

Kinetics of the Enthalpy Relaxation Process for an Epoxy Network as Determined with a Peak Shift Model

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ABSTRACT: The relaxation kinetics of the epoxy network diglycidyl ether of bisphenol A ($n = 0$) and *m*-xylylenediamine were studied with differential scanning calorimetry experimental data with a shift peak model. Nonlinear parameters were calculated with aging experiments. The nonexponential parameter and the apparent activation energy were found from intrinsic cycles. Adam–Gibbs theory was used to provide a molecular interpretation based on the

enthalpy relaxation. Different assumptions of the variation of specific heat capacity (c_p) were used to determine the macroscopic molar configurational entropy of the system. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2003–2008, 2005

Key words: differential scanning calorimetry (DSC); kinetics (polym.); modeling; relaxation; resins

INTRODUCTION

Methods based on the study of the physical aging process are together an indispensable tool for understanding the behavior of polymers. Characteristic kinetic parameters of the structural relaxation or physical aging can be used to show both nonlinear and nonexponential behavior.^{1,2} Calorimetric techniques have been used mostly to study these relaxation processes. Nonlinear behavior is depicted by the Tool–Narayanaswamy–Moynihan (TNM) equation:^{3–5}

$$\tau = \tau_0 e^{\frac{x \Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f}} \quad (1)$$

where τ_0 is the relaxation time, T is the aging temperature, x is the nonlinear parameter, Δh^* is apparent activation energy, T_f is the fictive temperature, and R is the gas constant. The temperature and structure are linked to the relaxation time and Δh^* through x . The nonexponential behavior is an outcome of the distribution of relaxation times that may be introduced to a Williams–Watts function.⁶ In a previous article,⁷ this equation was used to calculate the nonexponential parameter (β), which is related to the width of the distribution of relaxation times. The estimation of three characteristic parameters, x , Δh^* , and β , provides

valuable information about the crosslinked structure of polymers.

In this study, we studied the relaxation kinetics of the epoxy network diglycidyl ether of bisphenol A (BADGE; $n = 0$) and *m*-xylylenediamine (*m*-XDA) from differential scanning calorimetry (DSC) experimental data with a shift peak model. x was calculated with aging experiments. β and Δh^* were found from intrinsic cycles. Adam–Gibbs theory was used to provide a molecular interpretation based on the enthalpy relaxation.⁸ Different assumptions of the variation of c_p were used to determine the macroscopic molar configurational entropy of the system [$S_c(T)$].

EXPERIMENTAL

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.^{9,10} The curing agent was *m*-XDA (Aldrich Chemical Co., Milwaukee, WI) with an equivalent molecular weight of 31.2 g/equiv.

The experimental methodology (samples preparation and techniques) depicted in a previous article¹¹ allowed us to obtain the DSC aging data. These experiments were used to calculate x .

Δh^* and β were calculated with intrinsic cycles that involved cooling experiments from a upper transition temperature at different cooling rates (q_1 's), 0.5, 0.75, 1, 2.5, 5, and 7°C/min, in the DSC. After the cooling experiments, the materials were reheated at a heating rate (q_2) of 10°C/min, from which a T_f was calculated corresponding to each q_1 .

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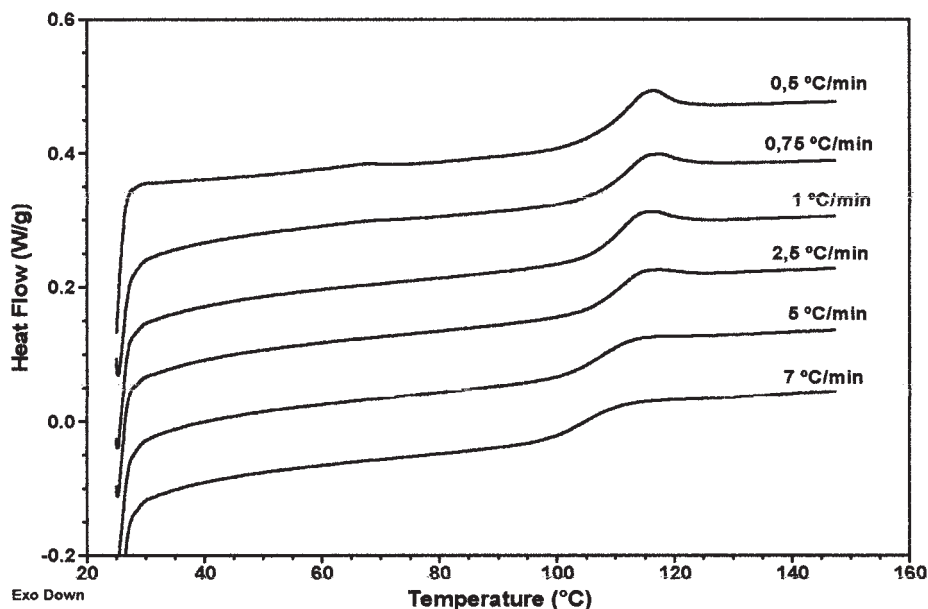


