin processing viscosity is a key factor. To improve the processibility of these materials, reactive diluents can be employed. Epoxy-based reactive diluents can participate, together with a resin and a curing agent, in

polymerization and crosslinking reactions, thus permitting the diluent to become chemically bound to the crosslinked network. In an attempt to preserve physico-mechanical properties at elevated temperatures, the use of a polyfunctional epoxy diluent was considered.² The objective of this work was to study the lifetime of a system that consists of a diglycidyl ether of bisphenol A ($n = 0$)/1,2-diaminecyclohexane [DGEBA ($n = 0$)/1,2-DCH] modified with the multi-functional epoxy reactive diluent vinylcyclohexene dioxide (VCHD).

The mass loss technique was used, despite that the useful life of a material may have ended long before a loss of mass is detected. Only determination of the glass-transition temperature by differential scanning calorimetry or dynamic mechanical analysis could help in such a case. Thermogravimetry remains a convenient technique for lifetime prediction, however. Lifetime is defined as reaching a 5% weight loss³ or a 5% conversion⁴ in a thermogravimetric analysis (TGA) experiment.

Kinetic methods

Kinetic information can be extracted from dynamic experiments by various methods. All kinetic methods utilize the basic rate equation that relates rate of conversion, $d\alpha/dt$, at constant temperature to some function of reagents, $f(\alpha)$, through a rate constant, k ⁵:

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

Correspondence to: L. Núñez (falisar1@uscmail.usc.es).

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,

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

where A is the preexponential factor, E is the activation energy, R is the gas constant, and T is the absolute temperature.

A combination of eqs. (1) and (2) gives

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

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, with this temperature dependent on the time of heating. Therefore, the reaction rate may be written as follows:

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

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

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

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

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

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

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_0^6 :

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

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

EXPERIMENTAL

Materials

The epoxy resin was Resin 332, a commercial DGEBA ($n = 0$) from Sigma Chemical Co. (St. Louis, MO), and the epoxy reactive diluent was vinylcyclohexane diox-

ide (Fluka, Switzerland), with equivalent molecular weights of 173.6 and 71.3 g/Eq, respectively, as determined by wet analysis.^{7,8} The curing agent was 1,2-diaminecyclohexane (DCH; Fluka, Switzerland), with an amine hydrogen weight of 28.5.

Sample preparation

Epoxy resin and reactive diluent were carefully and homogeneously mixed, at the proportion of 15% of diluent in weight of the total mass of the composed system, before being added the hardener. Then, the amounts of curing agent were added depending on the designed system. For the system noted as 15% VCHD (stoich.), a stoichiometric amount of curing agent was added taking into account the excess of epoxy introduced by the diluent. For the system noted as 15% VCHD (nonstoich.), the epoxy excess introduced through the reactive diluent was not taken into account. Thus, the amount of curing agent was the stoichiometric ratio corresponding to the two-component system DGEBA ($n = 0$)/1,2-DCH. Finally, the sample was introduced in a cylindrical frame.

For the 15% VCHD (stoich.) and 15% VCHD (nonstoich.) systems, the curing reactions were programmed according to the TTT diagrams calculated for the DGEBA ($n = 0$)/1,2-DCH/15% VCHD stoichiometric system⁹ and for the DGEBA ($n = 0$)/1,2-DCH system,¹⁰ respectively.

These curing reactions were:

- 35 min at 120°C in a stove for the 15% VCHD (stoich.) system;
- a first step of 24 h at 23°C and a second one of 16 h at 70°C in a stove, for the 15% VCHD (nonstoich.) system.

For thermogravimetric analysis the samples were cut into 6-mm-diameter discs that weighed between 15 and 25 mg.

Technique

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

The experiments were performed using a dynamic method in a temperature range between 100°C and 900°C at heating rates of 5°C, 15°C, 25°C, 35°C, and 45°C/min. All the experiments were performed under a nitrogen inert atmosphere, and the optimum gas flow rates were¹¹:

