

Thermal Stability and Kinetics Analysis of Rubber-Modified Epoxy Resin by High-Resolution Thermogravimetric Analysis

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ABSTRACT: A dynamic heating rate mode of high-resolution thermogravimetric analysis was used to study the thermal and thermal-oxidative stability, as well as kinetics analyses, of a model liquid rubber-modified epoxy resin, Ep/CTBN, made up of bisphenol A diglycidyl ether-based epoxy and carboxyl-terminated butadiene acrylonitrile rubber (CTBN). Results show that the thermal degradation of Ep/CTBN resin in nitrogen and air consists of two and three independent steps, respectively. Moreover, Ep/CTBN has a higher initial degradation temperature and higher activation energy than those of pure epoxy resin in both gases, indi-

cating that the addition of CTBN to epoxy can improve the thermal and thermal-oxidative stability of pristine epoxy resin. Kinetic parameters such as activation energy, reaction order, and preexponential factor of each degradation step of both Ep/CTBN and pure epoxy resins in air and nitrogen were calculated. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3594–3600, 2003

Key words: epoxy/CTBN resin; thermal degradation; kinetic analysis; thermogravimetric analysis (TGA); rubber

INTRODUCTION

Since the first epoxy resin patents were granted in the 1930s and 1940s, the properties of epoxy resins, such as excellent chemical resistance, very good adhesion, and ease of handling and processing, have been used in many applications including surface coatings, adhesives, castings, and laminates.^{1–9}

However, like other thermosetting resins, epoxy resin's brittleness is a major shortcoming in many applications. To overcome this disadvantage of epoxy resins, many attempts have been made to blend them with reactive liquid rubbers such as carboxyl- and amine-terminated butadiene acrylonitrile rubber (CTBN and ATBN). The properties of epoxy/CTBN or epoxy/ATBN systems, especially their mechanical properties, have been intensively studied, and results have proved that, with an appropriate weight of rubber, the rubber-modified resins have strongly improved toughness.^{10–15} To date, however, little is known about their thermal and thermal-oxidative sta-

bility up to elevated temperatures, and fundamental data are not available. We know that the thermal and thermal-oxidative stability of a polymer determine the upper service temperature and the environmental conditions under which the polymer can be employed. Because thermal/thermal-oxidative stability is related to both the initial degradation temperature and the degradation rate of a polymer,^{16,17} the determination of activation energy and reaction order associated with the degradation process is an absorbing topic.

In this study, a typical reactive liquid rubber-modified epoxy resin, made up of epoxy and CTBN, was chosen as a model system. Moreover, a dynamic heating rate mode of high-resolution thermogravimetric analysis (TGA) was used to study the decomposition behavior and kinetic parameters of resins because it gives reliable information on the frequency factor, the activation energy, and overall reaction order.^{18,19} The thermal decomposition behavior and kinetics of pristine epoxy resin were also investigated for comparative purposes.

EXPERIMENTAL

Materials

Epoxy resin used was Epon 828, a bisphenol A diglycidyl ether-based resin made by the Shell Chemical Co. (average molecular weight ~ 380 g/mol). Piperidine (Aldrich Ltd.) was the curing agent. CTBN (Hycar CTBN1300x9) was obtained from Noveon Asia

