

## **THERMAL STABILITY OF EPOXY SYSTEMS BADGE ( $n=0$ )/1,2-DCH AND BADGE ( $n=0$ )/ 1,2-DCH/VINYLCYCLOHEXENE DIOXIDE**

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### **Abstract**

The thermal degradation of the epoxy system diglycidyl ether of bisphenol A (BADGE  $n=0$ )/1,2-diamine cyclohexane (DCH) containing different concentrations of an epoxy reactive diluent was studied by thermogravimetric analysis in order to determine the reaction mechanism of the degradation process and to compare it with the results for the same system without diluent. The value of the activation energy, necessary for this study, was calculated using various integral and differential methods. Values obtained using the different methods were compared to the value obtained by the Flynn–Wall–Ozawa's method (between 193–240 kJ mol<sup>-1</sup> depending on the diluent concentration) which does not require a knowledge of the  $n^{\text{th}}$  order reaction mechanism. All the experimental results were compared to master curves in the range of Doyle's approximation (20–35% of conversion). Analysis of the results suggests that the reaction mechanism could be F<sub>2</sub>, F<sub>3</sub>, or A<sub>2</sub> type.

**Keywords:** activation energy, diluent, epoxy resins, reaction mechanism, thermogravimetry

### **Introduction**

Thermosets are materials with low tensile and storage moduli. For many end-uses, it is necessary to add other components to the resin in order to improve its properties. One of these components are reactive diluents, such as vinylcyclohexene dioxide, which are usually employed as a means of reducing viscosity in order to aid processability as well as allowing for greater incorporation of other formulatory ingredients as fillers. In addition to viscosity, other properties can be modified. These properties and its magnitude depend on both the type and quantity of diluent employed [1].

Since the behavior of thermosets is affected by the addition of diluents, it is important to investigate the changes that take place during the thermal degradation of these materials. The study of the degradation of a polymer is important because it can

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determine the upper temperature limit, the mechanism of a solid-state process, and the life-time for a thermoset.

The main objective of this work was to study the kinetics of thermal degradation of an epoxy resin containing different concentrations of an epoxy reactive diluent (vinylcyclohexenedioxide) in non-isothermal conditions. The results of this study were compared with those of same epoxy system without diluent [2].

### *Kinetic methods*

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

The degree of conversion can be expressed as:

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \quad (1)$$

where  $m$  is the measured experimental mass at temperature  $T$ ,  $m_0$  the initial mass, and  $m_\infty$  the mass at the end of non-isothermal experiments.

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,  $\alpha$ , that is:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (2)$$

Substituting Arrhenius equation into Eq. (2), one obtains:

$$\frac{d\alpha}{dt} = Af(\alpha)e^{-\frac{E}{RT}} \quad (3)$$

If the temperature of the sample is changed by a controlled and constant heating rate,  $\beta=dT/dt$ , 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:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} f(\alpha) \quad (4)$$

Integration of this equation from an initial temperature,  $T_0$ , corresponding to a null degree of conversion, to the peak temperature of the derivative thermogravimetric curve (DTG),  $T_p$ , where  $\alpha=\alpha_p$  gives [3]:

$$g(\alpha) = \int_0^{\alpha_p} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{T_p} e^{-\frac{E}{RT}} dT \quad (5)$$

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. In the bibliography it can be find different expressions

of  $g(\alpha)$  for the different solid state mechanisms [1, 2, 4, 5]. These functions were satisfactorily employed for the estimation of the reaction solid state mechanism from non-isothermal TG experiments [6].

*Differential method*

Analysis of the changes in thermogravimetric data brought about by variation of the heating rate,  $\beta$ , are the basis of the most powerful differential methods for the determination of kinetic parameters.

Kissinger's method [5]

Kissinger's method has been used in the literature to determine the activation energy of solid state reactions from plots of the logarithms of the heating rate vs. the inverse of temperature at the maximum of the reaction rate in constant heating rate experiments.

