

Thermal Degradation of the Epoxy System BADGE $n = 0/1,2$ -DCH Immersed in Hydrochloric Acid

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Received Received 1 April 2001; accepted 20 October 2001

ABSTRACT: The thermal degradation of an epoxy system consisting of diglycidyl ether of bisphenol-A and 1,2-diamine cyclohexane (BADGE $n = 0/1,2$ -DCH), immersed in hydrochloric acid for 30 days, was studied by thermogravimetric analysis, to determine the reaction mechanism of the degradation process. The results were compared with experimental data corresponding to the same epoxy system without exposure to the acid. It was found that the kinetic reaction mechanism changed with the immersion in HCl. The average activation energy of the solid-state process was determined by using the Flynn–Wall–Ozawa method, resulting in 81 ± 2 kJ/mol. Different integral and differential methods and different reaction mechanisms reported in the literature were used and compared to this value. Analysis of experimental results suggests that in the conversion range studied, 5–20%, the reaction mechanism is somewhere between the different types of phase boundary controlled reaction and random nucleation with one nucleus on the individual particle. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 371–375, 2002

Key words: thermogravimetric; epoxy resins; activation energy; hydrochloric acid

INTRODUCTION

Determination of kinetic parameters from curing kinetics and/or thermodegradation kinetics were shown to be very helpful to study thermoset behavior. Thermodegradation kinetics can be studied by thermogravimetric analysis, which is a very useful tool because important information can be obtained from a single thermogram. Kinetic parameters can be determined by using a large number of differential and integral methods and depend mainly on the treatment of experimental data.

Coating is one of the main uses of epoxidic materials. Because of that, in this article, the behavior of the epoxy system diglycidyl ether of

bisphenol-A and 1,2-diamine cyclohexane (BADGE $n = 0/1,2$ -DCH) is studied with the aim of considering its potential use as a coating for a basin containing leachates originated from municipal waste. Chemical analysis of these leachates shows a content of Cl^- to be taken into account. Owing to this, a kinetic study of the thermal degradation of the above-mentioned epoxy system immersed in hydrochloric acid in nonisothermal conditions was carried out. The results of the present study are compared to those corresponding to the original thermoset without exposure to HCl.

KINETIC METHODS

The rate of conversion, da/dt , is a linear function of a temperature-dependent rate constant, k , and some temperature-independent function of the conversion, α , that is,

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Journal of Applied Polymer Science, Vol. 85, 371–375 (2002)
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$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

Substituting the Arrhenius equation into eq. (1) leads to

$$\frac{d\alpha}{dt} = Af(\alpha) e^{-(E/RT)} \quad (2)$$

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.

The reaction rate may be written as

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT} \frac{dT}{dt} = \beta \frac{d\alpha}{dT} \quad (3)$$

and from it

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

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 $\alpha = \alpha_p$ gives¹

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

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.²⁻⁵

EXPERIMENTAL

Materials

The epoxy resin was a commercial 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.^{6,7} The curing agent was 1,2-diaminecyclohexane (DCH) (Fluka, Switzerland) with an amine hydrogen equivalent weight of 28.5.

Sample Preparation

The epoxy resin and curing agent were carefully and homogeneously mixed at a stoichiometric ratio of 100 : 16.42, and then the samples were introduced in a cylindrical frame.

The curing reaction was programmed according to a TTT diagram constructed for this system.^{8,9} It consists of two stages: a first step at room temperature for 24 h and a second step, in an oven, for 16 h at 70°C. After curing, the samples were removed from the frame.

For thermogravimetric analysis, the samples were cut in the form of 6-mm-diameter disks weighing 15–25 mg. Once cut, the samples were introduced in flasks containing hydrochloric acid for 30 days. This immersion time was chosen because experiments performed on samples of the material showed no change in the glass transition temperature, thus suggesting the nonexistence of degradation of the material during this period.

The thermogravimetric study was carried out by 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 100–900°C, at different heating rates of 5, 15, 25, 35, and 45°C/min.

RESULTS AND DISCUSSION

By using Kissinger's method¹⁰ and the experimental data recorded in the TG curves, the activation energy of the epoxy system BADGE $n = 0$ /1,2-DCH immersed in HCl for 30 days was calculated from a plot of $\ln(\beta/T_{\max}^2)$ versus $1000/T_{\max}$ and fitted to a straight line. T_{\max} is the inflection point temperature corresponding to the TG curves at different heating rates (Fig. 1). The value obtained for the activation energy was 131 kJ/mol. For the nonimmersed epoxy system, the activation energy was 144 kJ/mol. According to this method, the small difference between both activation energy values added to the fact that thermodegradation of both systems, immersed and nonimmersed, takes place at very close temperatures seem to suggest that HCl originates only a slight degradation of the epoxy system during the 30-days immersion.