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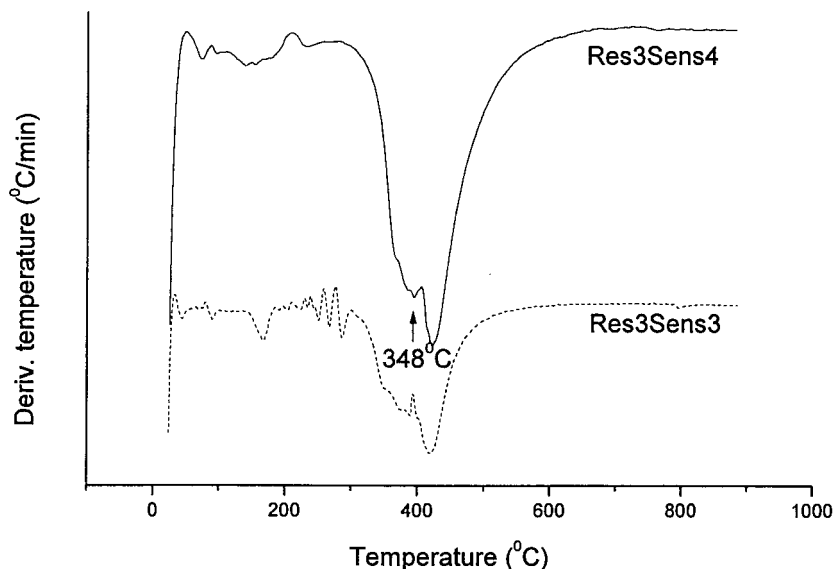


Figure 1 TGA plots of Ep/CTBN in nitrogen with varied sensitivities (initial heating rate is 20°C/min).

Pacific Ltd. (acrylonitrile content = 18%; nominal molecular weight = 3600).

Preparation of epoxy/CTBN and epoxy resins

Epon 828 (10 g) was added to a three-neck round-bottom flask equipped with a mechanical stirrer and a thermometer, and heated to 100°C with stirring, after which 2 g CTBN was added to the flask, and maintained at 100°C until the mixture was homogeneous. Then 0.5 g piperidine was added to the mixture with stirring. The blend was then poured into a stainless steel mold that had been preheated to 100°C, and degassed for 15 min under vacuum to remove trapped air. The blend was then cured at 120°C for 12 h in a conventional oven. The resultant cured sample was coded as Ep/CTBN.

Cured pristine epoxy resin was also prepared by a method similar to that described above except that no CTBN was added.

TGA analyses

All TGA analyses were performed on a TA Instruments Hi-Res TGA 2950 (TA Instruments, New Castle, DE) interfaced to a TA Instruments 2000 controller. Samples of 10–15 mg were heated to 900°C under a nitrogen or air atmosphere at a flow rate of 60 mL/min.

RESULTS AND DISCUSSION

Dynamic heating rate TGA mode^{20,21}

In the dynamic heating rate mode of high-resolution thermogravimetry, the heating rate is continuously and dynamically varied to maximize resolution. The observed heating rate is a function of resolution, sensitivity, initial heating rate, and weight loss rate with respect to time. Decomposition kinetics from this mode may be obtained by taking the second deriva-

TABLE I
Heating Rates and Temperatures at Maximum Degradation Rate and Temperature at Minimum Heating Rate of Ep/CTBN in Nitrogen

Operating parameter		First step			Second step		
Initial heating rate (°C/min)	Resolution	Heating rate (°C/min)	T_{\max}^a (°C)	T_{\min}^b (°C)	Heating rate (°C/min)	T_{\max}^a (°C)	T_{\min}^b (°C)
20	3	10.60	348.72	348.64	3.01	419.29	419.19
	4	3.44	335.87	335.64	0.89	398.46	398.45
	5	0.93	313.57	313.70	0.34	381.74	381.71
	6	0.25	295.02	295.09	0.064	359.51	359.43
40	3	8.60	393.10	394.82	2.88	421.94	421.27
	4	3.47	345.62	344.62	1.05	401.13	401.91

^a Temperature at maximum degradation rate.

^b Temperature at minimum heating rate.