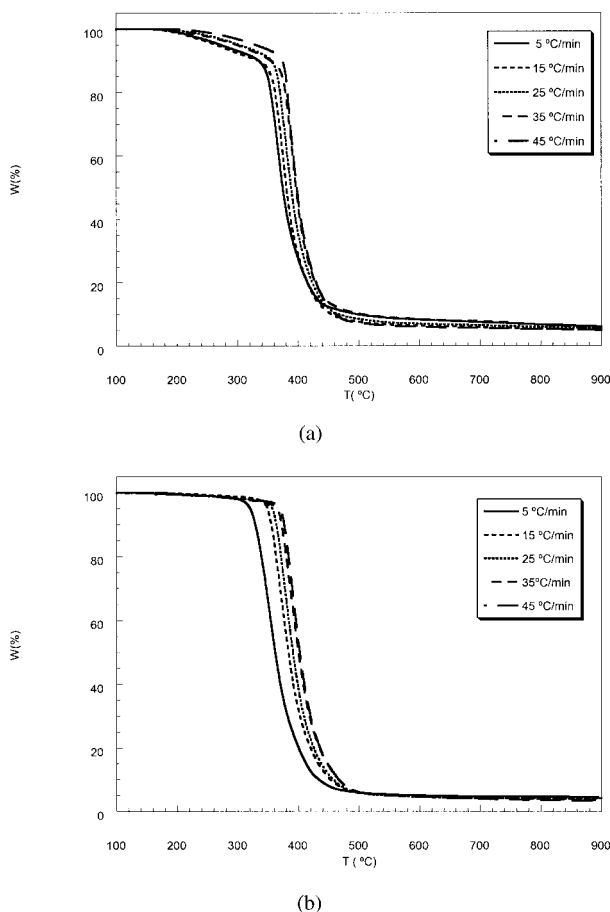


Figure 1 Experimental TG curves at the various heating rates used in this study for the a) DGEBA ($n = 0$)/12 DCH/15% VCHD (non stoich.) and b) DGEBA ($n = 0$)/12 DCH/15% VCHD (stoich.) systems.

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

RESULTS AND DISCUSSION

Lifetime determination without knowledge of the reaction mechanism

One method for studying the kinetics of thermodegradation is based on the 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.^{12,13} This method involves an approximate integration of eq. (7) using the Doyle¹⁴ approximation and then rearranging it 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. The dynamic mode was used to study thermal degradation at different heating rates: 5°C, 15°C, 25°C, 35°C, and 45°C/min. The curves presented in Figure 1(a,b) correspond to the 15% VCHD (nonstoich.) and 15% VCHD (stoich.) systems, respectively. These kind of curves are C-type curves,¹⁵ that is, curves with a single-stage decomposition reaction in which the starting and ending temperatures of degradation are used to characterize the curve. Comparing these curves with that obtained for the DGEBA ($n = 0$)/1,2-DCH system (without reactive diluent), it can be asserted that the reactive diluent did not have a significant effect on the characteristic step of the thermogravimetric curves. From these curves several isoconversion values of the degradation temperature can be experimentally obtained at every heating rate using an intercept method.¹⁶ To apply the Doyle approximation, conversions of 20%, 23%, 26%, 29%, 32%, and 35% were used.

From the fits of the plots of $\log \beta$ versus $1/T$ at the various conversions, the activation energies for both systems, 15% VCHD (nonstoich.) and 15% VCHD (stoich.), were calculated. The results are shown in Table I, and the average values of the activation energies are shown in Table II, together with the values obtained using the Kissinger method, which some authors¹⁶ have used to check their thermodegradation mechanism models. These values were compared with that obtained for the system without diluent.¹¹ From these data the lifetime at several temperatures was predicted, assuming the lifetime to be reached at 5% of conversion.

The ratio of two reaction rate constants is known as the scaling factor¹:

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

TABLE I
Activation Energies Obtained Using Flynn–Wall–Ozawa Method

α	(%) VCHD	$E_a \pm s(E_a)$ (kJ/mol)	R
0.20	15% (nonstoich.)	201.10 \pm 14.55	0.9922
	15% (stoich.)	157.91 \pm 6.70	0.9973
0.23	15% (nonstoich.)	206.70 \pm 14.01	0.9932
	15% (stoich.)	161.01 \pm 7.13	0.9971
0.26	15% (nonstoich.)	212.38 \pm 14.19	0.9934
	15% (stoich.)	164.39 \pm 7.61	0.9968
0.29	15% (nonstoich.)	217.20 \pm 14.01	0.9938
	15% (stoich.)	166.94 \pm 8.14	0.9964
0.32	15% (nonstoich.)	219.95 \pm 13.28	0.9946
	15% (stoich.)	169.34 \pm 8.78	0.9960
0.35	15% (nonstoich.)	222.64 \pm 13.64	0.9944
	15% (stoich.)	171.97 \pm 9.34	0.9956

TABLE II
Flynn–Wall–Ozawa and Kissinger Activation Energies

VCHD (%)	$\bar{E}_a(\text{Flynn}) \pm 2\sigma$ (kJ/mol)	$E_{a(\text{Kiss})} \pm s(E_a)$ (kJ/mol)
15% (nonstoich.)	213.33 \pm 6.10	237.61 \pm 36.83
15% (stoich.)	165.26 \pm 9.57	211.60 \pm 37.99
0% ¹¹	148.59 \pm 18.81	144.01 \pm 17.69

Using eq. (9) leads to calculation of the scaling factor, which allows a correction (or adjustment) of the time data. Tables III and IV show the experimental and theoretical values obtained using these scaling factors for the 15% VCHD (nonstoich.) and 15% VCHD (stoich.) systems. As shown, the lifetime calculated by the scaling factor did not essentially differ from the experimental values. The percentage error was less than 1%. In this way, using the scaling factor minimized the scattering with respect to the previously determined lifetime.

