Study of the Physical Aging of the Epoxy System BADGE $n = 0$/m-XDA/CaCO$_3$

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ABSTRACT: The physical aging of the epoxy network consisting of a diglycidyl ether of bisphenol A (BADGE $n = 0$), m-xylylenediamine (m-XDA), and calcium carbonate was studied by differential scanning calorimetry. The glass transition temperature and the variation of the specific heat capacities were calculated using the method based on the intersection of both enthalpy–temperature lines for glassy and liquid states. The apparent activation energy 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 filled calcium carbonate. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2456–2461, 2009

Key words: epoxy-amine reactions; physical aging; relaxation enthalpy; CaCO$_3$

INTRODUCTION

Epoxy resins are used in different industrial sectors. One of the main problems is its fragile structure, which can be improved by the introduction of a second component such as fillers. Several commercial fillers are suitable for use with epoxy resins for viscosity control, lower shrinking, lower thermal expansion, and mainly for the lower manufacturing cost. The fillers can be inorganic or organic elements. Usually inert inorganic fillers are used with a particle size of 0.015 µm or higher. Besides, they should be neutral or slightly basic and not to react with the resin or the agent of cured. This requirement avoids the use of some fillers with some classes of hardening. In this study an inorganic filler was used: calcium carbonate (CaCO$_3$).

We studied the physical aging for this epoxy network, diglycidyl ether of bisphenol A (BADGE $n = 0$)/m-xylylenediamine (m-XDA)/calcium carbonate (CaCO$_3$), using calorimetric measurements.

An objective of this study was to obtain calorimetric parameters (glass transition temperature, specific heat capacity, relaxation enthalpy, and so forth) to allow the characterization of physical aging and its kinetic data. Physical aging data are compared with those obtained without filling in a previous study.[1]

EXPERIMENTAL

Materials

The epoxy resin was a commercial diglycidyl ether of bisphenol A (BADGE $n = 0$) (Resin 332, Sigma Chemical, Saint Louis, MO, USA) with an equivalent molecular weight of 173.6 g/equiv, as determined by wet analysis.[2,3] The curing agent was m-XDA (Aldrich Chemical, Milwaukee, WI, USA) with an equivalent molecular weight of 31.2 g/equiv. The filled agent was a white powder, calcium carbonate (Panreac Chemistry Laboratories S.A) [Madrid, Spain]. These products have been used without previous purification for the sample preparation.

Sample Preparation

The resin solidifies easily, and this hinders its handling when making it react with other products; hence, it must be introduced in a stove at 40°C to maintain it in a liquid state. The hardening one stays in a desiccator to avoid hydration, oxidation, or carbonation. It is not necessary to give to the calcium carbonate any specific treatment. The samples are prepared using stoichiometric quantities of BADGE $n = 0$ and m-XDA. The intimate and homogeneous

TABLE I
Different Cooling Rates from Aging Temperature (T_a) in the Range of 60–110°C until Room Temperature (T_r)

T_0 (°C)	Cooling rate (°C/min)	T_a (°C)	Cooling rate (°C/min)	$T_a/2$ (°C)	Cooling rate (°C/min)	T_r (°C)
			Cooling ramp: 117.1°C → 25°C			
	40	100	35	50	25	
	35	90	25	45	20	
117.1	34	80	25	40	23	25
	32	70	25	35	23	
	30	60	24	30	23	

contact is favored among the two compounds by means of continuous stirring, as much as possible avoiding areas with different degrees of conversion. The best proportion has been determined in a previous study,[4] and it corresponds to (100 : 18). To carry out this study, 25 g of BADGE $n = 0$ and 4.5 g of curing agent were weighed. They were stirred for at least 5 min, and then 20% of the total weight of both components of calcium carbonate was added. In previous dynamic calorimetric experiments,[5] it was demonstrated that this percentage was correct, as the measures of the variation of enthalpy on the dynamic scanning were reproducible. It seems reasonable, since for very low (10–15%) proportions of filler the homogenization of the mixture is very difficult. It is impossible to ensure that the filler always assumes the same position, and it appears as different cross-linking densities. For high (25–30%) proportions, the quantity of filler is so high that in certain areas of the structure it can appear as barriers that prevent the system from reacting freely. This fact has been proved in a previous paper using scanning electronic microscopy (SEM).[5] After 5 min of agitation, the mixture was introduced into a cylindrical frame, previously waxed to avoid adherence. After 24 h at 25°C, the frames were placed into an oven at 120°C for 2 h. Finally, the samples were cut into small disks of about 6-mm diameter weighing approximately between 30 and 40 mg.

