Thermogravimetric Study of Degradation Process of Diglycidyl Ether of Bisphenol A–1,2-Diaminocyclohexane/Calcium Carbonate System

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ABSTRACT: The thermal degradation of the epoxy system consisting of diglycidyl ether of bisphenol A (BADGE, $n = 0$)–1,2-diaminocyclohexane (DCH) containing calcium carbonate filler is studied by thermogravimetric analysis to determine the reaction mechanism of the degradation process. The value of the activation energy, which is necessary for this study, is calculated using various integral and differential methods. The values obtained using the different methods are compared to the value obtained by Kissinger's method (234.84 $\pm$ 15.12 kJ/mol), which does not require knowledge of the n-order value of the reaction mechanism. All the experimental results are compared to master curves in the range of Doyle's approximation (5–35% of conversion). The analysis of the results suggests that the reaction mechanism is a sigmoidal A_2 type. The thermodegradation mechanism is similar to that found for the same epoxy system without additives. However, for this last system the sigmoidal mechanism is an A_4 type. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1528–1535, 2002

Key words: thermogravimetry; epoxy resins; activation energy; reaction mechanisms

INTRODUCTION

Thermosets are materials with low tensile and storage moduli. For many end uses, it is necessary to add other components to the resin to improve its properties. Some of these components are inert fillers, such as calcium carbonate ($CaCO_3$), which do not change the kinetic parameters significantly but change the mechanical properties, lifetime, and thermal degradation kinetics.

Because the behavior of thermosets is affected by the addition of fillers, 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 determine the upper temperature limit, the mechanism of a solid-state process, and the lifetime for a thermoset.

The main objective of this work was to study the kinetics of thermal degradation of an epoxy resin containing an inert filler ($CaCO_3$) in nonisothermal conditions. The results of this study were compared with those of the same epoxy system without filler.

Kinetic Methods

Thermogravimetric (TG) nonisothermal experiments register the change of the sample mass as a function of temperature. Kinetic parameters can be extracted from nonisothermal experiments.

The degree of conversion can be expressed as

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

where m is the measured experimental mass at temperature T, m_0 is the initial mass, and m_∞ is the mass at the end of the nonisothermal 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 (α), that is

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

Substituting the Arrhenius equation into eq. (2), one obtains

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

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, which is dependent on the time of heating.

Therefore, the reaction rate gives

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

Integration of this equation from an initial temperature (T_0) corresponding to a null degree of conversion to the peak temperature (T_p) of the derivative TG curve, where $\alpha = \alpha_p$, gives[1]

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

where $g(\alpha)$ is the integral function of conversion. To derive eq. (5) it was assumed that there is no reaction between 0 and T_0.

In polymers this integral function, $g(\alpha)$, is either a sigmoidal function or a deceleration function. Table I shows different expressions of $g(\alpha)$ for the different solid-state mechanisms.[2–5] These functions were satisfactorily employed for the estimation of the reaction solid-state mechanism from nonisothermal TG experiments.[6]

Differential Method

The analysis of the changes in the TG data brought about by variation of the heating rate are the basis of the most powerful differential methods for the determination of kinetic parameters. In this article the Kissinger's method[7] was used.

Integral Methods

The integral methods involve an approximate integration of eq. (5). Some of these methods were discussed in the literature by Flynn et al.,[8,9] Coats and Redfern,[10] Van Krevelen et al.,[11] and Horowitz and Metzger.[12]

Determination of Reaction Mechanism

The Criado et al.[3] method was used for the determination of the reaction mechanism. The activation energy of a solid-state reaction can be determined from several nonisothermal measurements, whatever the reaction mechanism.[13] If the value of the activation energy is known, the kinetic model of the process can be found by defining a function

$$Z(\alpha) = \frac{\left(\dfrac{d\alpha}{dt}\right)}{\beta} \prod (x)T \qquad (6)$$

where $x = (E/RT)$ and $\Pi(x)$ is an approximation of the temperature integral that cannot be expressed in a simple analytical form. In this study we used the fourth rational expression of Senum and Yang,[14] which gives errors lower than $10^{-5}\%$ for $x = 20$.