The activation energy can be calculated by Kissinger's method without a precise knowledge of the  $n$ -th order reaction mechanism, using the following equation:

$$\ln \frac{\beta}{T_{\max}^2} = \left\{ \ln \frac{AR}{E} + \ln[n(1 - \alpha_{\max})^{n-1}] \right\} - \frac{E}{RT_{\max}} \quad (6)$$

where  $\beta$  is the heating rate,  $T_{\max}$  is the temperature corresponding to the inflection point of the thermodegradation curves which corresponds to the maximum reaction rate,  $A$  is the pre-exponential factor,  $\alpha_{\max}$  is the maximum conversion, and  $n$  is the reaction order.

*Integral methods*

The integral methods involve an approximate integration of Eq. (5). Some of these methods discussed in the present paper are: Flynn–Wall–Ozawa and Coats–Redfern.

Flynn–Wall–Ozawa method [4, 6, 7]

Equation 5 is integrated using Doyle approximation [3]. The result of the integration after taking logarithms is:

$$\log \beta = \log \left[ \frac{AE}{g(\alpha)R} \right] - 2.315 - \frac{0.457E}{RT} \quad (7)$$

where  $\beta$ ,  $A$ ,  $E$  and  $T$  have the known meanings.

This is one of the integral methods that can determine the activation energy without the knowledge of the reaction order. It is used to determine the activation energy at given values of conversion.

Coats–Redfern method [8]

Coats–Redfern used an asymptotic approximation for resolution of Eq. (7) obtaining:

$$\ln \frac{g(\alpha)}{T^2} = \ln \frac{AR}{\beta E} - \frac{E}{RT} \quad (8)$$

Criado *et al.* [9] method for determination of reaction mechanism

The activation energy of a solid state reaction can be determined from several non-isothermal measurements whatever the reaction mechanism. If the value of the activation energy is known, the kinetic model of the process can be found defining a function

$$Z(\alpha) = \frac{\left( \frac{d\alpha}{dt} \right)}{\beta} \Pi(x)T \quad (9)$$

where  $x=E/RT$  and  $\Pi(x)$  is an approximation of the temperature integral which cannot be expressed in a simple analytical form. In this study, the fourth rational expression of Senum and Yang [10], which gives errors of lower than 10<sup>-5</sup>% for  $x=20$ , was used.

Combination of Eqs (2) and (9) gives:

$$Z(\alpha)=f(\alpha)g(\alpha) \quad (10)$$

This last equation was used to obtain the master curves as a function of the reaction degree corresponding to the different models.

Plotting the  $Z(\alpha)$  function calculated using both experimental data and Eq. (9), and comparing with the master curves leads to determine easily and precisely the mechanisms of solid state processes.

## Experimental

### *Materials*

The epoxy resin was a commercial BADGE ( $n=0$ ) (Resin 332, Sigman Chemical Co. San Louis, USA) with an equivalent molecular mass of 173.6 g/eq, as determined by wet analysis [11]. The curing agent was 1,2-diamine cyclohexane (DCH) (Fluka, Switzerland) with an amine hydrogen equivalent mass of 28.5. The epoxy reactive diluent was vinylcyclohexene dioxide (Fluka, Switzerland).

### *Sample preparation*

Epoxy resin and reactive diluent were carefully and homogeneously mixed, at different proportions of 5, 10, 15 and 20% in mass of the total mass of the composed system (epoxy, diamine, reactive diluent), before being added an amount of curing agent which corresponds to the stoichiometric amount for the system BADGE/1,2-DCH. Finally, the sample was introduced in a cylindrical frame.

The curing reaction was programmed according to a TTT diagram calculated for the system BADGE/1,2-DCH [12]. It consists of two stages: a first step 24 h at 23°C

and a second one 16 h at 70°C in a stove. After curing, the samples were removed from the frame.

For thermogravimetric analysis, the samples were cut in the form of 15–25 mg in mass and 6 mm in diameter discs.

Thermogravimetric analysis was performed using a thermogravimetric analyzer (TGA7) from Perkin Elmer controlled by a 1020 computer. This microbalance was calibrated making use of the discontinuous change in the magnetic properties of perkalloy and alumel on heating. The Curie point of every metal was calculated by the microbalance which was calibrated at different heating rates.

The system was operated in the dynamic mode in the temperature range 100–900°C, at different heating rates: 5, 15, 25, 35 and 45°C min<sup>-1</sup>.

