Kinetic Analysis of Relaxation Process for the Epoxy Network Diglycidyl Ether of Bisphenol A/*m*-Xylylenediamine

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ABSTRACT: The relaxation kinetic of the epoxy network diglycidyl ether of bisphenol A (BADGE $n = 0$) and *m*-xylylenediamine (*m*-XDA) was analyzed from DSC experimental data, using different theoretical models. Based on a Petrie model, which involved separate contributions of temperature and structure, three characteristic parameters were calculated: a preexponential factor A, an apparent activation energy E_H, and a parameter C, which indicate the dependency of relaxation time on structure. This model allowed us to calculate the relaxation function at different ageing temperatures. Another method used to study a relaxation ki-netic was the Kovacs–Hutchinson model, which takes into account the dependency of the relaxation time on temperature and structure. The last model used was a two-parameter equation from Williams–Watts, where the relaxation time is independent of temperature. Using data of characteristic times a master curve for the relaxation function was obtained. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1591–1595, 2005

Key words: resins; ageing; kinetics (polym.); relaxation; networks

INTRODUCTION

The changes produced by physical ageing show that the behavior of a thermoset polymer at temperatures below the glass transition are normally the result of slow relaxation of the glass from its initial nonequilibrium state toward its final thermodynamic equilibrium state.[1]

The properties of the network strongly influence the behavior of epoxy resin in such diverse applications as the automobile trade, building, surfboards, and golf clubs. Physical ageing can affect the degree of crosslinking of the epoxy resins and therefore decrease the long-term stability of the network, which is an important aspect of the performance of the material. This process is less obvious than crosslinking, but may lead to important changes in network properties such as embrittlement.

Many authors have recently studied the physical ageing of epoxy resins and blends by DSC, DMA, and other techniques. Gómez Ribelle et al.[2] examined the ageing behavior of poly(vinyl chloride) samples, both unplasticized and plasticized with dioctyl phthalate, by DSC. It was observed that the presence of plasticizer accelerates the ageing process. G'Sell and McKenna[3] measured the ageing of diglycidyl ether of bisphenol A amine-terminated poly(propylene oxide) network by measurements of the yield stress in uniaxial compression. Montserrat[4] related the physical ageing process of an anhydride fully cured epoxy resin monitored by DSC. The temperature dependency of enthalpy relaxation was analyzed in terms of the relaxation time and fictive temperature. Muzeau et al.[5] studied the ageing effects of poly(methyl methacrylate) by DSC and DMA and their influence over the quenching rate, time, and temperature of ageing. Aref-Azar et al.[6] investigated the thermal relaxation of polyethylene terephthalate using a range of thermal analytical techniques such as DSC, DMTA, and dielectric thermal analysis (DETA). Barral et al.[7] investigated the physical ageing of a terafunctional-phenol novolac epoxy mixture cured with diamine by DSC and DMA. Song[8] introduced modulated-temperature differential scanning calorimetry (M-TDSC) to study the process of ageing in polymers. In a previous article[9] we reported our study of the physical ageing of the epoxy network diglycidyl ether of bisphenol A (BADGE $n = 0$)/*m*-xylylenediamine (*m*-XDA). Herein the relaxation enthalpy was calculated using DSC data.

In this article we used the same DSC ageing data to analyze the kinetic of enthalpy relaxation process for this epoxy system. The study of the kinetic analysis of relaxation process in an epoxy resin makes it necessary to define a relaxation function $\phi(t)$ as a function of relaxation enthalpy of physical ageing. This relaxation function represents the kinetics of the epoxy resin approaching the equilibrium and can be defined by

$$\phi(t) = \frac{h(T_a, t_a) - h_\infty(T_a)}{h(T_a,0) - h_\infty(T_a)} = \frac{\delta}{\Delta h_\infty} = 1 - \frac{\Delta h}{\Delta h_\infty} \quad (1)$$

where T_a is the ageing temperature; t_a is the ageing time; δ (excess enthalpy) is the difference between the enthalpy of the aged glass $h(T_a, t_a)$ and the enthalpy at equilibrium $h_\infty(T_a)$ at the same ageing time; Δh_∞ is the limiting relaxation enthalpy; and Δh is the relaxation enthalpy.