Assuming an error equal to twice the standard deviation for the scaling factor, a 95% confidence interval can be obtained with

$$\text{error} = e^{\pm 2\sigma\Delta T/RT_1T_2} \quad (10)$$

This equation shows multiplicative exponential propagation for the error.

From eq. (10) the maximum and minimum values of the lifetime can be calculated. These values are also listed in Tables III and IV. As can be seen, the experimental data are within the confidence interval. Based on these assumptions and the data presented here, it can be argued that thermogravimetric analysis is a useful method for determining the lifetime of epoxy materials.

Comparing the experimental values with those previously reported for the system without diluent,¹⁷ it can be seen that the lifetime magnitude orders for the

TABLE III
Experimental, Theoretical, and Corresponding Maximum and Minimum Lifetime Values Obtained for DGEBA ($n = 0$)/1,2-DCH/15%-VCHD (Nonstoich.)

T (K)	t_{exp} (min)	t_{theor} (min)	t_{max} (min)	t_{min} (min)
413.16	3.00×10^{09}	2.92×10^{09}	6.68×10^{09}	5.50×10^{08}
433.16	1.76×10^{08}	1.71×10^{08}	3.87×10^{08}	2.96×10^{07}
453.16	1.32×10^{07}	1.29×10^{07}	2.90×10^{07}	2.06×10^{06}
473.16	1.24×10^{06}	1.21×10^{06}	2.69×10^{06}	1.78×10^{05}
493.16	1.41×10^{05}	1.38×10^{05}	3.03×10^{05}	1.87×10^{04}
513.16	1.89×10^{04}	1.85×10^{04}	4.05×10^{04}	2.34×10^{03}
533.16	2.95×10^{03}	2.90×10^{03}	6.30×10^{03}	3.41×10^{02}
553.16	5.28×10^{02}	5.19×10^{02}	1.12×10^{02}	5.70×10^{01}
573.16	1.06×10^{02}	1.05×10^{02}	2.25×10^{02}	1.07×10^{01}
593.16	2.39×10^{01}	3.43×10^{01}	5.03×10^{01}	2.26×10^{00}
613.16	5.91×10^{00}	3.99×10^{00}	1.24×10^{01}	0.53×10^{00}
633.16	1.59×10^{00}	1.57×10^{00}	3.32×10^{00}	0.13×10^{00}

TABLE IV
Experimental, Theoretical, and Corresponding Maximum and Minimum Lifetime Values Obtained for DGEBA ($n = 0$)/1,2-DCH/15% VCHD (Stoich.)

T (K)	t_{exp} (min)	t_{theor} (min)	t_{max} (min)	t_{min} (min)
413.16	4.19×10^{07}	4.12×10^{07}	8.96×10^{07}	5.06×10^{06}
433.16	4.62×10^{06}	4.55×10^{06}	9.82×10^{06}	5.12×10^5
453.16	6.20×10^{05}	6.11×10^{05}	1.31×10^{06}	6.31×10^{04}
473.16	9.84×10^{04}	9.71×10^{04}	2.07×10^{05}	9.25×10^{03}
493.16	1.81×10^{04}	1.79×10^{04}	3.80×10^{04}	1.58×10^{03}
513.16	3.82×10^{03}	3.78×10^{03}	7.97×10^{03}	3.08×10^{02}
533.16	9.03×10^{02}	8.94×10^{02}	1.88×10^{03}	6.78×10^{01}
553.16	2.37×10^{02}	2.35×10^{02}	4.91×10^{02}	1.66×10^{01}
573.16	6.83×10^{01}	6.77×10^{01}	1.41×10^{02}	4.47×10^{00}
593.16	2.14×10^{01}	2.12×10^{01}	4.42×10^{01}	1.31×10^{00}
613.16	7.23×10^{00}	7.17×10^{00}	1.49×10^{01}	0.42×10^{00}
633.16	2.61×10^{00}	2.59×10^{00}	5.37×10^{00}	0.14×10^{00}

system with the stoichiometric ratio (Table IV) and those for the system without diluent are practically the same in the entire range of temperatures studied. However, for the system with the nonstoichiometric ratio (Table III), the lifetimes are 2 orders of magnitude higher than the system without diluent. Therefore, depending on the working temperature, it would be better to choose one or the other of the systems.