The activation energy was also determined¹¹ by using the Flynn–Wall–Ozawa method,¹² from a linear fitting of $\ln\beta$ versus $1000/T$ at different conversions. This equation was derived by using Doyle's approximation^{13,14} and, for this reason,

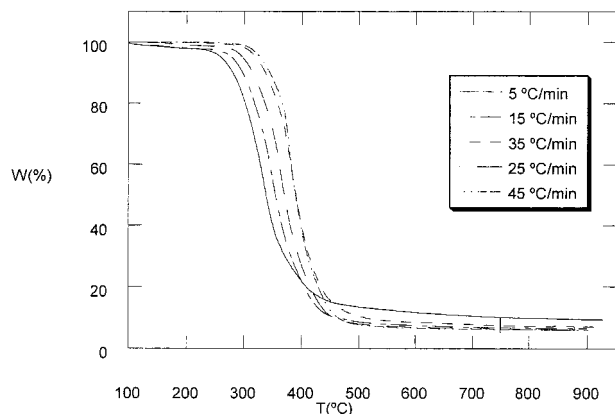


Figure 1 Experimental TG curves at different heating rates.

only conversion values in the range from 5 to 20% were used. The average activation energy obtained by this method was 81 ± 2 kJ/mol. For the nonimmersed system, the activation energy was 149 ± 4 kJ/mol. The wide difference between these two activation energies can be seen thus suggesting an influence of HCl on the TG curves.

If we considered only the nonimmersed system, both methods lead to very close activation energies: 144 and 149 kJ/mol by using Kissinger and Flynn–Wall–Ozawa methods, respectively. However, for the system immersed in HCl for 30 days, these activation energies show a wide deviation 131 of kJ/mol (Kissinger) and 81 kJ/mol (Flynn–Wall–Ozawa).

TG curves corresponding to the system immersed in HCl widen the thermodegradation temperature range (Fig. 2). The Kissinger method does not care about the shape of the TG curves as it keeps using the inflection point temperature.

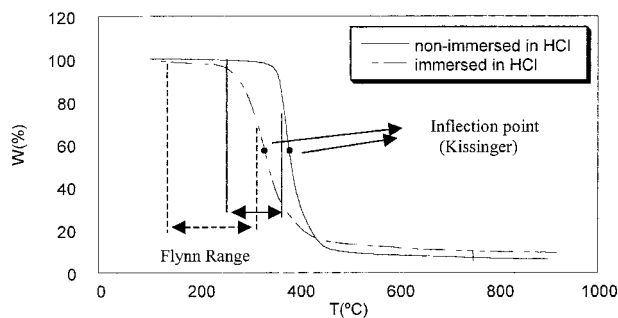


Figure 2 Experimental TG curves for the nonimmersed and immersed in HCl system at a constant heating rate of $15^\circ\text{C}/\text{min}$ showing the inflection point used by Kissinger and the temperature range used by Flynn–Wall–Ozawa method.

Table I Activation Energies (kJ/mol) Obtained by Using Coats–Redfern Method in the Range 5–20% for Different Heating Rate Values in the Range 5– $45^\circ\text{C}/\text{min}$

| Mechanism | Heating Rate ($^\circ\text{C}/\text{min}$) | | | | |
|-----------|--|--------|--------|--------|--------|
| | 5 | 15 | 25 | 35 | 45 |
| A_2 | 35.58 | 40.50 | 45.62 | 52.54 | 35.58 |
| A_3 | 20.71 | 23.85 | 27.16 | 31.68 | 20.71 |
| A_4 | 13.26 | 15.52 | 17.92 | 21.25 | 74.12 |
| R_1 | 75.25 | 84.83 | 94.73 | 108.00 | 105.72 |
| R_2 | 77.73 | 87.61 | 97.83 | 111.52 | 109.18 |
| R_3 | 78.57 | 88.55 | 98.89 | 112.72 | 110.35 |
| D_1 | 159.46 | 179.11 | 199.22 | 226.04 | 221.73 |
| D_2 | 162.73 | 182.78 | 203.32 | 230.69 | 226.27 |
| D_3 | 166.11 | 186.55 | 207.55 | 235.47 | 230.97 |
| D_4 | 163.86 | 184.03 | 204.73 | 232.28 | 227.84 |
| F_1 | 80.22 | 90.45 | 101.02 | 115.13 | 112.71 |
| F_2 | 1.21 | 2.04 | 3.09 | 4.54 | 3.99 |
| F_3 | 11.48 | 13.53 | 15.96 | 19.12 | 18.29 |

However, the Flynn–Wall–Ozawa method accounts for the curve shape as it considers the whole range of degradation within the Doyle approximation. For this reason, the activation energy calculated using this latter method was taken as a reference for discussion.