All the experiments were carried out under a dry nitrogen atmosphere. The TGA7 analyzer requires two purge lines: one to purge the balance chamber and a second one to purge the sample-furnace area. After various experiments, it was found that the optimum gas flow rates were: 25 mL min<sup>-1</sup> for the balance purge gas and 35 mL min<sup>-1</sup> for the sample purge gas.

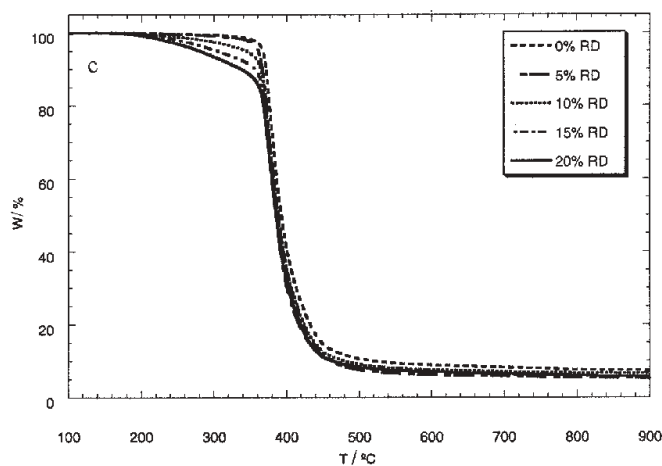
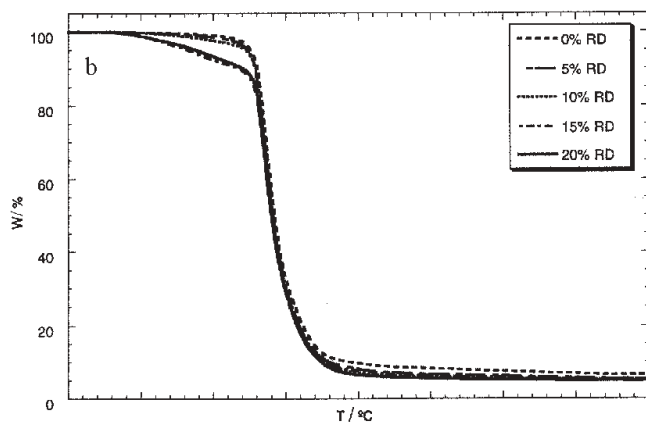
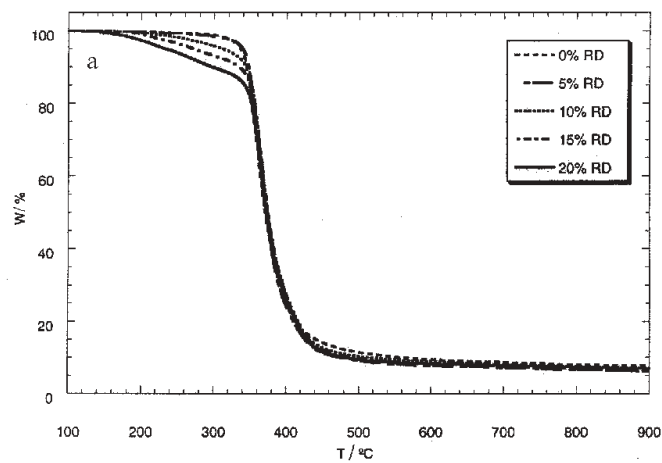
## Results and discussion

