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INFLUENCE OF THE CURING CYCLE SELECTION ON THE THERMAL DEGRADATION OF AN EPOXY-DIAMINE SYSTEM

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Polymers have a great interest for the study and design of new materials. Among these materials are epoxy resins, that have good properties, such as low shrinkage during cure, good adhesion, high water and chemical resistance, etc. They have also fast and easy cure in a broad range of temperatures.

TTT diagrams are very helpful to design new epoxy materials as they allow the search for very important final properties, such as thermal stability, conversion or glass transition temperature of a material cured through a selected curing cycle.

In this work the dependence of the thermal stability on the selected curing cycle for a DGEBA/1,2 DCH system was studied.

Keywords: *activation energy, curing cycle, epoxy resins, thermogravimetry, TTT diagram*

Introduction

Isothermal TTT cure diagrams are useful tools to predict, at least qualitatively, some important properties of thermosetting polymers [1–3]. To choose a curing cycle appropriated to a determined application of the material it is indispensable to know the desired values of the final properties of this epoxy system after being cured. Depending on temperature and time, and also on the component concentrations, the final properties can differ in a very significative way [4].

A TTT is calculated by plotting the experimental times to reach various events during an isothermal cure *vs*. the cure temperature. The TTT isothermal cure diagram records the phenomenological changes, such as vitrification and macroscopic gelation, taking place during the cure reaction of the epoxy. This diagram can include some other different contours, such as carbonization (char), or thermal degradation curve and isoconversion or iso-T_g curves, in which full cure or maximum experimental isoconversion are included [5, 6].

In previous articles, different TTT diagrams for the systems DGEBA/1,2 DCH [3], DGEBA/mxDA [7] and also the first one modified by the addition of a third component, such as an inert filler ($CaCO_3$) [8], or an epoxy reactive diluent (vinylcyclohexane dioxide) [9], were reported. The TTT diagram becomes different if the concentration of the components of the epoxy system changes, because the kinetics of the curing reaction can be altered through the change of the amount of the reaction materials, and therefore the isoconversion, vitrification and gelation curves will suffer an alteration.

In earlier works, we have studied the final properties of the system DGEBA/1,2 DCH cured through a selected curing sequence from its TTT diagram [3, 10–13]. The main objective of the present work was to study the influence of changing the curing cycle on the thermal stability of the system (to check if the kinetic parameters, the life-time, and the thermal degradation kinetics change significantly). The results obtained were compared with those corresponding to the same system but cured through a curing cycle previously described [10], thus showing the practical importance of the knowledge of the TTT diagram of a particular system. The study was carried out using thermogravimetric analysis.

Kinetic methods

TG non-isothermal experiments register the change of one sample mass as a function of temperature. Kinetic parameters can be extracted from non-isothermal experiments.

The degree of conversion can be expresed as:

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \tag{1}$$

where m is the measured experimental mass at temperature T, m_0 the initial mass and m_∞ the mass at the end of the non-isothermal experiment.

The rate of conversion, $d\alpha/dt$, is a linear function of a temperature-dependent rate constant, k, and a temperature-independent function of conversion, α, that is:

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$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha) \tag{2}$$

Substituting Arrhenius equation into Eq. (2), modifies to:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = Af(\alpha)\mathrm{e}^{-\frac{\mathrm{E}}{\mathrm{RT}}} \tag{3}$$

If the temperature of the sample is changed by a controlled and constant heating rate, $\beta=\mathrm{d}T/\mathrm{d}t$, the variation in the degree of conversion can be analyzed as a function of temperature, this temperature being dependent on the time of heating.

Therefore, the reaction rate gives:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta}\mathrm{e}^{-\frac{\mathrm{E}}{\mathrm{RT}}} f(\alpha) \tag{4}$$

Integration of this equation from an initial temperature, T_0, corresponding to a null, or negligible, degree of conversion, to the peak temperature of the derivative thermogravimetric curve (DTG), T_p, where $\alpha=\alpha_\mathrm{p}$ gives [14]:

$$g(\alpha) = \int_0^{\alpha_\mathrm{p}} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^{\mathrm{T_p}} \mathrm{e}^{-\frac{\mathrm{E}}{\mathrm{RT}}}\mathrm{d}T \tag{5}$$

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

In the case of polymers, this integral function, $g(\alpha)$, is either a sigmoidal function or a deceleration function. Depending on the solid-state mechanisms, $g(\alpha)$ can have different mathematical expresions [15–17]. These functions were satisfactorily employed for the estimation of the reaction solid-state mechanism from non-isothermal TG experiments [18].