Techniques

A differential scanning calorimeter (DSC) (Q100, 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 aluminium pans, were heated in the DSC to a temperature (T_0) of $\sim$ 30°C above T_g, during 10 min, to remove any thermal history of the samples. The samples were quenched from T_0 to the aging temperatures (T_a) and then from this last temperature to $T_a/2$ and finally to a room temperature (T_r) of approximately 25°C. Table I shows different

cooling rates from T_0 to T_a (60, 70, 80, 90, and 100°C), from T_a to $T_a/2$, and finally from $T_a/2$ to room temperature. After thermal history has been erased, we used different cooling rates for different aging temperatures. Based on the evidence of DSC experimental data obtained from a previous paper for the same system without filling[1] and with the thermoplastic Polyetherimide (PEI),[6] it was observed that the method applied is useful to reduce experimental scatter due to differences in cool transfer effects. The samples, once removed to differential scanning calorimeter, were annealed inside a glass tube in a thermostatic bath at different aging temperatures for aging times from 1 to 408 h. After annealing, the samples were introduced into the DSC cell, quenched to starting temperature (25°C), and immediately heated to 250°C at 10°C/min. A second scan was made by quenching to room temperature and reheating at 10°C/min to calculate the relaxation enthalpy. This scan will be used as the 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 81.29°C $\pm$ 1.10°C and 0.26 $\pm$ 0.01 J/g°C, respectively. These values were 17% and 15% lower than those obtained in a previous paper[1] for the system without filling. Both reductions are due to the impediments that it causes the filler in the reticulation process, increasing the hardness of the material but weakening the structural network.

Figure 1 shows DSC thermograms of the aged systems for the same time at temperatures close to T_g with and without filling. Structurally different relaxation for each system was observed. The endothermic peak (T_{ep}) in the area of glass transition was visible in the two cases, but, for the system with filler the intensity is smaller, since the filler reduces the reticulation in the epoxy network and hence it ages to lower temperatures. On the contrary, the area under the curve (Δh) for the samples that
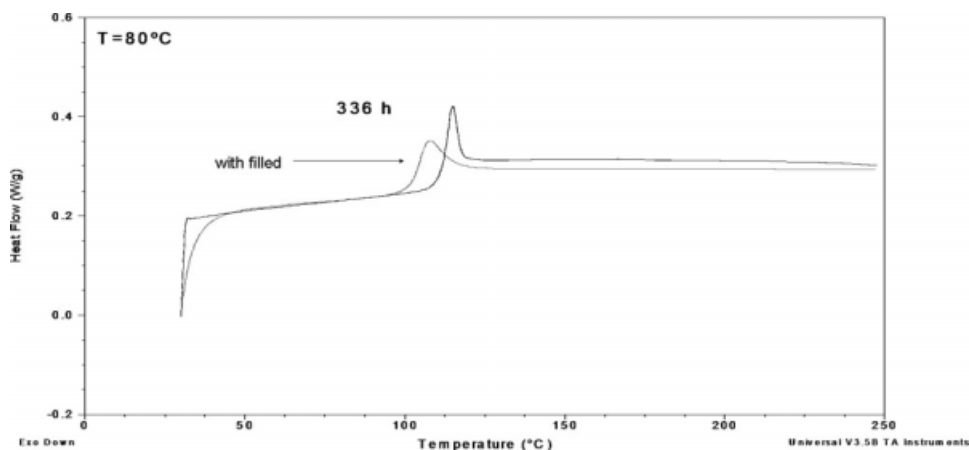
Figure 1 DSC scans of aged systems with and without filed at the aging time of 336 hours.

contain $CaCO_3$ to temperatures lower than the glass transition temperature ($T_g = 87.1°C$) is larger than for those that lack of filler, since $CaCO_3$, when located among the links, epoxy-diamine hinders the relaxation of the same ones; therefore, it needs a larger contribution of heat. However, above T_g the opposite occurs because to these temperatures a rejuvenating of the material associated with a molecularly larger movement takes place that produces a promoting of the structural relaxation.