A combination of eqs. (2) and (6) gives

$$Z(\alpha) = f(\alpha)g(\alpha) \qquad (7)$$

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

Plotting the $Z(\alpha)$ function calculated using both the experimental data and eq. (6) and comparing them with the master curves leads to easy and precise determinations of the mechanisms of solid-state processes.

EXPERIMENTAL

Materials

The epoxy resin was a commercial diglycidyl ether of bisphenol A (BADGE, $n = 0$, Resin 332,

Table I   Algebraic Expressions for $g(\alpha)$ for Most Frequently Used Mechanisms of Solid-State Processes

Symbol	$g(\alpha)$	Solid-State Processes
	Sigmoidal Curves	
A_2	$[-\ln(1 - \alpha)]^{1/2}$	Nucleation and growth [Avrami eq. (1)]
A_3	$[-\ln(1 - \alpha)]^{1/3}$	Nucleation and growth [Avrami eq. (2)]
A_4	$[-\ln(1 - \alpha)]^{1/4}$	Nucleation and growth [Avrami eq. (3)]
	Deceleration Curves	
R_1	α	Phase boundary controlled reaction (1-D movement)
R_2	$[1 - (1 - \alpha)^{1/2}]$	Phase boundary controlled reaction (contracting area)
R_3	$[1 - (1 - \alpha)^{1/3}]$	Phase boundary controlled reaction (contracting volume)
D_1	α^2	1-D diffusion
D_2	$(1 - \alpha)\ln(1 - \alpha) + \alpha$	2-D diffusion
D_3	$[1 - (1 - \alpha)^{1/3}]^2$	3-D diffusion (Jander equation)
D_4	$(1 - 2/3\alpha) - (1 - \alpha)^{2/3}$	3-D diffusion (Ginstling–Brounshtein equation)
F_1	$-\ln(1 - \alpha)$	Random nucleation with one nucleus on the individual particle
F_2	$1/(1 - \alpha)$	Random nucleation with two nuclei on the individual particle
F_3	$1/(1 - \alpha)^2$	Random nucleation with two nuclei on the individual particle

Sigma Chemical Co., St. Louis) with an equivalent molecular weight of 173.6 g/eq as determined by wet analysis.[15,16] The curing agent was 1,2-diaminocyclohexane (DCH, Fluka) with an amine hydrogen equivalent weight of 28.5. The inert filler was calcium carbonate (Analema).

Sample Preparation

The epoxy resin and curing agent were carefully and homogeneously mixed at a stoichiometric ratio before adding an amount of inert filler equivalent to 20% of the total mass of the composed
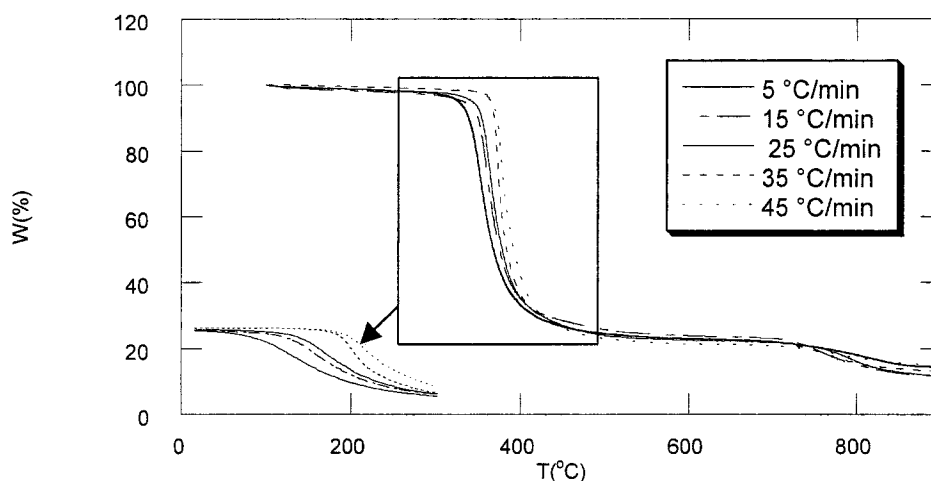

Figure 1   The experimental TG curves at different heating rates.