Figure 1 DSC curves obtained at $q_2 = 10^\circ\text{C}/\text{min}$ after the sample was cooled at different q_1 's.

RESULTS AND DISCUSSION

Δh^* was calculated with the equation proposed by Moynihan et al.:⁵

$$\frac{\Delta h^*}{R} = - \left[\frac{\partial \ln|q_1|}{\partial(1/T_f)} \right]_{\Delta H_0} \quad (2)$$

where T_f is the fictive temperature for each q_1 and ΔH_0 is the maximum relaxation enthalpy.

Figure 1 shows the DSC data obtained at a q_2 of $10^\circ\text{C}/\text{min}$ after the sample was cooled at different q_1 's. The T_f values calculated with these DSC curves are given in Table I.

The linear fitting of $\log q_1$'s versus $1/T_f$ allowed us to calculate from the slope the value of Δh^* . The value obtained for the slope $\Delta h^*/R$ was 159.35 kK. Compared to the activation energy for similar epoxy systems,^{1,2} this value was higher. The higher value indicated a large number of chain segments in the relaxation process.

TABLE I
 T_f Values at Different q_1 Values

q_1 (K/min)	T_f (K)
0.5	372.7
0.75	373.3
1	373.9
2.5	374.4
5	374.8
7	375.0

x was calculated from the aging experiment results by the peak shift method,^{1,12} where the following dimensionless peak shift was obtained:

$$\hat{S}(\bar{D}) = \Delta c_p \left(\frac{\partial T_p}{\partial \Delta h} \right)_{q_1, q_2, T_a} \quad (3)$$

where Δc_p is the specific heat capacity, T_p is a maximum peak temperature, T_a is the aging time and Δh is a relaxation enthalpy.

The following equation is a function of x , where $F(x)$ is a dimensionless function independent of distribution of relaxation times:

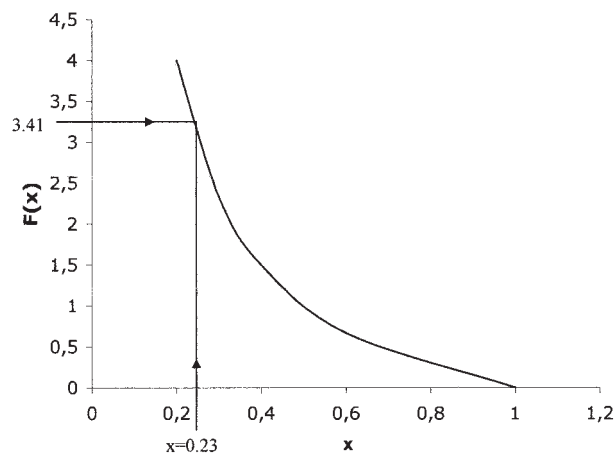


Figure 2 Master curve depicting the variation of $F(x)$ versus x .

