

Comparative Study of the Physical Aging of the Epoxy Systems BADGE $n = 0/m$ -XDA and BADGE $n = 0/m$ -XDA/PEI

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ABSTRACT: The physical aging of the epoxy network consisting of a diglycidyl ether of bisphenol A, *m*-xylylenediamine, and polyetherimide was studied by differential scanning calorimetry. The glass transition temperature and the variation of the specific heat capacities have been calculated using the method, based on the intersection of both enthalpy–temperature lines for glassy and liquid states. The apparent activation energy (E_H) was calculated using a

single method that involved separate temperature and excess enthalpy dependency. All calorimetric data were compared with those obtained for the epoxy network without thermoplastic. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3931–3935, 2006

Key words: epoxy-amine reactions; physical aging; relaxation enthalpy

INTRODUCTION

Although epoxy resins are used in different industrial sectors, one of the major problems is its fragile structure that can be improved by the introduction of a second component that is capable of phase separation, such as rubbers and thermoplastic polymers. Thermoplastic polymers are inherently tough and can reduce the brittleness of the resin, without affecting their advantageous ultimate properties.^{1–5}

Another handicap of the epoxy system without thermoplastic is its higher amount of water kept in the system and the originated plasticization effect that produces a decrease of glass transition temperature. Introducing a thermoplastic causes the disappearance of a part of polar groups of the epoxy network that lowers the water uptake.

One of the thermoplastics used in epoxy formulations is polyetherimide (PEI), which is a clear, amorphous high performance polymer. Some authors like Girard et al.⁶ have used this PEI to toughen epoxy resin, and found that the effective improvement in toughness is only obtained at high fractions of the thermoplastic, where the blends form sponge-like (a dispersion of thermoset-rich particles in a thermoplastic matrix) or sandwich-like (consisting of a dispersion

of macroscopic irregular thermoplastic-rich domains showing a sponge-like structure in a thermoset-rich matrix, exhibiting a dispersion of thermoplastic-rich particles) morphology. Similar results were also reported by other authors.^{7,8}

Physical aging produces structural changes, and shows that the behavior of a thermoset 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.⁹ The physical aging of the blends of PEI has been investigated by Goodwin,¹⁰ Echeverria et al.,¹¹ Simon et al.,¹² and Belana et al.¹³

We have studied the physical aging for this epoxy network diglycidyl ether of bisphenol A (BADGE $n = 0$)/*m*-xylylenediamine (*m*-XDA)/PEI, using calorimetric measurements.

An objective of this study has been to obtain calorimetric parameters (glass transition temperature, specific heat capacity, relaxation enthalpy, etc.) to allow the characterization of physical aging and its kinetic data. Physical aging data are compared with those obtained without thermoplastic in a previous study.¹⁴

EXPERIMENTAL

Materials

The epoxy resin was a commercial diglycidyl ether of bisphenol A (BADGE $n = 0$) (Resin 332, Sigma Chemical Co., St. Louis, USA) with an equivalent molecular

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TABLE I
Different Cooling Rates from Aging Temperature (T_a) in the Range of 40–80°C Until
Cooling ramp
Room Temperature (T_r) $T_0=113^\circ\text{C} \longrightarrow T_r=25^\circ\text{C}$

T_0 (°C)	Cooling rate (°C/min)	T_a (°C)	Cooling rate (°C/min)	$T_a/2$	Cooling rate (°C/min)	T_r (°C)
113	34	80	26	40	23	25
	32	70	25	35		
	30	60	24	30		
	34	50	23	25		
	28	40	22	20		

weight of 173.6 g/equiv, as determined by wet analysis.^{15,16} The curing agent was *m*-xylylenediamine (*m*-XDA, Aldrich Chemical Co., Milwaukee, WI) with an equivalent molecular weight of 31.2 g/equiv. The used thermoplastic was a clear, amorphous high performance polymer named polyetherimide (PEI, Aldrich Chemical Co.).

Sample preparation

In the first step, 2.5 g of PEI was dissolved in 50 mL of methane dichloride, with continuous stirring at room temperature. In the second step, epoxy resin and the dissolution of PEI were carefully and homogeneously mixed in a thermostatic bath with continuous stirring, and the mixture was heated to 90°C in a thermostatic bath during 4 h, until dichloride methane was evaporated. Then, the curing agent (*m*-XDA) was added at a stoichiometric ratio. The mixture was introduced in a cylindrical frame of 6 mm diameter, previously waxed to avoid adherence. After 24 h, at room temperature, the frames were placed for 2 h in an oven at 120°C. Finally, the samples were cut into 6-mm diameter discs, weighing ~10 mg.