EXPERIMENTAL

The epoxy resin was a commercial diglycidyl ether of bisphenol A (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.[10,11] The curing agent was *m*-xylylenediamine (*m*-XDA; Aldrich Chemical Co., Milwaukee, WI) with an equivalent molecular weight of 31.2 g/equiv.

Experimental methodology depicted in a previous report[9] allowed us to obtain the DSC ageing data used herein.

RESULTS AND DISCUSSION

The kinetic parameters of the relaxation process can be obtained using a phenomenologic model proposed by Cowie and Ferguson[12]:

$$\frac{d\phi(t)}{dt} = -\frac{\phi(t)}{\tau_{\text{eff}}(t)} \quad (2)$$

In this equation $\tau_{\text{eff}}(t)$ represents the effective relaxation time and can be calculated from the experimental results as follows:

$$\frac{1}{\tau_{\text{eff}}(t)} = -\frac{1}{\phi(t)}\frac{d\phi(t)}{dt} \quad (3)$$

where $d\phi(t)/dt$ is the instantaneous rate of approach toward equilibrium, assuming that the effective relaxation time depends on the ageing temperature and ageing time and on the glass structure. For a given temperature there is an ageing time t_a that allows us to calculate the effective relaxation time as
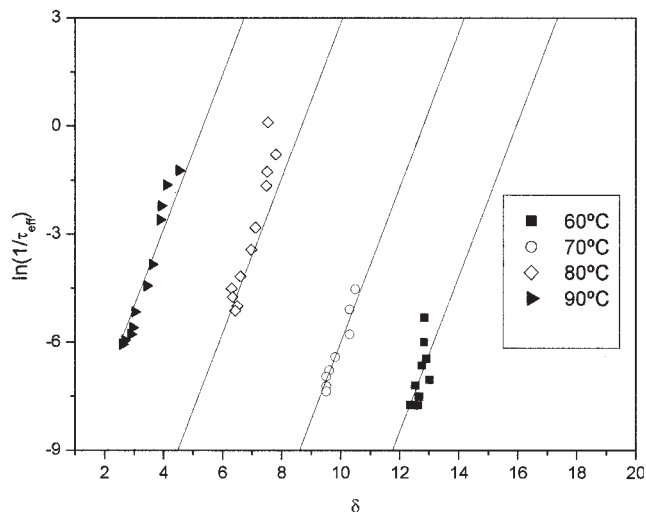

Figure 1 Plots of ln $1/\tau_{\text{eff}}$ versus excess enthalpy for different ageing temperatures. Solid lines are the values predicted by a Petrie model.

$$\tau_{\text{eff}}(t_a) = -\frac{t_a}{\ln \phi(t_a)} \quad (4)$$

Figure 1 shows the plots of rate of relaxation $\ln(1/\tau_{\text{eff}})$ versus excess enthalpy for different ageing temperatures: 60, 70, 80, and 90°C. Equation (4) was used to calculate effective relaxation times $\tau_{\text{eff}}(t_a)$, using eq. (1) to determine the relaxation function values $\phi(t_a)$. The rate of relaxation of this epoxy network decreases as the excess enthalpy decreases for all ageing temperatures. As the system approaches equilibrium, because the relaxation enthalpy is practically constant, the rate of relaxation decreases.