The thermodegradation activation energy of the epoxy system was studied using two different methods. One of them, the Kissinger method, is a differential method that analyzes the changes in thermogravimetric data with the variation of the heating rate to obtain the kinetic parameters [19]. The other method was the Flynn–Wall–Ozawa method. This is a method that involves an approximate integration of Eq. (5) [18–20].

Determination of the reaction mechanism using Criado et al. method [16]

Once the activation energy of a given solid-state reaction is known, the kinetic model of the process can be found using different methods. One of them is that proposed by Criado *et al.* that defined a function

$$Z(\alpha) = \frac{\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)}{\beta}\Pi(x)T \tag{6}$$

where $x=(E/RT)$ and $\Pi(x)$ is an approximation of the temperature integral which cannot be expressed in a simple analytical form. The present study was carried out using the fourth rational expression of Senum and Yang [21] that gives errors of lower than 10^{-5}% for x=20.

Combination of Eqs (2) and (6) gives:

$$Z(\alpha)=f(\alpha)g(\alpha) \tag{7}$$

that was used to obtain master curves as a function of the reaction extent for the different models reported in [15–17].

Plotting the $Z(\alpha)$ function calculated using both experimental data and Eq. (6), and comparing with the master curves leads to determine easily and precisely the mechanisms of solid-state processes.

Lifetime

Lifetime prediction is a technique frequently used in industry to find out the probable behavior of a new material. The viewpoint of lifetime prediction is to detect the decisive reaction that limits the life of a material, then to measure its kinetics quantitatively at high temperature where the reaction is fast.

The lifetime is considered when 5% mass loss [22] or 5% conversion [23] is reached from a thermogravimetric analysis experiment (TG).

Experimental

Materials

The epoxy resin was a commercial DGEBA (n=0) (Resin 332, Sigma Chemical Co., St. Louis, MO, USA), with an equivalent molecular mass of 173.6 g/Eq, as determined by wet analysis [24, 25]. The curing agent was 1,2-diaminecyclohexane (DCH) (Fluka, Switzerland), with an amine hydrogen equivalent mass of 28.5.

Sample preparation

Epoxy resin and cure agent were carefully and homogeneously mixed, at stoichiometric ratio, before being introduced in a cylindrical frame.

The curing reaction was programmed according to a TTT diagram described for this material [3]. It consists of two stages: a first step at 23°C during 7.5 h and a second one in a stove, at 70°C during 24 h. The system cured through this sequence will be named B system, and the system to whom we will make reference because was the first system studied will be named A system. The 'old' curing cycle consisted also of two stages: a first step at 23ºC during 24 h and a second one in a stove at 70ºC during 16 h. As can be

Table 1 Inflection point temperature at different heating rates for A and B systems

Heating rate/K min^{-1}	$T_{\text{inflection point}}$/°C		T_f–T_d	
	A system [10]	B system	A system [10]	B system
5	343.76	335.63	49.65	50.08
15	368.75	356.72	48.60	49.69
25	376.25	363.73	41.99	50.62
35	383.75	371.32	40.96	45.35
45	390.00	379.29	39.60	41.68

seen, both sequences are very similar, because our aim was to check if a small change in the curing cycle implies a significative difference on the thermal stability of the system. After curing, the samples were removed from the frame. Checking the TTT diagram [3] it can be seen that, at the end of the first step of each cycle, curing conversions of the material differ in 20, being 80 and 60% for the old and new cycles, respectively. For the old system during the first step of the curing, the sample gelates and vitrifies, while the second one (B system) only gelates after the first step. Our question is to know if those differences will affect to the thermal stability of our system.