The activation energy corresponding to different $g(\alpha)$ for the sigmoidal and decelerated mechanism can be obtained at constant heating rates by using the equation proposed by Coats and Redfern¹⁵ from fitting $\ln[g(\alpha)/T^2]$ versus $1000/T$ plots. The study was carried out by using the same conversion values as those used for the previous method.

Table I shows the activation energies calculated by using the Coats and Redfern method at constant heating rate values in the range of 5– $45^\circ\text{C}/\text{min}$. Analysis of this table suggests that the solid-state thermodegradation mechanism followed by our immersed epoxy system is a de-

Table II Activation Energies (kJ/mol) Obtained by Using Van Krevelen Method for the F_1 and R_n Mechanisms

| Mechanism | Heating Rate ($^\circ\text{C}/\text{min}$) | | | | |
|-----------|--|--------|--------|--------|--------|
| | 5 | 15 | 25 | 35 | 45 |
| F_1 | 93.53 | 104.54 | 114.71 | 128.32 | 124.19 |
| R_1 | 87.98 | 98.35 | 107.88 | 120.69 | 116.81 |
| R_2 | 90.70 | 101.41 | 111.26 | 124.46 | 120.46 |
| R_3 | 91.65 | 102.44 | 112.40 | 125.74 | 121.69 |

Table III Activation Energies (kJ/mol) Obtained by Using Horowitz–Metzger Method for the F_1 and R_n Mechanisms

| Mechanism | Heating Rate (°C/min) | | | | |
|-----------|-----------------------|--------|--------|--------|--------|
| | 5 | 15 | 25 | 35 | 45 |
| F_1 | 120.17 | 132.83 | 141.58 | 155.89 | 151.86 |
| R_1 | 102.15 | 113.39 | 121.35 | 135.10 | 127.13 |
| R_2 | 105.15 | 116.63 | 124.72 | 138.57 | 130.67 |
| R_3 | 105.15 | 116.63 | 128.09 | 138.57 | 134.20 |

celerated (F_1 ; R_n) type, because activation energies are closer to the value calculated through the Flynn–Wall–Ozawa method. This degradation mechanism is different for the nonimmersed in hydrochloric acid epoxy system, as for this system, the thermodegradation mechanism seemed to be a sigmoidal A_n type.¹¹ This change in thermodegradation mechanism on the surface layers of the system is caused by HCl.

The use of the equations proposed by Van Krevelen et al.¹⁶ and Horowitz and Metzger,¹⁷ allow calculation of activation energy for solid-state thermodegradation-decelerated mechanism (F_1 , R_n). Van Krevelen obtained activation energies through a linear fitting of $\log g(\alpha)$ versus $\log T$, whereas the Horowitz–Metzger model used a linear fitting of $\log g(\alpha)$ versus $(T - T_r)$. Table II shows the activation energies obtained at the different heating rates using the Van Krevelen model. These values are not very different from those calculated through Flynn–Wall–Ozawa, mainly because of a decelerated mechanism R_1 at a heating rate of 5°C/min. Table III shows activa-

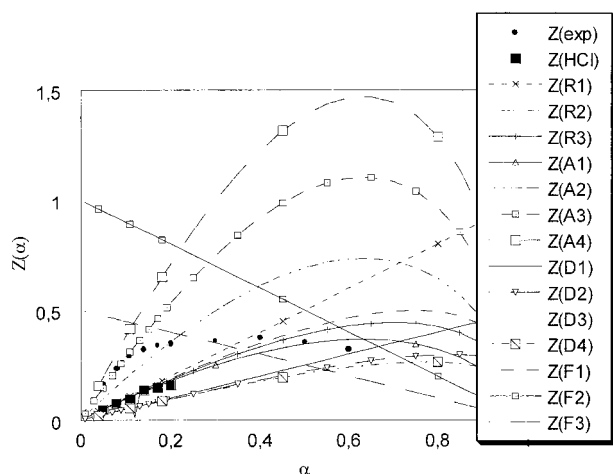


Figure 3 Master plot curves $Z(\alpha)$ versus α .