Figure 2 shows DSC thermograms of the aged system for different times at different temperatures: (a) 60, (b) 70, (c) 80, (d) 90, and (e) 100°C. The temperature of the endothermic peak increases in intensity with aging temperatures and displaces to higher temperatures with aging time. This behavior has been observed in the system without filling[1] and in the same system with a thermoplastic[6] and for similar epoxy systems.[7–13] A linear increase of the T_{ep} with aging time has been observed for all aging temperatures. This behavior is the same as was observed for the system without filling[1] and is the same as was observed by other authors,[11–14] where the deviation from linearity begins at 10°C below T_g, as can be seen in Figure 3.

The relaxation enthalpy, Δh, is plotted versus logarithm scale 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, whereas for the system without filling it increases with temperature. Similar behavior was observed in the epoxy system with a thermoplastic. Some discrepancies appear for higher temperatures in which the values of enthalpy are lower when increasing the temperature; therefore the molecular movement has a smaller free volume for the relaxation.

The dependence of enthalpy relaxation does not follow the relaxation of Bauwens-Crowet and Bau-

wens.[15] On the contrary, the formulation without filling verifies this relationship to the temperature of 100°C, which is close to a glass transition temperature.[1] The relaxation enthalpies increase up to an aging time when 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.[11,13] This value cannot be determined experimentally in this study because it increases even after the upper aging time. However, there are several methods that allow us to calculate (Δh_∞). The two methods we have selected have been used previously by us and others.[6,11,13,16] The first one is based in the extrapolation of the liquid enthalpy curve of the unaged sample:

$$\Delta h_\infty = \int_{T_a}^{T_0} \left(c_{p,l} - c_{p,\text{ref}}\right) \cdot dT \qquad (1)$$

where T_a is aging temperature, $T_0 < 90.94°C$, and $c_{p,l}$ and $c_{p,\text{ref}}$ are the specific heat capacities of liquid state and reference sample, respectively. The second one is a method that supposes the approximation of the previous method, taking into account that