A Petrie model[13] was applied involving separate temperature and excess enthalpy dependency:

$$\tau_{\text{eff}} = A e^{E_H/RT} e^{-C\delta} \quad (5)$$

where A is a preexponential factor, E_H is the apparent activation energy, and C is a parameter that shows the dependency of relaxation time on structure. Equation (5) can be rewritten as

$$\ln \tau_{\text{eff}} = \ln A + \frac{E_H}{RT} - C\delta \quad (6)$$

The linear fitting of $\ln \tau_{\text{eff}}$ versus δ at all ageing temperatures makes it possible to calculate the three characteristic parameters: $\ln A = -241.5 \pm 26.6$, $E_H = 764.8 \pm 83$ kJ/mol, and $C = 2.1 \pm 0.3$ g/J. This single method gives a value for E_H similar to that of other systems calculated following this model.[4,12,14,15] The apparent activation energy has a lower value, which indicated an easier structural relaxation, because this epoxy system is characterized by large dis-
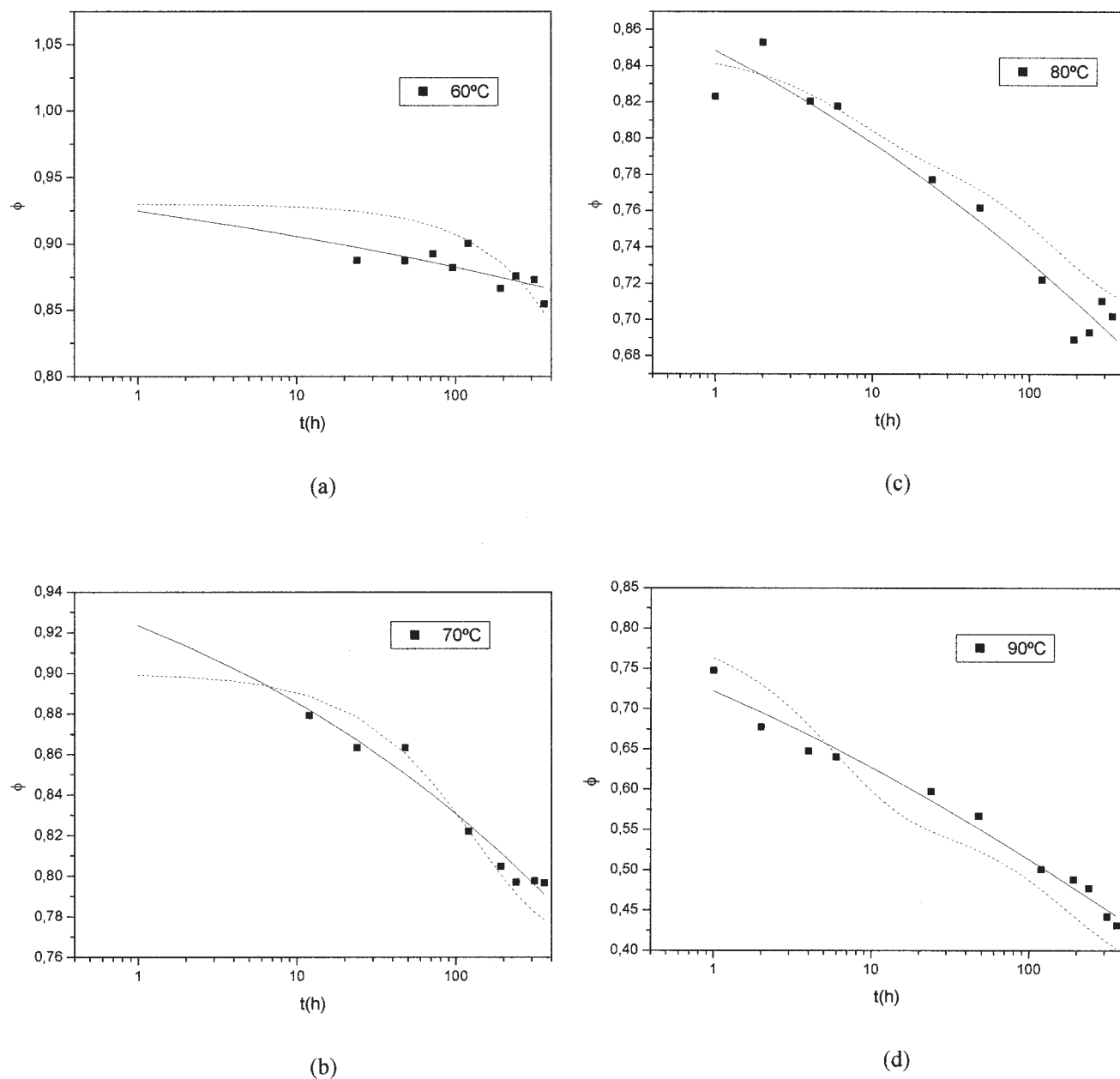
Figure 2 Relaxation function versus logarithm of time: (a) at 60°C; (b) at 70°C; (c) at 80°C; and (d) at 90°C. Solid line represents the predicted values according to a Petrie model. Dashed line shows the data obtained to the Williams–Watts function.