Calculation of lifetime using thermodegradation mechanism

The results of a study now underway in our laboratories that will be submitted for publication next confirm that the thermodegradation kinetics of the DGEBA ($n = 0$)/1,2-DCH/15% VCHD (nonstoich.) and DGEBA $n = 0$ /1,2-DCH/15% VCHD (stoich.) systems follow a deceleratory-type mechanism, R_2 , R_3 , or F_3 and R_2 or R_3 , respectively.

Taking into account the expression for the function of conversion, $g(\alpha)$,

TABLE V
Theoretical Lifetime Values (in Minutes) for the DGEBA ($n = 0$)/1,2-DCH/15% VCHD (Nonstoich.) system, Knowing the Thermodegradation Mechanism

T (K)	t (R_2)	t (R_3)	t (F_3)
413.16	1.10×10^{08}	7.35×10^{07}	4.80×10^{09}
433.16	6.43×10^{06}	4.30×10^{06}	2.81×10^{08}
453.16	4.83×10^{05}	3.24×10^{05}	2.12×10^{07}
473.16	4.53×10^{04}	3.03×10^{04}	1.98×10^{06}
493.16	5.14×10^{03}	3.44×10^{03}	2.25×10^{05}
513.16	6.91×10^{02}	4.62×10^{02}	3.02×10^{04}
533.16	1.08×10^{02}	7.23×10^{01}	4.72×10^{03}
553.16	1.93×10^{01}	1.29×10^{01}	8.88×10^{02}
573.16	3.89×10^{00}	2.60×10^{00}	1.70×10^{02}
593.16	0.87×10^{00}	0.58×10^{00}	3.82×10^{01}
613.16	0.15×10^{00}	0.01×10^{00}	6.48×10^{00}
633.16	0.06×10^{00}	0.04×10^{00}	2.56×10^{00}

TABLE VI
Theoretical Lifetime Values (in Minutes) for the DGEBA
($n = 0$)/1,2-DCH/15% VCHD (Stoich) System, knowing
the Thermodegradation Mechanism

T (K)	t (R_2)	t (R_2)
413.16	1.53×10^{06}	1.02×10^{06}
433.16	1.69×10^{05}	1.13×10^{05}
453.16	2.26×10^{04}	1.52×10^{04}
473.16	3.60×10^{03}	2.41×10^{03}
493.16	6.63×10^{02}	4.44×10^{02}
513.16	1.40×10^{02}	9.34×10^{01}
533.16	3.30×10^{01}	2.21×10^{01}
553.16	8.66×10^{00}	5.79×10^{00}
573.16	2.49×10^{00}	1.67×10^{00}
593.16	0.78×10^{00}	0.52×10^{00}
613.16	0.26×10^{00}	0.18×10^{00}
633.16	0.95×10^{00}	0.064×10^{00}
653.16	0.037×10^{00}	0.025×10^{00}

$$g(\alpha) = Kt \quad (12)$$

and that lifetime was defined as the time necessary for a 5% conversion, it can be calculated through the following equation:

$$t = \frac{g(\alpha)}{K(T)} \quad (13)$$

This equation allows the calculation of lifetime as a function of temperature through the constant rate k . Tables V and VI show lifetime values as a function of temperature for the nonstoichiometric and the stoichiometric systems, respectively. Comparison of lifetime values obtained using this method with those calculated without knowledge of the reaction mechanism shows important differences. It may be concluded that the lifetimes predicted by this last method are less reliable than those obtained using experimental data. That may be because the thermodegradation kinetics do not fit into any of the solid-state mechanisms used for comparison. It would be interesting to develop a design of mechanism, a combination of known mechanisms, able to fit the experimental results in the whole range of conversions.

CONCLUSIONS

Thermal analysis was used to estimate the half-lives of two epoxy systems. These values depend on the temperature. For example, to work at about 413 K (140°C), the best system would be that with the nonstoichiometric relation of diluent because its half-life is about 5700 years (for the other system with diluent it is about 79 years, and for the two-component system it is about 27 years). Anyway, it would be interesting to study the mechanical properties for selecting the best material to be applied for a specific use. For example, the material studied here, at a stoichiometric ratio and cured through the selected curing reaction, could be an interesting adhesive with high thermal stability at 140°C.

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