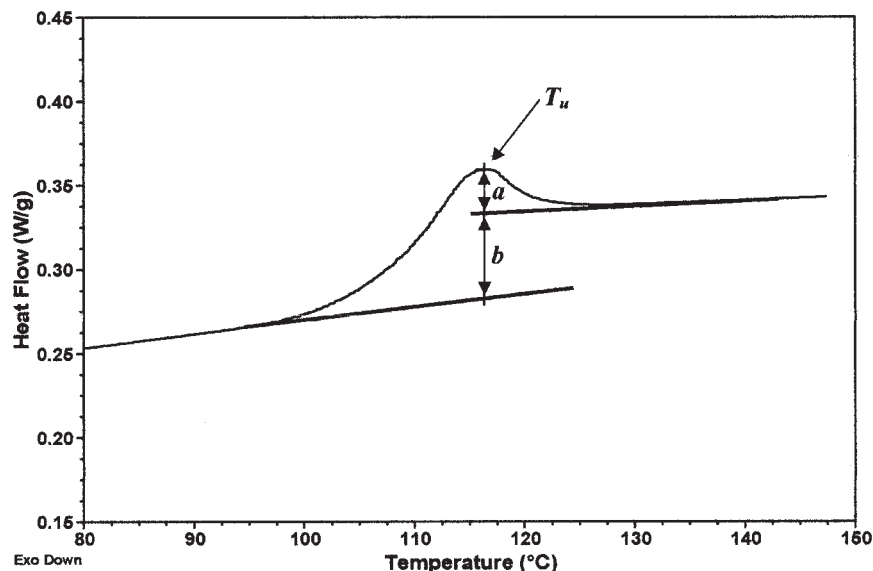


Figure 3 Curve, with q_1 of $0.5^\circ\text{C}/\text{min}$, used for the estimation of $c_{p,u}^N$ through the experimental values a and b . T_u is indicated in the plot.

$$F(x) = \hat{s}(\bar{D}) \quad (4)$$

$F(x)$ was calculated theoretically from a master curve and allowed us to calculate the x parameter, as shown in Figure 2. From the values of $\Delta c_p = 0.31 \text{ J g}^{-1} \cdot \text{K}^{-1}$ and

$$\left(\frac{\partial T_p}{\partial \Delta h} \right)_{q_1, q_2, T_a} = 11.16 \text{ g/J}$$

calculated for our epoxy system $\hat{s}(\bar{D}) = F(x) = 3.41$ and from the dependence of $F(x)$ on x (Fig. 2), we calculated a value of $x = 0.23$, which was close to the result obtained by Montserrat et al.² for ethylenediamine (FEDA) and was in good agreement with the value obtained in a previous article⁷ with the Kovacs and Hutchinson equation.¹³

From these intrinsic cycles (Fig. 1), where the upper peak showed a dependence on q_1 , a normalized upper peak height ($c_{p,u}^N$) could be defined:¹⁴

$$c_{p,u}^N = \frac{c_{p,u} - c_{p,g}}{c_{p,l} - c_{p,g}} = \frac{a + b}{b} \quad (5)$$

where $c_{p,u}$ is the value of c_p at the upper peak temperature (T_u) and $c_{p,l}$ and $c_{p,g}$ are the values of c_p corresponding to the equilibrium liquid and the glassy states, respectively, extrapolated to the upper peak. $c_{p,u}^N$ was obtained through the experimental measurements of the values a and b , as shown in Figure 3.

In Figure 4, the dependence between $c_{p,u}^N$ and the quotient between q_1 and q_2 (q_1/q_2) for these epoxy system are shown. Comparison of the theoretical

curves of $c_{p,u}^N$ corresponding to the Kohlrausch-Williams-Watts (KWW) function⁶ for $x = 0.2$ with the experimental data allowed us to estimate β , which had a value close to 0.3. This value for β was in good agreement with those obtained by Lee and McKenna,¹⁵ Montserrat et al.,² Morancho and Salla,¹⁶ and Hutchinson et al.¹⁷

Adam-Gibbs theory⁸ provided the molecular interpretation of the material based on the fact that the enthalpy relaxation involved cooperative rearrangements of main-chain molecular segments in the case of linear polymers. If a cooperative rearrangement region consists of z molecular segments, the activation energy for a transition from one state to the other one

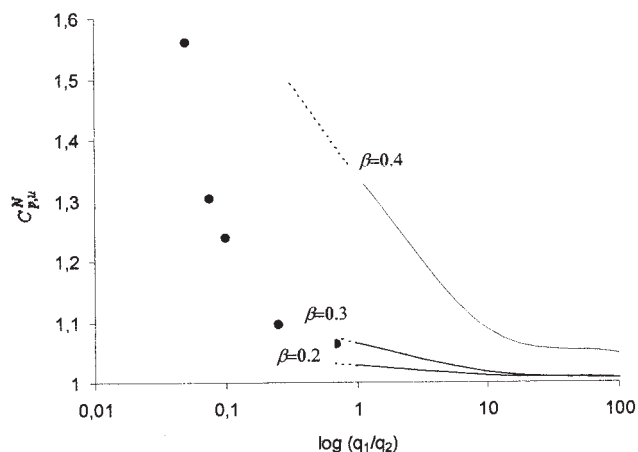


Figure 4 Variation of $c_{p,u}^N$ with q_1/q_2 . Full lines represent the theoretical variation for different values of β . Circles represent the experimental data for $x = 0.2$.