$$\Delta h_\infty = \Delta c_p \left(T_g - T_a\right) \qquad (2)$$

Table II shows the values of (Δh_∞) at different aging temperatures. For both methods, Δh_∞ decreases when the aging temperature increases. Also, at higher aging temperatures a bigger discrepancy exists among the methods. At the temperature of 80°C, a larger approach is observed among the theoretical data calculated by means of eq. (1) and the experimental data showed in Figure 4, since, at temperatures lower than glass transition temperature the epoxy network quickly reaches the structural equilibrium. For the system with filler, the values
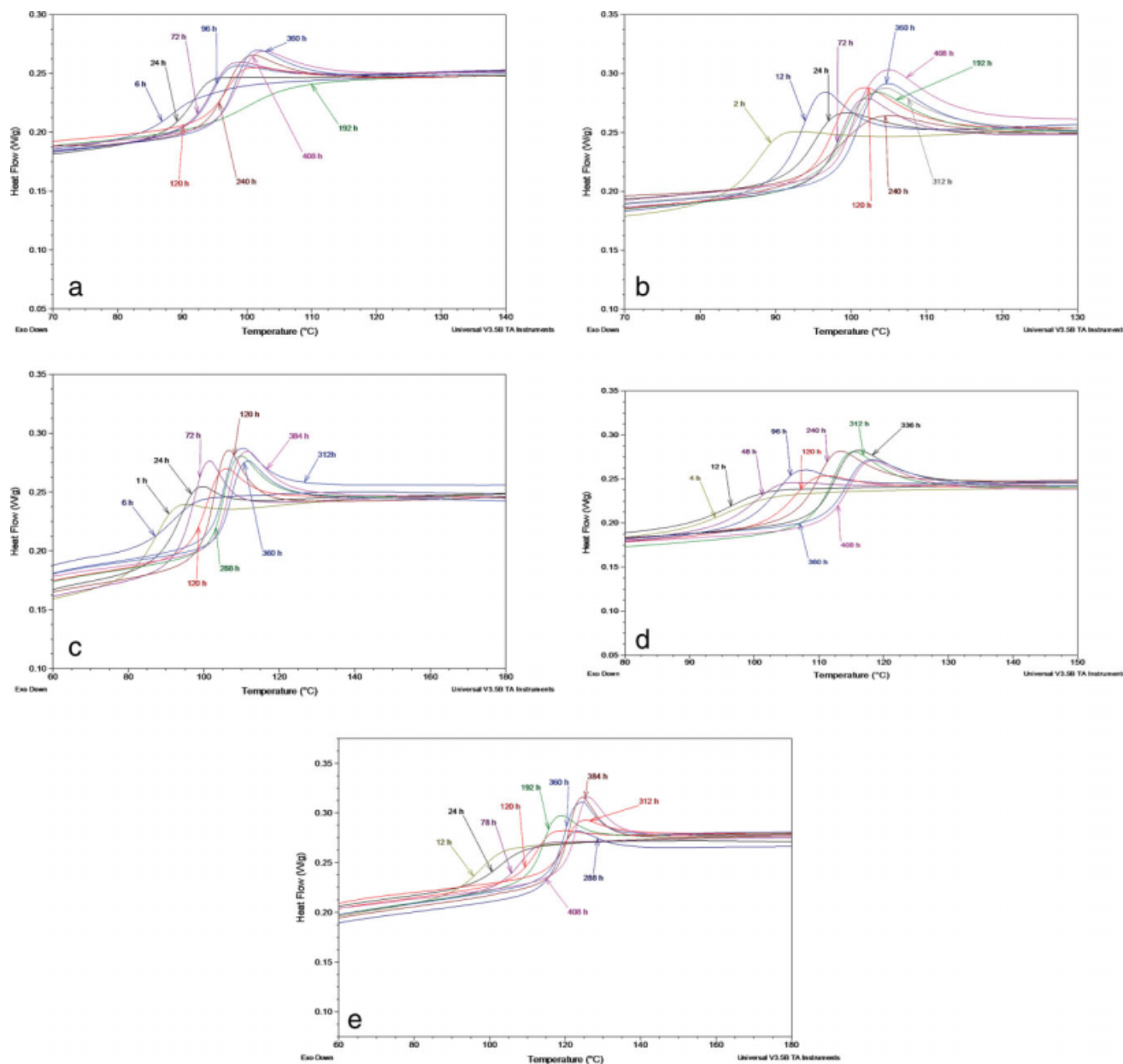
Figure 2 (a) DSC scans of aged sample at 60°C; (b) at 70°C; (c) at 80°C; (d) at 90°C; (e) at 100°C for different aging times. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]
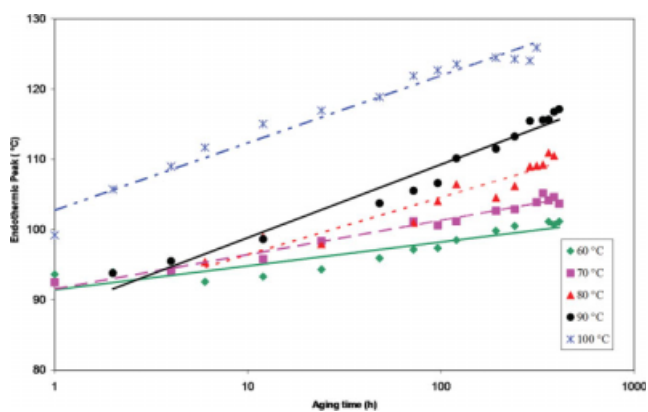
Figure 3 Temperatures of endothermic peak versus logarithm of the aging time at different aging temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]
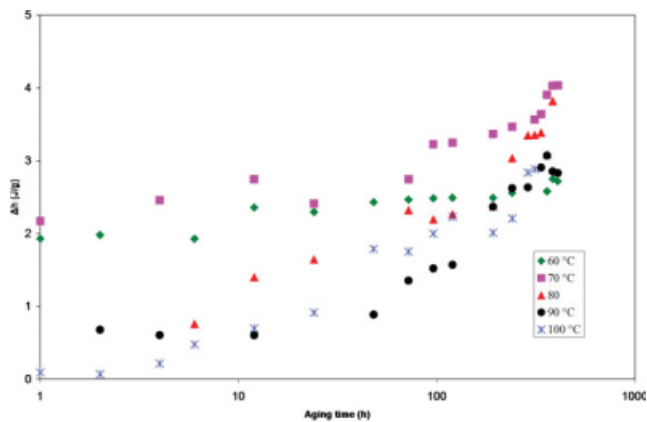
Figure 4 Relaxation enthalpy versus logarithm of the aging time at different aging temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

| T_a (°C)	Δh_∞ (J/g) [eq. (1)]	Δh_∞ (J/g) [eq. (2)]
60	8.42	7.05
70	5.60	4.44
80	2.87	1.84
90	0.24	–
100	–	–

are smaller because the structural equilibrium is reached more easily when there is a smaller number of links of epoxy-diamine that they should relax.