Techniques

A differential scanning calorimeter Q100 of TA Instruments was used to obtain all the experimental data reported in this work. Before performing the isothermal aging experiments, the samples were submitted to the following thermal history: the samples encapsulated in aluminum pans were heated in DSC to a temperature (T_0) ~30°C above T_g , during 10 min, to remove any thermal history of the samples. The samples were quenched from T_0 to aging temperatures (T_a), and then from this last temperature to $T_a/2$, and finally to a room temperature (T_r) of ~25°C. Table I shows different cooling rates from T_0 to T_a (40, 50, 60, 70, and 80°C), from T_a to $T_a/2$, and finally from $T_a/2$ to temperature room. After thermal history has been erased, we use different cooling rates for different aging temperatures. Based on the evidence of DSC

experimental data and data obtained in a previous paper¹⁴ for the same system without thermoplastic, it can be observed that the method applied is useful to reduce experimental scatter because of differences in cool transfer effects. Then the samples, once removed to differential scanning calorimeter, were annealed inside a glass tube in a thermostatic bath at different aging temperatures for different aging times: 24, 48, 72, 120, 192, 200, 240, 288, and 360 h. After annealing, the samples were introduced into the DSC cell, quenched to starting temperature (25°C) and immediately heated until 250°C at 10°C/min. A second scan was made by quenching to room temperature and reheated at 10°C/min, to calculate the relaxation enthalpy. This scan will be used as reference scan.

RESULTS AND DISCUSSION

The average values obtained for the glass transition temperature (T_g) and the variation of the specific heat capacities (Δc_p) were 83.9 ± 0.6 °C and 0.19 ± 0.03 J/g °C, respectively. These values were 20 and 40% lower than those obtained in a previous paper¹⁴ for the system without thermoplastic.

Figure 1 shows DSC thermograms of the aged sys-

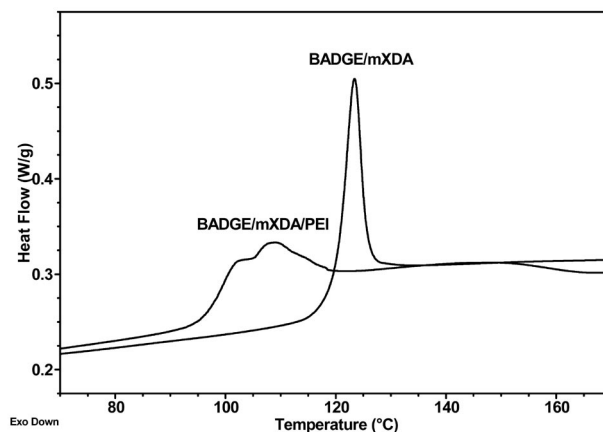


Figure 1 DSC scans of aged systems with and without thermoplastic.