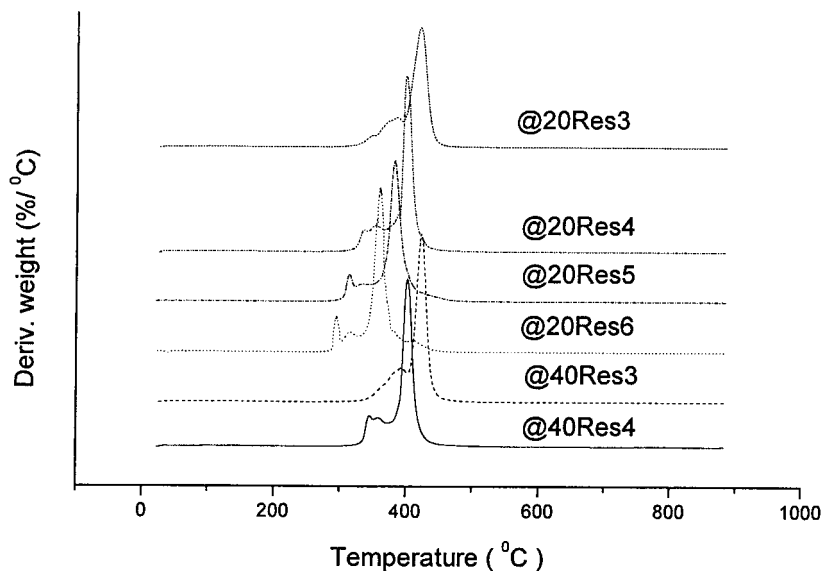


Figure 2 TGA plots of Ep/CTBN in nitrogen.

tive of the Arrhenius equation versus temperature and the natural log to get the following expression:

$$\ln(Hr/T^2) = (-Ea/R)(1/T) - \ln[ARn(1-\alpha)^{n-1}/Ea] \quad (1)$$

where Hr is the heating rate at maximum degradation rate ($^{\circ}\text{C}/\text{min}$), T is the temperature at maximum degradation rate (K), Ea is the activation energy (J/mol), R is the gas constant (8.314 kJ/mol), A is the preexponential factor (1/s), n is the reaction order, and α is the fraction of decomposition.

The plot of $\ln(Hr/T^2)$ versus $1/T$ should give a straight line with the slope $-Ea/R$, giving the activation energy Ea . The reaction order and preexponential factor can be calculated by using the intercept value (I) determined from eqs. (2) and (3).

$$n = (d\alpha/dT)^{-1} e^{(-Ea/RT+I)} Ea(RHr)^{-1} \quad (2)$$

$$A = Hr(d\alpha/dT)(1-\alpha)^{-n} [e^{-Ea/RT}]^{-1} \quad (3)$$

It is worth noting that, although the dynamic heating rate mode requires at least three experiments at

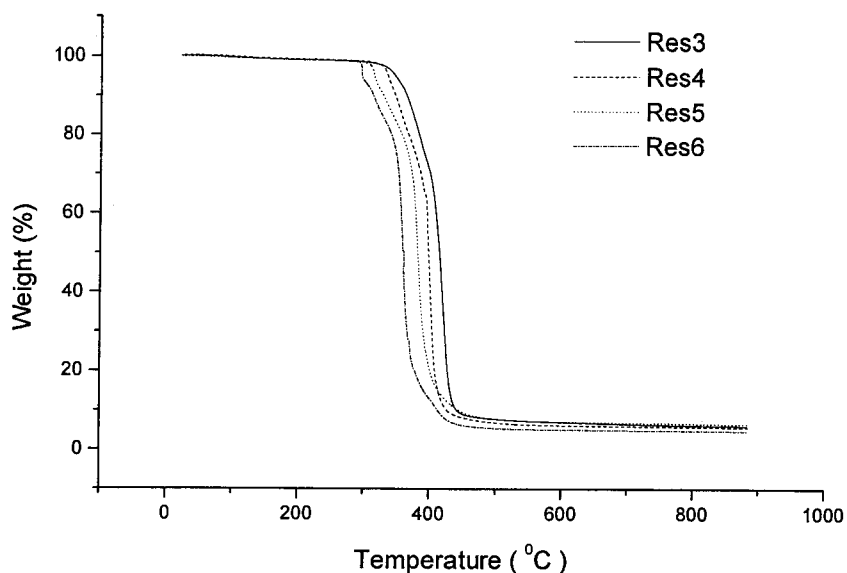


Figure 3. TGA plots of Ep/CTBN in nitrogen.