Table IV Activation Energies (kJ/mol) at a Heating Rate of 5°C/min for the Linear Combination of the F_1 and R_n ($n = 1, 2, 3$) Mechanisms

| | Coats | Van Krevelen | Horowitz |
|-------------------|-------|--------------|----------|
| TER1(F_1+R_1) | 77.80 | 90.85 | 105.15 |
| TER2(F_1+R_2) | 79.39 | 92.74 | 108.16 |
| TER3(F_1+R_3) | 79.80 | 93.11 | 108.16 |

tion energies calculated by using the Horowitz–Metzger model. Values in this table deviate markedly from the Fynn–Wall–Ozawa values. These differences could be associated with the choice of the reference temperature, T_r , which was chosen as that corresponding to the inflection point of the TG curves (Fig. 1) at the different heating rates. This choice does not account for the shape of the thermodegradation main period. Activation energies calculated by the Horowitz–Metzger method are in better agreement with those obtained through the Kissinger equation, which also does not account for the shape of the TG curves.

To check that the thermodegradation curves followed by the immersed epoxy system were either phase boundary controlled reaction or random nucleation with one nucleus on the individual particle, we used the method proposed by Criado et al.³ This method was used to construct the master curve of the epoxy system. Master curves corresponding to the different thermodegradation decelerated type mechanisms were constructed and then compared to the experimental curve constructed by using the following equation at different heating rates:

$$Z(\alpha) = \frac{\left(\frac{d\alpha}{dt}\right)}{\beta} \Pi(x) T \quad (6)$$

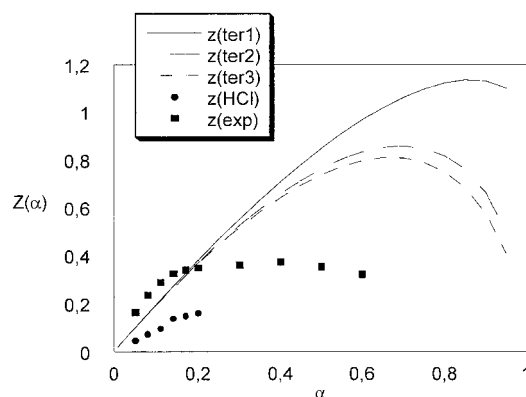


Figure 4 Master plots for the mechanisms TER1, TER2, and TER3.

where $x = E/RT$ and $\Pi(x)$ is an approximation of the temperature integral which cannot be expressed in a simple analytical form. For the present study, the fourth rational expression of Senum and Yang was used.

For the present study, it was found through the study of different integral methods that the optimum heating rate value corresponds to 5°C/min. Experimental values used for determination of $Z(\alpha)$ were those corresponding to 5°C/min. The reason for this choice was that the activation energy obtained by Coats–Redfern method corresponding to this heating rate value is the one in best agreement with the mean value calculated through the Flynn–Wall–Ozawa method. Figure 3 shows $Z(\alpha)$ versus α plots. In this figure, $Z(\text{HCl})$ and $Z(\text{exp})$ correspond to experimental values for the 30 days immersed in HCl and the nonimmersed systems, respectively. It can be seen that, at low conversions, experimental values fit better decelerated R_n and F_1 mechanisms. However, in the range of 10–20% of experimental conversion, values seems to fit a F_1 thermodegradation mechanism. Beyond 20% of conversion, not properly represented in this figure, experimental results do not show a special trend. This could suggest that experimental data correspond to a combination of different R_n and F_1 mechanisms. Three possible combinations, TER1 ($F_1 + R_1$), TER2 ($F_1 + R_2$), and TER3 ($F_1 + R_3$), were used for this study. Table IV shows activation energies at a heating rate of 5°C/min. It can be seen that activation energies calculated by using Coats–Redfern, Van Krevelen, and Horowitz–Metzger methods are in good agreement with the value obtained by the Flynn–Wall–Ozawa method.

However, Figure 4 shows that master curves obtained by using these three mechanisms substantially deviate from experimental results. This indicates that the thermodegradation behavior of the studied epoxy system is more complex than the models used in the present study.

From the previous results, it can be concluded that the thermodegradation behavior of the BADGE ($n = 0$)/1,2-DCH system changes after being immersed for 30 days in hydrochloric acid, going from a nucleation and growth mechanism, corresponding to the original system, to a possible

contracting volume or random nucleation with one nucleus on the individual particle, after being immersed in HCl. This change could be originated by the break of bonds in the pendant chains caused by HCl, thus making the material to lose crosslinking and decreasing the energy necessary to begin thermodegradation.

CONCLUSIONS

The thermodegradation behavior of the epoxy system BADGE ($n = 0$)/1,2-DCH immersed for 30 days in hydrochloric acid was studied by TGA. Observed was a change from a nucleation and growth mechanism to a contracting volume or random nucleation with one nucleus on the individual particle.

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