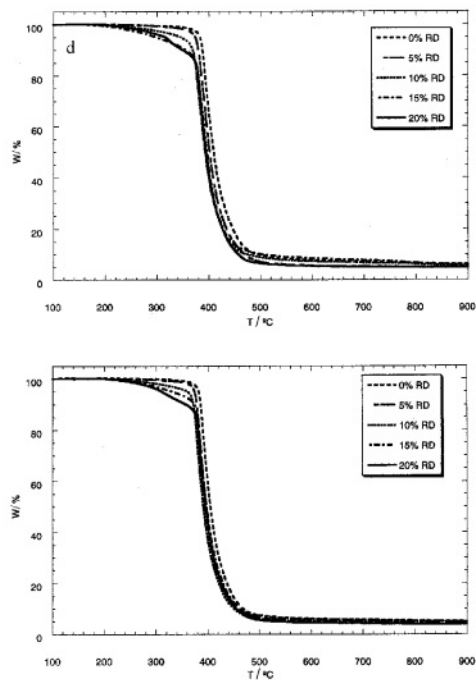
Figure 1 shows thermal degradation curves corresponding to dynamic experiments carried out at the heating rates of 5, 15, 25, 35 and 45°C min<sup>-1</sup> for the different proportions used. These curves are C type [9], which corresponds to a single-stage decomposition reaction where the procedural decomposition temperatures (initial and final) are well defined. This step is due to the thermal degradation of the epoxy resin and corresponds to a temperature around 350°C. The inflection point temperature corresponding to the first step,  $T_m$ , can be determined from the minimum of the derivative of these curves. As it can be seen, an increase in the reactive diluent content, makes the initial decomposition smoother, but the main decay in the change of mass is similar for all the compositions.

Owing to the thermodegradation behavior of the epoxy system here studied, intervals of 10°C min<sup>-1</sup>, instead of those of 5°C min<sup>-1</sup> used by other authors [13–15], were chosen, to avoid the overlapping of the inflection point temperatures. This same procedure was followed in the study of similar epoxy system without diluent [16–18].

Using Kissinger method, Eq. (6), and the inflection point temperature corresponding to the thermogravimetric curves obtained at the heating rates of 5–45°C min<sup>-1</sup> for the different concentrations of diluent, the activation energy can be calculated from a plot of  $\ln(\beta/T_{max})$  vs.  $1000/T_{max}$  and fitting to a straight line. The activation energies obtained using this method are shown in Table 1.

The activation energy can also be determined using the method of Flynn–Wall–Ozawa (Eq. (7), from a linear fitting of  $\ln\beta$  vs.  $1000/T$  at a different conversions. According to Doyle approximation, conversion values 20, 23, 26, 29, 32 and 35% were used. The fitting straight lines were nearly parallel, thus indicating the applicability of this method to our epoxy system in the conversion range studied. This fact suggests





**Fig. 1** Thermal degradation curves at different heating rates a – 5°C min<sup>-1</sup>; b – 15°C min<sup>-1</sup>; c – 25°C min<sup>-1</sup>; d – 35°C min<sup>-1</sup>; e – 45°C min<sup>-1</sup>

that a single reaction mechanism is operative [15, 19]. The mean activation energies obtained for the different concentrations of diluent are shown in Table 2.

**Table 1** Activation energies obtained using Kissinger method

<i>R.D./%</i>	$\bar{E}_a \pm 2\sigma(E_a)/\text{kJ mol}^{-1}$
5	235.63±26.94
10	302.70±30.93
15	237.61±36.83
20	244.04±13.30

**Table 2** Mean activation energies obtained using Flynn–Wall–Ozawa method

<i>R.D./%</i>	$\bar{E}_a \pm 2\sigma(E_a)/\text{kJ mol}^{-1}$
5	192.94±4.25
10	239.83±6.07
15	213.33±6.10
20	196.87±7.67

Compared to the activation energies for the epoxy system without diluent  $144.01 \text{ kJ mol}^{-1}$  (Kissinger method) and  $148.59 \text{ kJ mol}^{-1}$  (Flynn–Wall–Ozawa method [16]), values for the system with diluent are higher although the beginning of degradation of the epoxy system with diluent takes place at the same temperature ranges.

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. Some authors [13, 20] used the activation energies obtained using these two methods in order to check their thermodegradation mechanism models.

Using Eq. (8), proposed by Coats and Redfern, the activation energy for every  $g(\alpha)$  [1, 9] can be obtained at constant heating rates from fitting of  $\ln(g(\alpha)/T^2)$  vs.  $1000/T$  plots. For this study same conversion values than those used in the previous methods were used.