Table II   Inflection Point Temperature and Residual Mass at 800°C at Different Heating Rates

Heating Rate (°C/min)	$T_{\text{inflection point}}$ (°C)	W (%)
5	342.51	16.62
15	358.75	15.18
25	362.50	16.14
35	368.75	16.44
45	372.50	15.58

system (epoxy, diamine, and filler). This amount was found to be optimum through scanning electron microscopy and curing kinetics studies on this same system using different amounts of CaCO$_3$.[17] Finally, the sample was introduced into a cylindrical frame.

The curing reaction was programmed according to a TTT diagram especially calculated for this material. It consists of two stages: the first step is for 67 min at 50°C and the second step is for 18 h at 85°C in a stove. After curing, the samples were removed from the frame.

For TG analysis (TGA) the samples were cut into 6-mm diameter disks weighing 15–25 mg.

The TGA was performed using a TGA7 analyzer (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 a temperature range of 100–900°C at heating rates of 5, 15, 25, 35, and 45°C/min.

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 for the balance purge gas and 35 mL/min for the sample purge gas.

RESULTS AND DISCUSSION

Figure 1 shows thermal degradation curves corresponding to dynamic experiments carried out at heating rates of 5, 15, 25, 35, and 45°C/min. These curves are the D type,[3] which correspond to a two-stage decomposition reaction where the procedural decomposition temperatures (initial and final) are well defined. The first step is due to the thermal degradation of the epoxy resin and the second step corresponds to the degradation of the calcium carbonate (at around 825°C). Pérez-Maqueda et al.[18] concluded that the degradation of CaCO$_3$ under a high vacuum fitted an R_3 contracting sphere kinetic model with an activation energy of 179 kJ/mol. The inflection point temperature corresponding to the first step (T_m) can be determined from the minimum of the derivative of these curves, and the residual mass (W) after
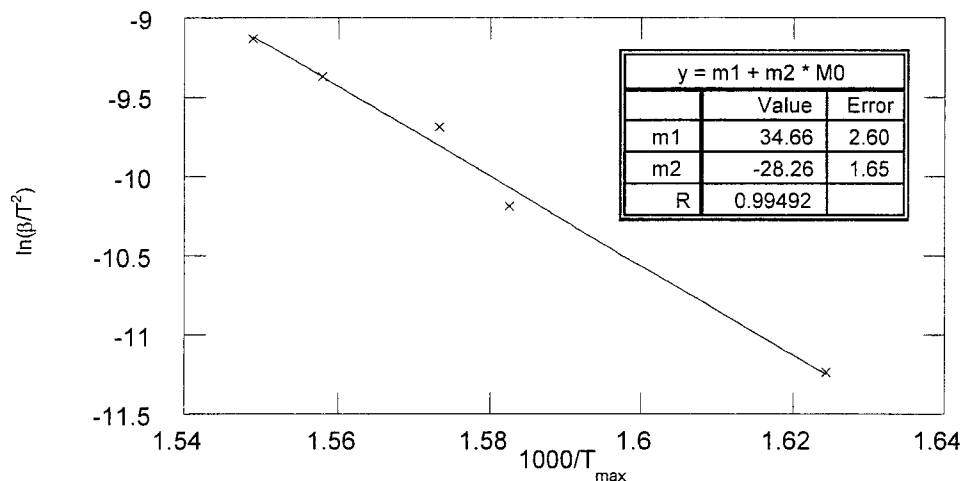