The thermogravimetric study was carried out using a Thermogravimetric Analyzer (TGA7) from Perkin Elmer controlled by a 1022 computer. The system was operated in the dynamic mode in the temperature range 100–900ºC, at different heating rates of: 5, 15, 25, 35 and 45 K min^{-1}. All the experiments were carried out under a dry nitrogen atmosphere.

Results and discussion

Figure 1 shows the thermal degradation curves resulting from dynamic experiments carried out at different heating rates (5, 15, 25, 35 and 45 K min^{-1}), for the A [10] and B systems. These curves are C type [15], that correspond to a one stage decomposition reaction where the procedural decomposition temperatures (initial and final) are well defined. The step is due to the thermal degradation of the epoxy resin. The inflection point temperature corresponding to the first step, T_m, can be determined from the minimum of the derivative of these curves, the onset and endset of the main degradation step and the residual mass can be measured from TG curves. Table 1 shows the inflection point temperatures of the first step, T_m, and the width of the thermodegradation step at different heating rates, for A [10] and B systems, calculated as the difference between the onset, T_d, and the endset, T_f, of the main thermodegradation step. Table 2 shows the residual mass, measured at 890ºC. Analysis of these tables show that all the inflection temperatures corresponding to B system are lower than those measured for A system, although the differences are within the 5% of error allowed by the IUPAC. The width of the main thermodegradation step is almost the same for both systems, and shows a little decrease with increasing the heating rate of the experiment. However, there are significant differences in the residue values. The highest values correspond to A system. It can be seen that, in all the cases, the residual mass is nearly independent of the heating rate.

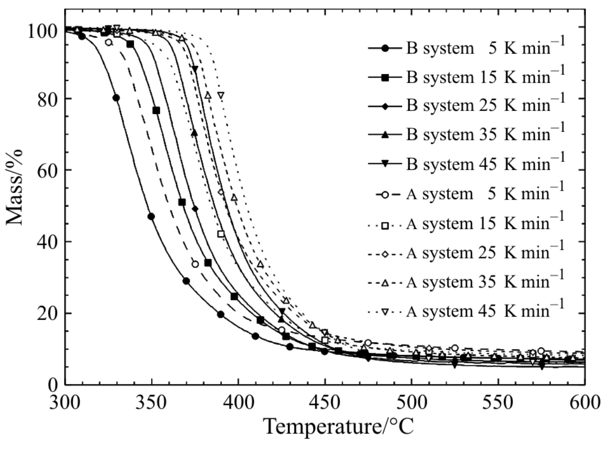

Fig. 1 TG curves of A [10] and B systems at different heating rates

Owing to the thermodegradation behavior of the epoxy systems here studied and to avoid the overlapping of inflection point temperatures, we have chosen 10 K min^{-1} heating rates intervals between measurements, instead of 5 K min^{-1} intervals used by some authors [26, 27]. This same procedure was followed in the study of the A system [10]. Recently Dakka [28] has studied the effect of the heating rate

Table 2 Residue (%) at 890°C at different heating rates for A and B systems

System	Heating rate/K min^{-1}				
	5	15	25	35	45
A	7.60	6.51	7.31	6.13	5.22
B	6.53	6.44	4.97	5.28	4.08

and also of the particle size on the production of evolved gases of other polymeric systems.

Using Kissinger equation [19] and the inflection point temperature corresponding to the curves showed in Fig. 1, the activation energies were calculated from a plot of $\ln(\beta / T^2_{\max})$ *vs.* $1000/T_{\max}$ and fitting to a straight line. The activation energies for both systems obtained using this method are shown in Table 3.

Table 3 Activation energies obtained using Kissinger and Flynn–Wall–Ozawa methods

System	$E_{\mathrm{a\,Kissinger}} \pm sE_{\mathrm{a\,Kissinger}}$/ kJ mol^{-1}	$E_{\mathrm{a\,Flynn}} \pm \sigma E_{\mathrm{a\,Flynn}}$/ kJ mol^{-1}
A [10]	144.01±17.69	148.59±18.81
B	160.74±17.34	131.58±11.36

The activation energy can also be determined using the method of Flynn–Wall–Ozawa [18, 20], from a linear fitting of lnβ *vs.* 1000/*T* at different conversions. Owing to the fact that this equation was derived using Doyle approximation [29], only conversion values in the range 5–35% were used. The activation energies obtained at different conversions give a mean value that is shown in Table 3. The values obtained using Kissinger and Flynn–Wall–Ozawa methods are different for the A and B systems, but are in reasonable agreement taking into account the ranges limited by the errors.