tances between crosslinks that produce a larger free volume.

Using these parameters we can recalculate the value of rate of relaxation $\ln(1/\tau_{\text{eff}})$. These values are represented in Figure 1 as solid lines. There is a good agreement between the experimental and model values for all ageing temperatures. The discrepancies are smaller as the system approaches equilibrium for all temperatures. The behavior of these epoxy systems is not the same as that observed by other authors for amorphous polymers,[4,14] where the discrepancies are substantial where sub-T_g peaks appear ($\sim$ 60°C).

Figure 2 shows the relaxation function versus ageing times. The relaxation function was calculated using values of limiting relaxation enthalpy and relaxation enthalpy obtained in our previous study.[9] This function tends to values close to zero for longer times at 90°C. At lower temperatures this behavior cannot be observed, probably because of an overestimation of limiting relaxation enthalpy. The limiting relaxation enthalpies calculated in a previous study using a theoretical model show discrepancies with values calculated graphically.[9]

The relaxation function values obtained using Petrie model data are shown in Figure 2 (solid lines). It can be observed that deviations from experimental data

TABLE I
Characteristic Times t_c and β Calculated Using a
Williams–Watts Function for Different
Ageing Temperatures (T_a)

T_a (°C)	β	$\ln t_c$ (t_c in h)
60	0.102 ± 0.07	25.07 ± 0.20
70	0.123 ± 0.04	15.80 ± 0.10
80	0.139 ± 0.02	12.98 ± 0.03
90	0.156 ± 0.01	7.21 ± 0.01

are >60°C, where endothermic peaks appear below the glass-transition temperature. A good agreement is observed at 70, 80, and 90°C. This behavior is similar to that predicted by Montserrat.[4] The relaxation time in equilibrium (τ_r) at an arbitrary temperature, which is taken as the glass-transition temperature,[9] can be calculated using eq. (6), taking into account that δ is zero. The value obtained is around 7.5 h, which is not possible because in a previous report[9] it was observed that the equilibrium is achieved above 360 h.

For similar systems Kovacs and Hutchinson[16] used an equation where the relaxation time involves separate temperature and structure dependencies:

$$\tau = \tau_r e^{[\theta(T_r - T)]} e^{[-(1-x)\theta\delta/\Delta_{c_p}]} \tag{7}$$

where $\theta = E_H/RT_g^2$, taking E_H as the value obtained using Petrie's model and $T_g = 378$ K, a value obtained in our previous study.[9] This parameter has a value of 0.64 K^{-1}, which is close to the universal parameter of Williams–Lander–Ferry, whose value for polymer glasses is 0.768 K^{-1} and lower than that obtained by Monserrat.[4] In eq. (7) there appears a structural parameter x that measures the relative contribution of temperature to relaxation time and parameter C. This parameter can be calculated using the equation: $x = 1 - (C\Delta c_p/\theta)$, where $\Delta c_p = 0.31$ J/gK was previously calculated.[9] The estimated value of x is close to zero. These data are lower than those obtained by Montserrat[4] for epoxy resin. Moreover, this value is too low compared to that of other studies, which give a value of 0.42.[17] This disagreement can be inferred because the estimation of the data is based on the assumption that there is a single relaxation model instead of a distribution of relaxation times.