Figure 2   The Kissinger method applied to experimental data at different heating rates.
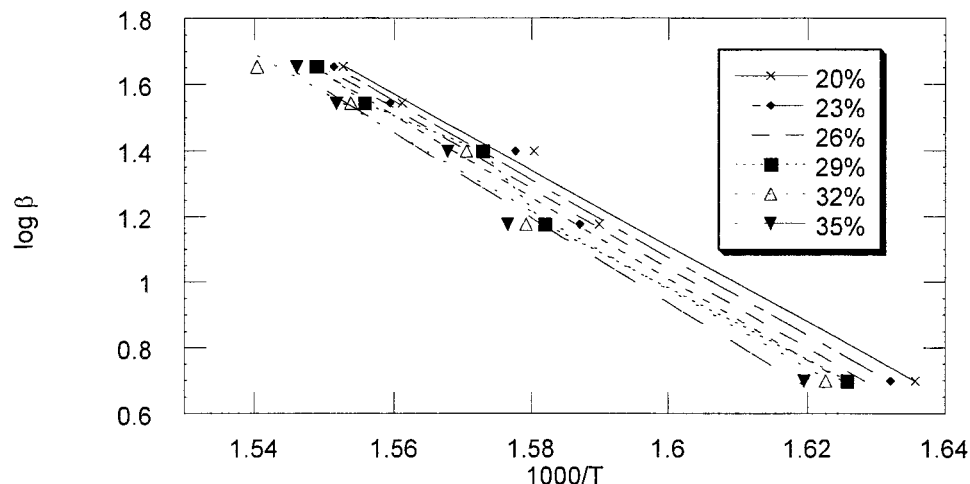
Figure 3 Typical plots of log β versus 1000/T at various conversion values in the 20–35% range in steps of 3%.

degradation can be measured from these TG curves after complete degradation. Table II shows the T_m and the W at different heating rates. An analysis of this table shows that the W keeps nearly constant at a value of around 16%. This value increased 8% with respect to the system without filler.[19] This increment is obviously caused by the calcium carbonate residue.

Because of the thermodegradation behavior of the epoxy system studied here, we chose 10°C/ min heating rates intervals instead of 5°C/min intervals used by some authors[20–22] to avoid the overlapping of the inflection point temperatures. This same procedure was followed in a study of the same epoxy system without filler.[19]

Using Kissinger's approximation equation and the inflection point temperature corresponding to the thermograms shown in Figure 1, the activation energy (E_a) can be calculated from a plot of $\ln(\beta/T_{max}^2)$ versus $1000/T_{max}$ and fit to a straight line. Figure 2 shows the activation energy obtained using this method, which was 234.84

$\pm$ 15.12 kJ/mol. Compared to the activation energy for the epoxy system without filler,[19] this value is higher because the beginning of degradation of the epoxy system with filler takes place at higher temperatures.

The activation energy can also be determined using the method of Flynn et al.[8,9] from a linear fitting of ln β versus 1000/T at different conversions. Because of the fact that this equation was derived using the Doyle approximation,[23] only conversion values in the 5–35% range can be used. Compared to the system without filler,[19] the conversion increases by 15%. For the present study we used conversion values of 20, 23, 26, 29, 32, and 35%. Figure 3 shows that the fitting

Table III Activation Energies Obtained Using Flynn et al. Method

α (%)	E_a (kJ/mol)	R
20	209.84	0.9942
23	215.16	0.9945
26	220.75	0.9947
29	225.48	0.9945
32	230.39	0.9939
35	239.70	0.9939

Table IV Activation Energies Obtained Using Coats–Redfern Method for Solid-State Processes at Heating Rate of 5°C/min

Mechanism	E_a (kJ/mol)	R
A_2	158.39	0.9989
A_3	102.21	0.9989
A_4	74.12	0.9987
R_1	276.64	0.9981
R_2	301.15	0.9986
R_3	309.63	0.9988
D_1	563.50	0.9982
D_2	595.20	0.9985
D_3	629.40	0.9988
D_4	606.55	0.9986
F_1	203.01	0.9984
F_2	96.40	0.9983
F_3	327.08	0.9990

Table V   Activation Energies Obtained Using Coats–Redfern Method for Solid-State Processes at Heating Rate of 15°C/min

Mechanism	E_a (kJ/mol)	R
A_2	191.55	0.9975
A_3	123.57	0.9973
A_4	89.58	0.9972
R_1	334.39	0.9963
R_2	364.06	0.9970
R_3	374.28	0.9972
D_1	681.09	0.9964
D_2	719.56	0.9968
D_3	760.81	0.9972
D_4	733.36	0.9970
F_1	395.47	0.9976
F_2	116.84	0.9994
F_3	246.06	0.9995