Compared to others, these two methods present the advantage that they do not require the previous knowledge of the reaction mechanism for determining the activation energy, and are continuously employed in [30]. Some authors [18, 21] used the activation energies obtained using these two methods to check their thermodegradation mechanism models. In a future work, the Flynn–Wall–Ozawa energy values will be considered as reference, to compare with those obtained through the different integral methods cited before. The Flynn–Wall–Ozawa results will be considered for comparison purposes because the Kissinger method takes only one point of the thermodegradation curve whereas the Flynn–Wall–Ozawa method takes different points corresponding to different conversion values.

As a first approximation, to estimate which kind of mechanism of thermodegradation follows our epoxy systems, we have used the method proposed by Criado *et al*. This method uses reference theoretical curves called master plots which are compared to experimental data. Experimental results were obtained from Eq. (6) at the heating rate of 45 K min^{-1}.

Figures 2a and b show master curves and experimental results corresponding to the A and B systems. This figure suggests that the mechanism better describing the thermodegradation behavior of both, A [10] and B systems at 45 K min^{-1}, correspond to A$_4$, showing the data corresponding to B system a closer fitting than those associated to A system.

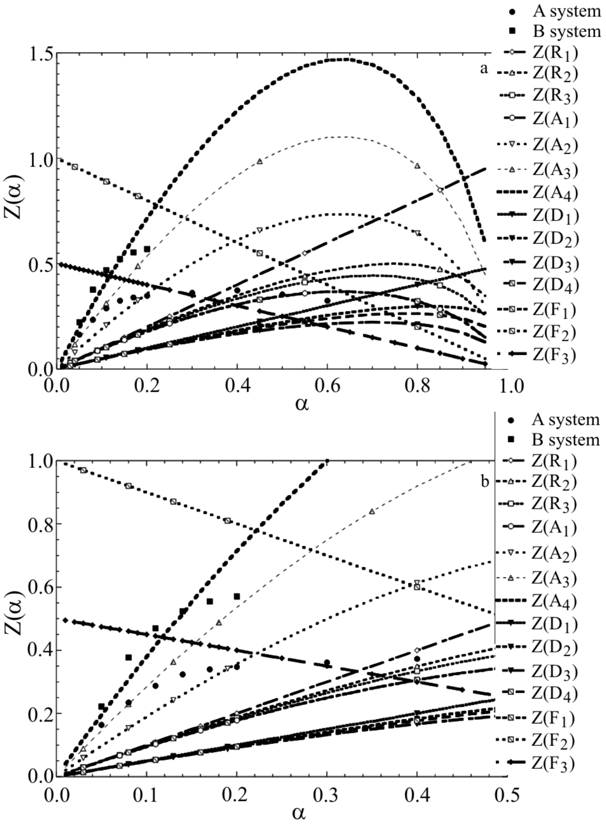

Fig. 2 a – Master plot curves $Z(\alpha)$ and experimental data for A and B systems at 45 K min^{-1} and b – detail from 2a at low conversion values

We can conclude that, as a result of changing the curing cycle, the activation energies for the thermodegradation of the system have changed, but not considerably. However, this change in the energy values has only affected to the experimental $Z(\alpha)$ data by shifting these data to higher values. Because of this displacement, the experimental data for B system fit better to the A$_4$ mechanism than those corresponding to A system.