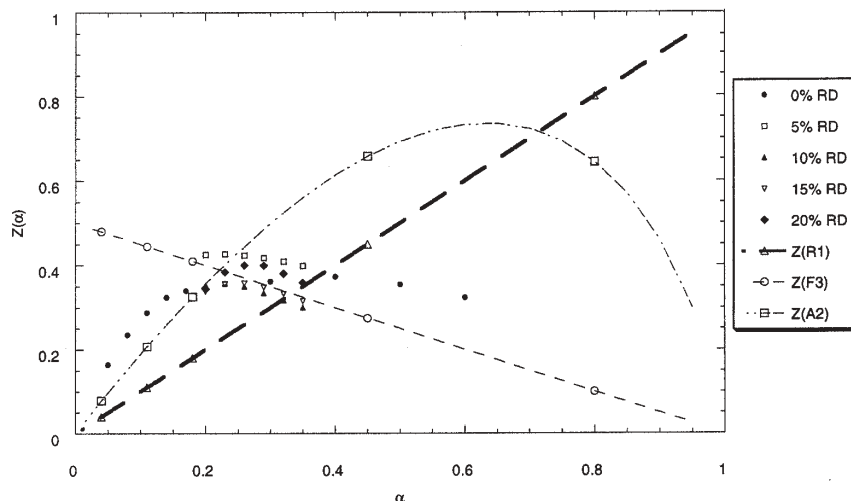


Fig. 2 Master curve resulting from plots of  $Z(\alpha)$  vs.  $\alpha$

Table 3 shows activation energies in the range 20–35% of conversion (Doyle approximation) for the different diluent concentrations, at the constant heating rate value of  $45^\circ\text{C min}^{-1}$ . Analysis of this table shows that the activation energies in better agreement with those obtained using Kissinger and Flynn–Wall–Ozawa, depend on the concentration of diluent. The best-fitting models for the different concentrations of diluent, at the heating rate of  $45^\circ\text{C min}^{-1}$ , are shown in Table 4. This table suggests that the solid state thermodegradation mechanism followed by our epoxy systems is, in most cases, a deceleration ( $F_3$ ) type. For the system without filler this mechanism was  $A_4$  (sigmoidal) [16].



**Table 3** Activation energies (kJ mol<sup>-1</sup>) obtained using Coats–Redfern method for the different concentrations of diluent at the heating rate value of 45°C min<sup>-1</sup>

Mechanism	Concentration of diluent/%			
	5	10	15	20
A2	175.03	174.70	159.71	168.84
A3	113.03	112.84	102.83	108.91
A4	82.020	81.909	74.379	78.957
R1	305.36	304.58	279.19	294.81
R2	332.42	331.65	304.06	320.94
R3	341.80	341.03	312.68	330.00
D1	621.71	620.07	569.35	600.54
D2	656.77	655.13	601.56	634.39
D3	694.58	692.96	636.31	670.92
D4	669.34	667.70	613.12	646.61
F1	361.07	360.32	330.39	348.61
F2	95.810	106.97	97.31	102.85
F3	224.61	224.83	205.57	216.63

To corroborate that our epoxy system follows a deceleratory thermodegradation mechanism, the method proposed by Criado *et al.* was used [9]. This method uses reference theoretical curves called master plots which are compared to the experimental data. Experimental results were obtained from Eq. (9) at a heating rate 45°C min<sup>-1</sup>.

**Table 4** Best-fitting mechanisms of solid state processes according to Kissinger and Flynn–Wall–Ozawa methods

R.D./%	Best fitting mechanisms according to	
	Kissinger method	Flynn–Wall–Ozawa method
5	F <sub>3</sub> , A <sub>2</sub>	A <sub>2</sub> , F <sub>3</sub>
10	R <sub>1</sub>	F <sub>3</sub>
15	F <sub>3</sub>	F <sub>3</sub>
20	F <sub>3</sub>	F <sub>3</sub>

Figure 2 shows master curve resulting from plots of Z(α) vs. α, showing that, in the range of conversion used for this study, the better agreement between experimental results and Z master curves corresponds to a deceleratory mechanism.

## Conclusions

The thermal degradation of the epoxy system BADGE ( $n=0$ )/1,2-DCH with different amounts of the epoxy reactive diluent vinylcyclohexene dioxide was studied by TG in order to determine the reaction mechanisms of the decomposition process. Various differential and integral methods were used. The study of the master curves, together with the interpretation of integral methods, allows confirmation that the system follows a deceleratory  $F_3$  thermodegradation mechanism for all the compositions with diluent.

The activation energies for the systems with diluent are higher than that obtained for the system without diluent [16].

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