Table VII   Activation Energies Obtained Using Coats–Redfern Method for Solid-State Processes at Heating Rate of 35°C/min

Mechanism	E_a (kJ/mol)	R
A_2	267.83	0.9950
A_3	172.76	0.9948
A_4	125.31	0.9946
R_1	467.35	0.9933
R_2	508.99	0.9943
R_3	523.36	0.9946
D_1	951.99	0.9934
D_2	1005.93	0.9941
D_3	1063.76	0.9947
D_4	1025.29	0.9943
F_1	553.03	0.9951
F_2	163.96	0.9999
F_3	345.20	0.9999

straight lines are nearly parallel, thus indicating the applicability of this method to our epoxy system in the conversion range studied. This fact suggests that a single reaction mechanism is operative.[22,24] The activation energies corresponding to the different conversions are listed in Table III. These activation energy values give a mean value of 223.55 kJ/mol. Table III also shows the close agreement between the activation energy corresponding to 32% conversion and the value obtained using Kissinger's method.

Compared to others, these two methods present the advantage that they do not require the previous knowledge of the reaction mecha-

nism for determining the activation energy. Some authors[4,20] used the activation energies obtained using these two methods in order to check their thermodegradation mechanism models.

Using the method proposed by Coats and Redfern,[10] the activation energy for every $g(\alpha)$ listed in Table I can be obtained at constant heating rates from fitting of $\ln[g(\alpha)]/T^2$ versus $1000/T$ plots. We used the same conversion values for this study as those used in the previous methods.

Tables IV–VIII show activation energies and correlations in the 5–35% range at constant heating rate values of 5, 15, 25, 35, and 45°C/min, respectively. Analysis of these tables shows that,

Table VI   Activation Energies Obtained Using Coats–Redfern Method for Solid-State Processes at Heating Rate of 25°C/min

Mechanism	E_a (kJ/mol)	R
A_2	206.42	0.9980
A_3	133.21	0.9979
A_4	96.56	0.9976
R_1	360.40	0.9969
R_2	392.31	0.9975
R_3	403.45	0.9977
D_1	734.10	0.9970
D_2	775.49	0.9974
D_3	819.95	0.9978
D_4	790.36	0.9975
F_1	426.22	0.9980
F_2	125.81	0.9987
F_3	264.84	0.9988

Table VIII   Activation Energies Obtained Using Coats–Redfern Method for Solid-State Processes at Heating Rate of 45°C/min

Mechanism	E_a (kJ/mol)	R
A_2	394.89	0.9958
A_3	254.70	0.9957
A_4	184.65	0.9955
R_1	689.06	0.9943
R_2	750.31	0.9952
R_3	771.58	0.9955
D_1	1403.56	0.9945
D_2	1483.00	0.9950
D_3	1568.26	0.9956
D_4	1511.51	0.9952
F_1	815.21	0.9960
F_2	241.40	0.9998
F_3	508.32	0.9999

Table IX   Activation Energies Obtained Using Van Krevelen et al. Method for Sigmoidal Processes at Different Heating Rates

Reaction Rate (°C/min)		Mechanism			
		A_2	A_3	A_4	F_2
5	E_a (kJ/mol)	163.87	107.54	79.35	106.82
	R	0.9989	0.9989	0.9989	0.9987
15	E_a (kJ/mol)	198.75	130.75	101.98	124.03
	R	0.9976	0.9976	0.9976	0.9996
25	E_a (kJ/mol)	214.62	141.30	104.64	133.90
	R	0.9981	0.9981	0.9981	0.9990
35	E_a (kJ/mol)	279.56	184.62	137.09	175.76
	R	0.9952	0.9952	0.9952	0.9999
45	E_a (kJ/mol)	415.06	274.92	204.85	261.61
	R	0.9960	0.9960	0.9960	0.9998

at all the heating rate values, the activation energies are in better agreement with those obtained using the Kissinger and Flynn et al. methods correspond to an A_2-type mechanism. From these tables it also can be seen that the optimum heating rate value is 25°C/min, at which the corresponding activation energy is 206.42 kJ/mol, which is very close to the 223.55 kJ/mol obtained by the Flynn et al. method. These facts suggest that the solid-state thermodegradation mechanism followed by our epoxy system is a sigmoidal (A_n) type. This degradation mechanism is the same for the epoxy system without filler, but the sigmoidal type mechanism is different: it is A_4 for the system without filler and A_2 for the system with filler incorporated; both are nucleation and growth TG mechanisms.