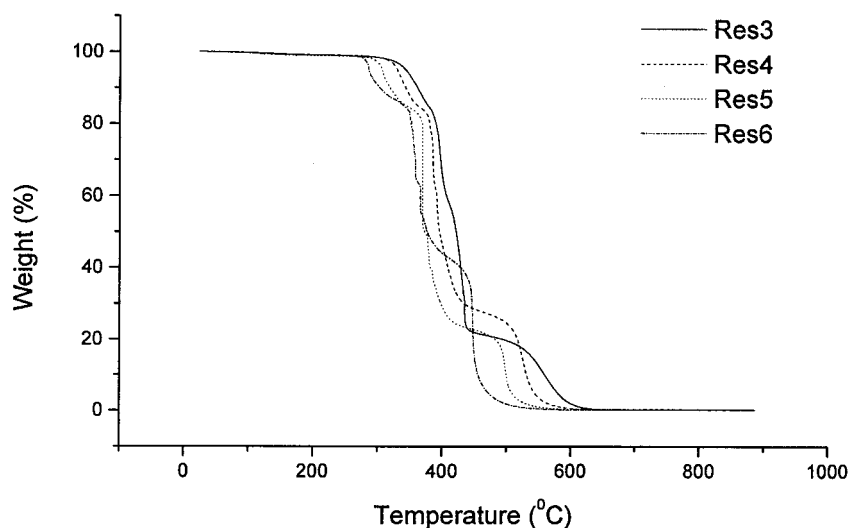


Figure 4 TGA plots of Ep/CTBN in air.

different maximum degradation rates to obtain kinetic information, the calculation of activation energy is independent of reaction order and the reaction mechanism, so it is very useful when studying a material for which the degradation mechanism is not completely understood.

Optimum conducting parameters

As seen from the above, to calculate activation energy, the temperature and heating rate at maximum degradation rate must be determined from experimental data. However, both parameters are dependent on operating parameters such as initial heating rate, resolution, and sensitivity, so investigating the effect of experimental conditions on these two factors and consequently finding the optimum operating parameters are very important.²¹

Figure 1 shows the TGA plots of Ep/CTBN resin in nitrogen with various sensitivities. When the sensitivity was lower than 4, the corresponding plots did not have sufficient sensitivity to separate the first degradation step at about 348°C, so the sensitivity was fixed at 4 for all further experiments.

Two initial heating rates and four resolutions were chosen to conduct the experiments: the data of heating rate and temperature at maximum degradation rate of

Ep/CTBN in nitrogen are shown in Table I. When the initial heating rate was fixed and resolution was varied from 3 to 6, temperature and heating rate values at maximum degradation rate spanned a wide range of values; the temperature values were shifted to lower ones. When the resolution was fixed, and the initial heating rate was varied from 20 to 40°C/min, the peak temperatures and heating rates were also significantly affected, and the temperatures were shifted to higher values, as shown in Figure 2 and Table I. However, when the initial heating rate was 20°C/min, the minimum heating rate and maximum degradation rate occurred at almost the same temperature: the maximum difference between them was less than 0.13°C, whereas when the initial heating rate was 40°C/min, the maximum difference between them was higher than 1°C. As a result, the initial heating rate was fixed at 20°C/min, and resolution was varied from 3 to 6 for further analyses.