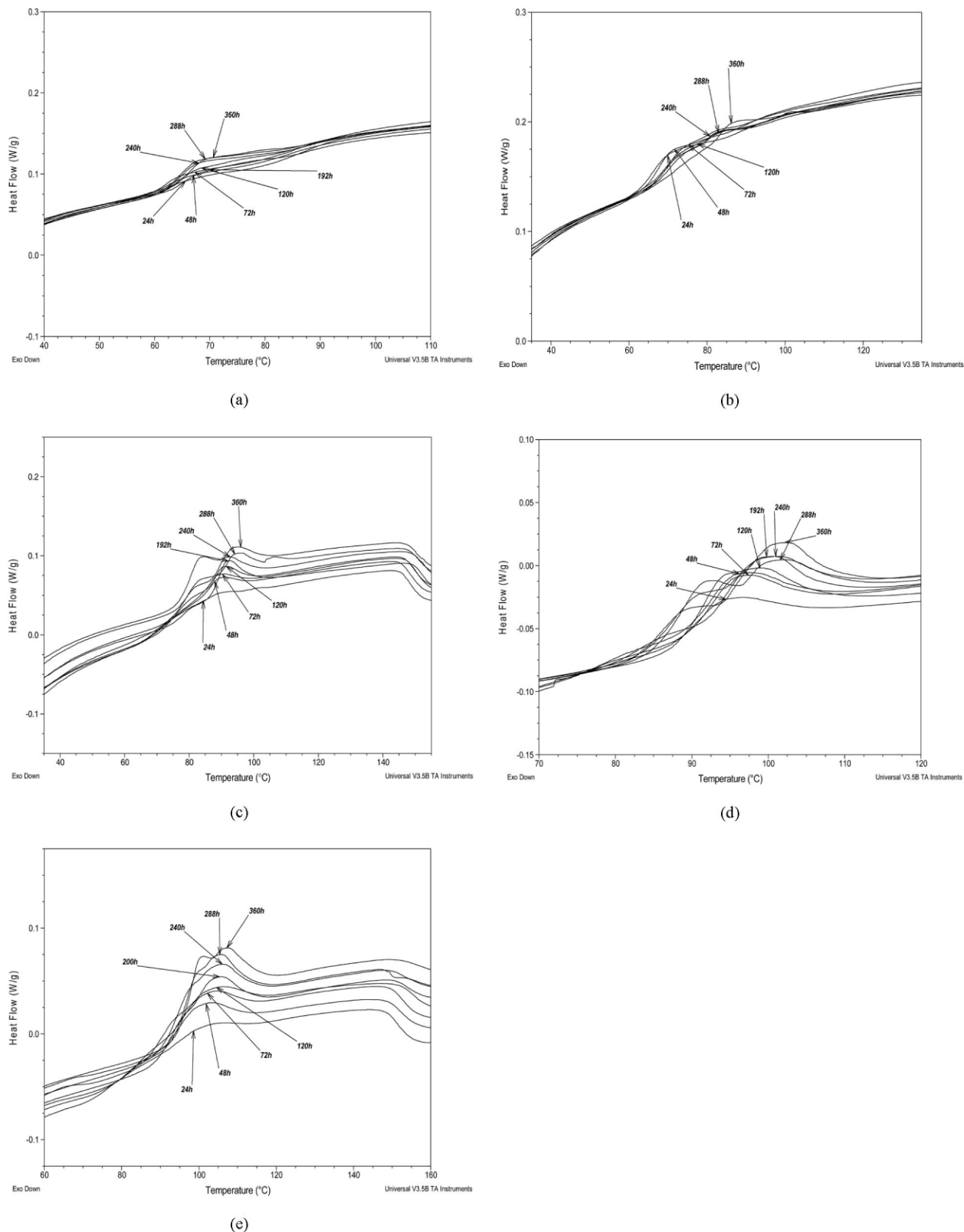


Figure 2 DSC scans of aged sample at (a) 40°C, (b) 50°C, (c) 60°C, (d) 70°C, and (e) 80°C for different aging times.

tems for the same time at temperatures close to $T_{g,r}$ with and without thermoplastic. *m*-XDA is an aliphatic diamine and contains two aliphatic groups with

different positions. PEI can compete with the epoxy to react with the *m*-XDA and exhibit different reactivities. A different structural relaxation can be seen and,

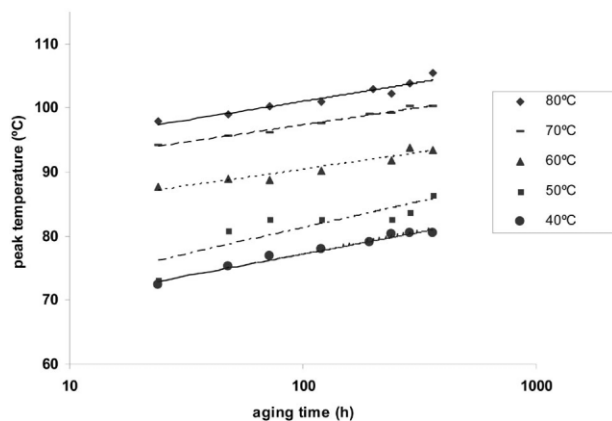


Figure 3 Temperatures of endothermic peak (T_{ep}) versus logarithm of the aging time at different aging temperatures.

for the system with thermoplastic, two peaks appear that can be associated to different ways of structural relaxation caused by a position of the thermoplastic in the epoxy network. Figure 2 shows DSC thermograms of aged system with PEI for different times at different temperatures: (a) 40°C, (b) 50°C, (c) 60°C, (d) 70°C, and (e) 80°C. In these figures, at upper aging temperatures 60, 70, and 80°C, the temperature becomes high enough to afford mobility, and then the network turns to the liquid equilibrium line, producing the T_g -overshoot. At low aging temperatures (40 and 50°C), the endothermic peak can be situated below T_g . This behavior has been observed in the system without thermoplastic and for several authors in similar epoxy systems.^{17–22} The temperature of the endothermic peak increases in intensity with aging temperatures and displaces to higher temperatures with aging time. Figure 3 shows the temperature of endothermic peak (T_{ep}) versus logarithm of the aging time at different aging temperatures. In this figure, a linear increase of T_{ep} with aging time can be seen for all aging temperatures. This behavior is not the same as was observed for the system without thermoplastic and neither is the same as was observed by other authors,^{12,21–23} where the deviation from linearity begins at 10°C below T_g . This linearity behavior can be related to the extension of the molecular chains because of the presence of thermoplastic in the epoxy network, which compensates a lower molecular motion at lower temperatures that cause a deviation from linearity as the aging time increases.