In order to confirm this sigmoidal behavior, we calculated activation energies and correlations using the Van Krevelen et al. and Horowith–Metzger models.[11,12] The activation energy is obtained through a linear fitting of log α versus log T plots. Table IX shows activation energies and correlation values for A_n mechanisms at different constant heating rate values. As can be seen, mechanism A_2 at heating rate of 25°C/min gives an activation energy of 214.62 kJ/mol, which is in good agreement with the value obtained using Flynn et al.'s method (223.55 kJ/mol).

Table X shows activation energies and correlations using the A_n mechanism and the Horowitz and Metzger model, which uses ln $g(\alpha)$ versus ($T - T_r$) plots.[13] Once more the best agreement with the Kissinger and Flynn et al. methods corre-

Table X   Activation Energies Obtained Using Horowitz–Metzger Method for Sigmoidal Processes at Different Heating Rates

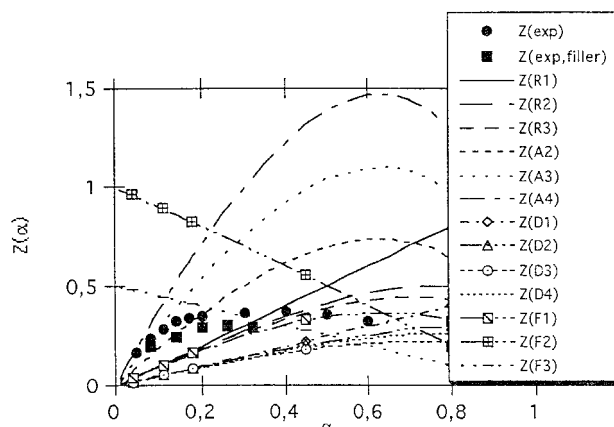| Reaction Rate (°C/min)		Mechanism			
		A_2	A_3	A_4	F_2
5	E_a (kJ/mol)	169.14	112.86	84.73	107.09
	R	0.9989	0.9989	0.9989	0.9987
15	E_a (kJ/mol)	204.07	136.04	101.87	129.41
	R	0.9975	0.9975	0.9975	0.9996
25	E_a (kJ/mol)	219.93	146.73	110.13	137.66
	R	0.9980	0.9980	0.9980	0.9998
35	E_a (kJ/mol)	284.54	189.69	142.44	181.47
	R	0.9951	0.9951	0.9951	0.9998
45	E_a (kJ/mol)	420.55	280.25	211.31	266.74
	R	0.9960	0.9960	0.9960	0.9998

Figure 4 The master curves $Z(\alpha)$ of the experimental data for the system with and without filler.

sponds to the A_2 mechanism and a heating rate of 25°C/min, at which $E_a = 219.93$ kJ/mol.

To corroborate that our epoxy system follows a sigmoidal thermodegradation mechanism, we used the method proposed by Criado et al.[3] This method uses reference theoretical curves called master plots that are compared to experimental data. The experimental results are obtained from eq. (6) at a heating rate of 25°C/min, which is considered the optimum through studies based on integral methods.

Figure 4 shows master curve plots $[Z(\alpha)]$ versus α, which show that, in the range of conversions used for this study, the better agreement between the experimental results and Z master curves corresponds to a sigmoidal mechanism.

CONCLUSIONS

The thermal degradation of the epoxy system BADGE ($n = 0$)/1,2-DCH with CaCO$_3$ filler was studied by TGA in order to determine the reaction mechanism 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 sigmoidal A_2 thermodegradation mechanism within the conversion range (Doyle approximation) considered here. A

comparison with the system without filler was made. The activation energy of the filled system is much higher than that of the nonfilled system as a consequence of the higher temperature necessary for the beginning of degradation of the first epoxy system.

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