Lifetime

The activation energy was calculated from the fit of a plot of logβ *vs.* 1/*T* at the various conversions. The average activation energy value obtained using Flynn–Wall–Ozawa method was 131.58 kJ mol^{-1}. From this data, the lifetime at several temperatures was predicted, taking into account that the lifetime is assumed to be reached at 5% of conversion. Lifetime values corresponding to temperatures between 100 and 360°C are summarized in Table 4. From this table, it can be seen that the lifetime values obtained for B system are, at low

Table 4 Experimental lifetimes for A and B systems

Temperature/K	t_{exp}/min B system	t_{exp}/min A sytem [11]
373.16	5.30E+07	1.38E+09
393.16	6.44E+06	1.25E+08
413.16	9.52E+05	1.42E+07
433.16	1.68E+05	1.98E+06
453.16	3.45E+04	3.28E+05
473.16	8.11E+03	6.32E+04
493.16	2.14E+03	1.39E+04
513.16	6.28E+02	3.45E+03
533.16	2.02E+02	9.51E+02
553.16	7.04E+01	2.88E+02
573.16	2.64E+01	9.45E+01
593.16	1.06E+01	3.35E+01
613.16	4.51E+00	1.24E+01
633.16	2.02E+00	5.10E+00

temperatures, two magnitude orders lower than those calculated for A system [10]. This is in good agreement with the fact that the thermodegradation curves for B system showed the main thermodegradation step at earlier temperatures. It can also be observed from same table, for both systems, the sharp fall of lifetime with increasing temperature, as lifetime corresponding to 360°C is only 5.10 or 2.02 min for A and B systems, respectively. As it can be seen the optimal temperature range is 100–140°C in which the corresponding lifetime range is 2633–27 and 100–1.8 years for A [10] and B systems, respectively. It is clear that the durability of this material depends not only on the temperature but also on the selected curing cycle.

The study of thermodegradation kinetics of the system BADGE n=0/1,2 DCH confirms that this epoxy system follows a sigmoidal A_4 mechanism; that is, a nucleation and growth solid-state process (Avrami equation) [15–17]. The corresponding equation is

$$[-\ln(1-\alpha)]^{1/4}=kt \tag{8}$$

Using the mean activation energy value calculated by Flynn–Wall–Ozawa method, and the pre-exponential factor value, the rate constant can be derived from Arrhenius equation as a function of temperature. Table 5 shows k values obtained for B system.

Equation (8) allows the calculation of the conversion degree as a function of time:

$$\alpha = 1-e^{-k^4t^4} \tag{9}$$

Taking into account that lifetime was defined as the time necessary for a 5% conversion, Eq. (9) leads to

$$t=\frac{0.476}{k} \tag{10}$$

Table 5 Lifetimes for B system corresponding to the A_4 mechanism

Temperature/K	k/T	A_4/min
373.16	1.30E-08	3.67E+07
393.16	1.08E-07	4.42E+06
413.16	7.28E-07	6.54E+05
433.16	4.13E-06	1.15E+05
453.16	2.00E-05	2.38E+04
473.16	8.55E-05	5.57E+03
493.16	3.23E-04	1.47E+03
513.16	1.10E-03	4.33E+02
533.16	3.44E-03	1.39E+02
553.16	9.85E-03	4.83E+01
573.16	2.62E-02	1.82E+01
593.16	6.54E-02	7.28E+00
613.16	1.54E-01	3.10E+00
633.16	3.42E+01	1.39E-02
653.16	7.24E-01	6.57E-01

This equation allows the calculation of lifetime as a function of temperature through the constant rate k. Table 5 shows lifetime values as a function of temperature corresponding to A_4 mechanism. Comparison of lifetime values obtained using this method with those calculated without the knowledge of the reaction mechanism shows small differences, but, for all temperatures, they are of the same magnitude orders.

Conclusions

The thermal degradation of two epoxy systems DGEBA (n=0)/1,2 DCH cured through different curing sequences was studied and compared. Although different activation energy values were obtained depending on the considered system, both of them follow the same thermodegradation kinetic mechanism, A_4. However, B system experimental data fit better to the theoretical master curve. Lifetime has also been evaluated. The system previously studied (A system) shows at low temperatures, lifetime values two orders of magnitude higher than those corresponding to B system. For example, the experimental lifetime value corresponding A system at 100ºC was 2633 years and only 100 years for B system.

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