TABLE II
Values of Adam–Gibbs Parameters with Hyperbolic Variation Assumed for $\Delta c_p = CT_2/T$

B (kK)	T_2 (K)	T_g/T_2	C (J g ⁻¹ K ⁻¹)	$N_A S_c^* \Delta\mu/k$ (kJ g ⁻¹)	$S_c(T_g)$ (J g ⁻¹ K ⁻¹)	$z^*(T_g) \Delta\mu/k$ (kK)	$T_g - T_2$ (K)
6.37	302.26	1.25	0.38	2.435	0.072	33.68	75.56

(E) may be determined as $E = z\Delta\mu$, where $\Delta\mu$ is the energy hindering the motion of each segment. This theory shows that there is a lower limit (z^*), which may be determined by the critical configurational entropy (s_c^*) and by $S_c(T)$, as follows:

$$z^*(T) = \frac{N_A S_c^*}{S_c(T)} \quad (6)$$

where N_A is Avogadro's number.

If it is assumed that the change in specific heat capacity at the glass-transition temperature (T_g) is configurational, $S_c(T_g)$ may be written as:

$$S_c = \int_{T_0}^T \frac{\Delta c_p(T)}{T} dT \quad (7)$$

If the configurational entropy in the glassy state is a function of T_f , the relaxation time is a function of both temperature and structure:

$$\tau(T, T_f) = A e^{(N_A S_c^* \Delta\mu / k T S_c(T_f))} \quad (8)$$

where k is Boltzmann's constant.

The evaluation of $S_c(T)$ from eq. (7) requires a knowledge of the temperature dependence of the variation of heat capacity. If one considers a hyperbolic variation of c_p ($\Delta c_p = CT_2/T$), eq. (8) can be rewritten as

$$\tau(T, T_f) = A e^{\left[\frac{B}{T \left(1 - \frac{T_2}{T_f} \right)} \right]} \quad (9)$$

where

$$B = \frac{N_A S_c^* \Delta\mu}{kC} \quad (10)$$

If the TNM equation (equation 1) and the nonlinear Adam–Gibbs expression [eq. (9)] are compared, the parameters from the two models may be obtained:

$$x \approx 1 - \frac{T_2}{T_f} \quad (11)$$

$$\frac{\Delta h^*}{R} \approx \frac{B}{x^2} \quad (12)$$

It is possible to calculate the nonlinear Adam–Gibbs parameters B and T_2 from the experimental parameters x , $\Delta h^*/R$, and T_f . Table II shows the Adam–Gibbs parameters and related values. The value of B was close to that obtained by Montserrat et al.² for FEDA. The value of T_2 was much below T_g and close to those obtained by Montserrat and coworkers.^{1,2} The experimental value of $T_g - T_2$ was in good agreement with the WLF value, which rarely exceeds 100 K, and its value was 51.6 K. On the other hand, $S_c(T)$ was determined from $z^*(T_g) \Delta\mu/k$, which could be calculated from eqs. (6) and (10).

If one uses the assumption $\Delta c_p = C' = \text{Constant}$, the following equations may be used to calculate the Adam–Gibbs parameters B' and T_2 :

$$\frac{x}{1-x} \approx \ln\left(\frac{T_f}{T_2}\right) \quad (13)$$

$$B' \approx \frac{x^2}{(1-x)} \frac{\Delta h^*}{R} \quad (14)$$

Table III shows the Adam–Gibbs parameters and related values with a constant variation of c_p assumed. The value of $T_g - T_2$ was close to the upper value of the Williams-Lander-Ferry (WLF) value. $S_c(T_g)$ and $z^*(T_g) \Delta\mu/k$ were independent of the temperature dependence of Δc_p . The value of T_2 was similar to that

TABLE III
Values of Adam–Gibbs Parameters with $\Delta c_p = C'$ Assumed

B' (kK)	T_2 (K)	T_g/T_2	C (J g ⁻¹ K ⁻¹)	$N_A S_c^* \Delta\mu/k$ (kJ/g)	$S_c(T_g)$ (J g ⁻¹ K ⁻¹)	$z^*(T_g) \Delta\mu/k$ (kK)	$T_g - T_2$ (K)
7.97	294.25	1.28	0.31	2.438	0.068	36.02	83.57

TABLE IV
Values of Adam–Gibbs Parameters with $T_2 = T_g - 51.6$ K and Hyperbolic Variation for $\Delta c_p = CT_2/T$ Assumed