Other methods that describe the structural relaxation process have been applied by several authors in polymers.[2,4,12] This method is based on an equation called Williams–Watts function[18] or a two-parameter equation:

$$\phi(t_a) = e^{[-(t_a/t_c)]^\beta} \tag{8}$$

where β is a nonexponential parameter ($0 < \beta \leq 1$), related to the width of the underlying relaxation time spectrum for the enthalpic ageing process; and t_c is a characteristic time. The characteristic time t_c and the nonexponential parameter β do not repre-

sent a specific molecular process. These parameters were calculated from a nonlinear fitting of $\ln \phi(t_a)$ versus t, where $\phi(t_a)$ was calculated using eq. (1). The Williams–Watts model was applied to depict the shape of the experimental relaxation function. Table I shows these parameters and the standard errors corresponding to different ageing temperatures. The values of β are in the range between 0.10 and 0.16, in good agreement with values obtained by other authors for similar systems.[4,12,19] These values are slightly dependent on ageing temperatures. This slow increase in temperatures indicates a faster approach to equilibrium.

The characteristic time t_c decreases as the ageing temperature increases because higher ageing temperatures make it easier to achieve the thermodynamics equilibrium. Several authors reported a similar tendency in amorphous polymers and blends.[4,19,20]

Figure 2 shows the values obtained using a Williams–Watts model (dashed lines). A worse fit to experimental data can be observed for all ageing temperatures. Therefore, the Petrie model, taking into account the dependencies of temperature and structure, seems to better describe the structural relaxation process.

The logarithm of characteristic time can be considered as a shift factor of ageing time.[4,12,19,21] Figure 3 shows a plot of $\phi(t')$ versus $\log t'$, where t' is a reduced ageing time that was previously calculated as $t' = t_a/t_c$. This plot can be considered as a master curve. From this master curve, values of relaxation function may be obtained at any ageing temperature.

CONCLUSIONS

The relaxation kinetic was studied using different methods. The Petrie model makes it possible to calculate the relaxation function at different ageing temper-
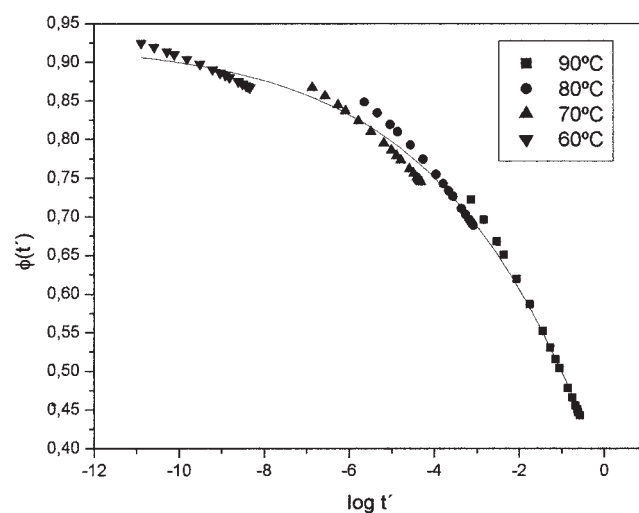

Figure 3   Relaxation function versus $\log t'$.

atures. These data are in good agreement with experimental relaxation data at all ageing temperatures, where endothermic peaks appear above the glass-transition temperature.

Using the Kovacs–Hutchinson model, we obtained a value of structural parameter x too low compared to that of other studies for similar systems. This model was thus not applied to study the kinetic relaxation of this epoxy system.

Another model used to study the relaxation kinetic is a Williams–Watts model that seems to describe more poorly the behavior of experimental relaxation function; besides it does not take into account the dependency of the relaxation time on temperature and structure. Moreover, this model seems to describe the decay of the experimental relaxation function during the ageing process.

The application of characteristic time allows us to obtain values of relaxation function independently of temperature. The plot of $\phi(t')$ versus log t' is considered to be a master curve because the relaxation function may be obtained at any ageing temperature.

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