The fictive temperature T_f is a hypothetical temperature at which the structure of glass would be in equilibrium. According to Perez et al.,[17] and assuming that the fictive temperature of the unaged sample is practically equal to glass transition temperature, the fictive temperature can be calculated using the following equation:

$$T_f \approx T_g - \frac{\Delta h}{\Delta c_p} \quad (3)$$

where T_g is the glass transition temperature, Δh is the relaxation enthalpy, and Δc_p is the variation of the specific heat capacity.

Figure 5 shows fictive temperature versus aging temperature at different aging times. The fictive temperature decreases when the annealing time increases. Besides for a fixed aging time, the fictive temperature presents a minimum value. This minimum decreases with the aging time because the glass is close to the structural equilibrium. This effect in epoxy resins was observed for us and other authors.[1,18,19]
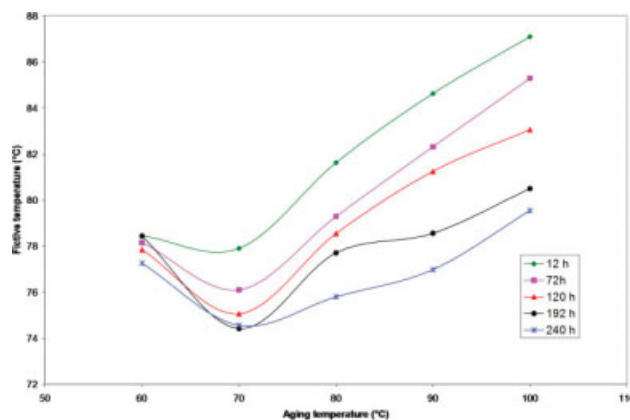
Figure 5 Fictive temperatures versus aging temperature at different aging times. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley. com]
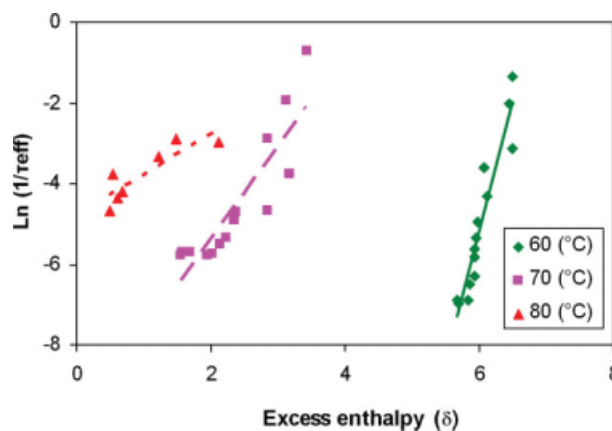
Figure 6 Rate of relaxation $\ln(1/\tau_{\text{eff}})$ versus excess enthalpy for different aging temperatures: 60, 70, and 80°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

The kinetic parameters of the relaxation process can be obtained using a phenomenologic model proposed by Cowie and Ferguson[20]:

$$\frac{d\phi(t)}{dt} = -\frac{\phi(t)}{\tau_{\text{eff}}(t)} \quad (4)$$

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 ageing temperature and ageing time 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

$$\tau_{\text{eff}}(t_a) = -\frac{t_a}{\ln \phi(t_a)} \quad (5)$$

Figure 6 shows the plots of rate of relaxation $\ln(1/\tau_{\text{eff}})$ versus excess enthalpy for different ageing temperatures: 60, 70, and 80°C. The rate of relaxation of this epoxy network decreases as the excess enthalpy decreases for all ageing temperatures. A Petrie model[21] was applied involving separate temperature and excess enthalpy dependency:

$$\tau_{\text{eff}}(t_a) - Ae^{E_H/RT}e^{-C\delta} \quad (6)$$

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 ageing 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: $\ln A = -125.2 \pm 30$, $E_H = 380 \pm 88$ kJ/mol, and $C = 1.2 \pm 0.3$ g/J. The value of the energy of activation of the equation of Petrie is

smaller for the system with filler, since $CaCO_3$ is placed in the structure of the epoxy network, avoiding the union of some links between the resin and the hardening agent. With a smaller number of links, less energy is needed for the formation of the activated complex.

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