The relaxation enthalpy, Δh , is plotted versus logarithm of aging time in Figure 4, where it can be seen that the enthalpy relaxation increases with aging time. At temperatures below T_g , the relaxation enthalpy decreases with temperature at the same aging times, while for the system without thermoplastic it increases with temperature. Some discrepancies appear for lower times where the values of enthalpy at 40°C are

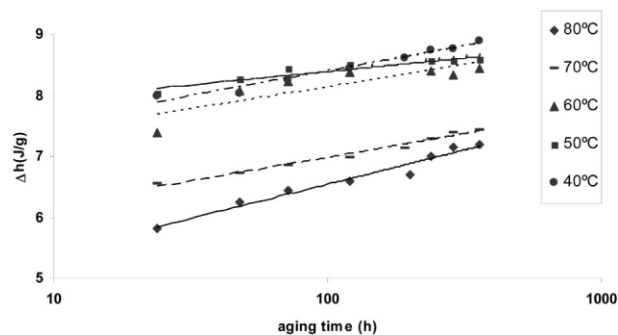


Figure 4 Relaxation enthalpy versus logarithm of the aging time at different aging temperatures.

lower than those obtained at 50°C. This is because the thermoplastic cause to the structural relaxation is slower above all at low aging temperatures. The dependence of enthalpy relaxation seems to follow the relaxation of Bauwens-Crowet and Bauwens²⁴ at 70°C. The relaxation enthalpies increase up to an aging time, where it becomes practically constant because the structural equilibrium is achieved. It is very difficult to achieve experimentally a limiting enthalpy of relaxation (Δh_∞) for each aging temperature. It can be calculated only experimentally for values of aging temperature close to glass transition temperature.^{20,22} This value cannot be determined experimentally in this study, since it increases even after the upper aging time. However, there are several methods that let us calculate (Δh_∞). The two methods, we have selected, have been used previously by us and other authors.^{20,22,25} Table II shows the values of (Δh_∞) at different aging temperatures. The values obtained for both methods present deviations that increase with annealing temperatures. Besides, the values were between 20 and 40%, lower than those obtained for the system without thermoplastic.

The kinetic parameters of the relaxation process can be obtained using a phenomenologic model proposed by Cowie and Ferguson:²⁶

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

TABLE II
Limiting Relaxation Enthalpy Calculated Using Eqs. (3) and (4) at Different Aging Temperatures (T_a)

T_a (°C)	Δh_∞ (J/g) [from eq. (3)]	Δh_∞ (J/g) [from eq. (4)]
40	11.44	8.13
50	10.35	6.28
60	8.76	4.43
70	7.33	2.58
80	3.38	0.73

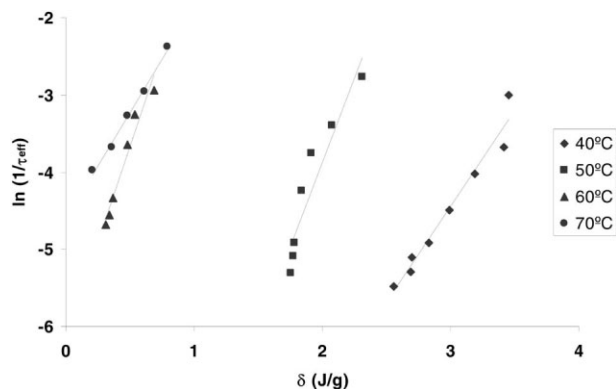


Figure 5 $\ln 1/\tau_{\text{eff}}$ versus excess enthalpy for different aging temperatures. Solid lines are the values predicted by Petrie model.

In this equation, $\phi(t)$ represents a function of relaxation enthalpy and $\tau_{\text{eff}}(t)$ represents the effective relaxation time, and can be calculated from the experimental results. Assuming that the effective relaxation time depends on the aging temperature, and aging time and on the glass structure, and for a given temperature, there is an aging time t_a that allows us to calculate the effective relaxation time as follows:

$$\tau_{\text{eff}}(t_a) = -\frac{t_a}{\ln\phi(t_a)} \quad (2)$$

Figure 5 shows the plots of rate of relaxation $\ln(1/\tau_{\text{eff}})$ versus excess enthalpy for different aging temperatures: 40, 50, 60, and 70°C. The rate of relaxation of this epoxy network decreases as the excess enthalpy decreases for all aging temperatures. A Petrie model²⁷ was applied, involving separate temperature and excess enthalpy dependency:

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

where A is a preexponential factor, E_H is the apparent activation energy, 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 aging time, and C is a parameter that shows the dependency of relaxation time on structure. The linear fitting of $\ln \tau_{\text{eff}}$ versus δ at all aging temperatures makes it possible to calculate the three characteristic parameters: $\ln A = -48 \pm 10$, $E_H = 547 \pm 102$ kJ/mol, and $C = 1.4 \pm 0.3$

g/J. This single method gives a value for E_H similar to that of other systems calculated, following this model.^{22,28–30} The apparent activation energy has a higher value compared to the value obtained for the system without thermoplastic,¹⁴ which indicated a complicated structural relaxation, because this epoxy system is characterized by large distances between crosslinks that produce a larger free volume.

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