B' (kK)	T_2 (K)	T_g/T_2	C' (J g ⁻¹ K ⁻¹)	$N_A s_c^* \Delta\mu/k$ (kJ/g ⁻¹)	S_c (T_g) (J g ⁻¹ K ⁻¹)	$z^*(T_g)\Delta\mu/k$ (kK)	$T_g - T_2$ (K)
2.97	326.22	1.16	0.36	1.051	0.049	21.53	51.60

TABLE V
Values of Adam–Gibbs Parameters with $T_2 = T_g - 51.6$ K and $\Delta c_p = C'$ Assumed

B' (kK)	T_2 (K)	T_g/T_2	C (J g ⁻¹ K ⁻¹)	$N_A s_c^* \Delta\mu/k$ (kJ/g)	$S_c(T_g)$ (J g ⁻¹ K ⁻¹)	$z^*(T_g)\Delta\mu/k$ (kK)	$T_g - T_2$ (K)
3.44	326.22	1.16	0.31	1.054	0.042	24.94	51.60

TABLE VI
Values of $\Delta\mu/k$ and $z^*(T_g)$ with Two Possible Values for W^* Assumed

$\Delta c_p = CT_2/T$				$\Delta c_p = CT_2/T, T_2 = T_g - 51.6$ K			
$W^* = 2^3$		$W^* = 2^4$		$W^* = 2^3$		$W^* = 2^4$	
$\Delta\mu/k$	$z^*(T_g)$	$\Delta\mu/k$	$z^*(T_g)$	$\Delta\mu/k$	$z^*(T_g)$	$\Delta\mu/k$	$z^*(T_g)$
4.8	7	3.6	9.3	2.1	12	1.6	16

obtained with the hyperbolic variation, whereas the values obtained by Montserrat and coworkers^{1,2} for similar systems differed significantly.

We considered the Adam–Gibbs parameters by assuming a value of T_2 of $T_g - 51.6$ K and taking $T_f = T_{g'}$ and we calculated these values from eqs. (11) and (12) assuming hyperbolic variation. These results are shown in Table IV. Table V shows that similar data was obtained from eqs. (13) and (14) if one assumes that $\Delta c_p = C'$. As shown in Tables IV and V, the values of $S_c(T)$ and $z^*(T_g)\Delta\mu/k$ were lower than those shown in Tables II and III. This behavior was observed by Montserrat and coworkers^{1,2} for different epoxy systems.

The configurational entropy of the little chain segment was calculated from

$$s_c^* = k \ln W^* \quad (15)$$

where W^* is the minimum number of configurations needed for cooperative rearrangement. When we considered a value of W^* of 2^3 as proposed by Hodge^{18–20} for linear polymers and a value of 2^4 proposed by Montserrat et al.² for crosslinked polymers, we calculated $\Delta\mu/k$ and $z^*(T_g)$ with the values obtained in Tables II and IV. We based our calculations on the unit related to segmental mobility known as a *bead*. A bead has a heat capacity of 11 J mol⁻¹ K⁻¹. To calculate $\Delta\mu/k$ and $z^*(T_g)$ for one bead, we defined the molecular weight of the constitutional repeating unit as the sum of 173.6 g for the epoxy and 31.2 g for the *m*-XDA. This gave us a value of 204.8 g/mol. The specific heat capacity ($\Delta c_p = 0.31$ J g⁻¹ K⁻¹) obtained in a previous

study¹¹ could be converted to units of Joules per mole per degree Kelvin as 63.5. With this last value, we determine that the number of beads per constitutional repeating unit was approximately 6 and that the molecular weight was 34.1 g/mol of bead. Table VI shows the values of $\Delta\mu/k$ and $z^*(T_g)$ for one bead. The value of $\Delta\mu/k$ was much lower for $W^* = 2^4$, corresponding to crosslinked polymers; therefore, the relaxation process was easier than a for a linear polymer. The minimum size of a cooperative rearrangements region (z^*) increased to $W^* = 2^4$ because the number of molecular segments increases in crosslinked polymers.

CONCLUSIONS

The relaxation parameters were evaluated by the peak shift method. Δh^* was higher than those of similar epoxy systems,^{1,2} which indicated a large number of chain segments in the relaxation process. x was close to the value obtained in a previous study⁷ with the Kovacs and Hutchinson equation.¹³

Adam–Gibbs theory was used to provide a molecular interpretation. The hyperbolic and constant assumptions of the variation of c_p gave low values for T_2 , around 80 K below T_g , and high values for $S_c(T)$, which seemed unrealistic. However, the assumption of a value of T_2 equal to $T_g - 51.6$ gave lower values for $S_c(T)$.

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