TABLE III
Initial Temperatures and Char Yields of Ep/CTBN Resin and Epoxy Resin

Operating parameter		Ep/CTBN		Epoxy	
Purge gas	Resolution	T_i^a (°C)	Y_c^b (%)	T_i^a (°C)	Y_c^b (%)
N ₂	3	350.06	6.097	349.31	9.738
	4	334.52	5.728	327.02	8.007
	5	311.12	6.196	310.46	8.040
	6	295.26	4.824	292.43	5.672
Air	3	342.84	0.2542	333.02	0.3216
	4	325.58	0.2387	321.10	0.2877
	5	305.89	0.2016	304.47	0.1660
	6	285.55	0.1450	278.58	0.1428

^a Initial degradation temperature, defined as the temperature of 5% weight loss.

^b Char yield at 880°C.

TABLE II
Start and End Temperatures of Each Degradation Step

Purge gas	Step	Ep/CTBN	Epoxy
N ₂	First	295–340	290–340
	Second	340–450	340–410
Air	First	285–340	280–340
	Second	350–410	340–430
	Third	450–550	450–500

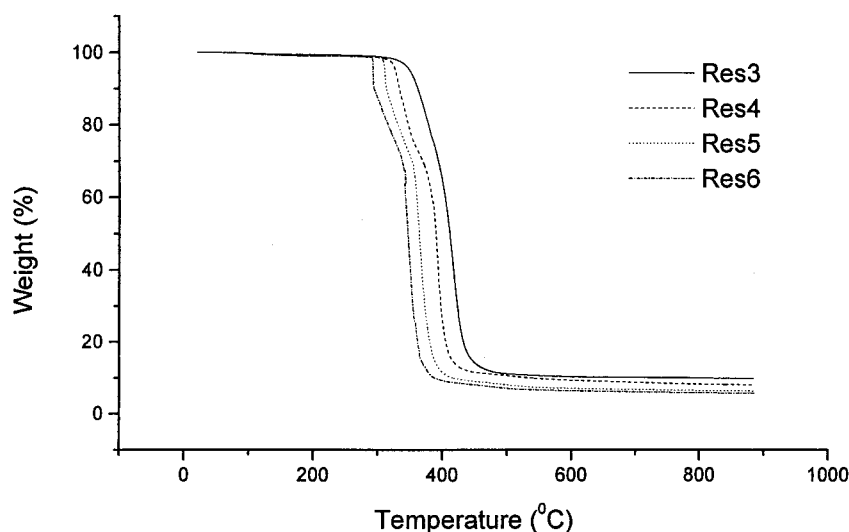


Figure 5 TGA plots of pristine epoxy in nitrogen.

Degradation behavior and kinetic analyses

Typical TGA curves of Ep/CTBN in nitrogen (Fig. 3) and air (Fig. 4) reveal that the thermal degradation of the resin consists of two and three independent steps, respectively. The start and end temperatures of each step varied with operating parameters and are listed in Table II. In addition, the initial degradation temperature (T_i), cited as the characteristic temperature for assessing thermal stability, in nitrogen is 4–9°C (varied with the experimental parameters) higher than that in air, as expected (Table III). Similar phenomena were also observed in pristine epoxy resin (Fig. 5 and Fig. 6) except that its T_i in nitrogen was 6–16°C higher than that in air. Comparison of T_i values of the two resins shows that Ep/CTBN has higher T_i than that of pure epoxy resin in both gases, indicating that the addition of CTBN to epoxy can improve the thermal

and thermal-oxidative stability of the epoxy resin. This conclusion will be further addressed in the following activated energy (E_a)-related discussion.

The char yields at 880°C of both resins in air were much lower than that in nitrogen (Table III). Moreover, in nitrogen the char yield of Ep/CTBN was somewhat smaller than that of epoxy, whereas in air both values were about zero. It is important to note that, when comparing TGA plots in nitrogen (Figs. 3 and 5) with those in air (Figs. 4 and 6), an interesting phenomenon can be observed; that is, char yields of both resins at 400–480°C in air were about two times those in nitrogen, implying that the intermediates formed in air after the second degradation reaction are relatively stable at temperatures from 400–480°C. Detailed determination of the more complicated stoichiometry of degradation reactions needs further investigation.

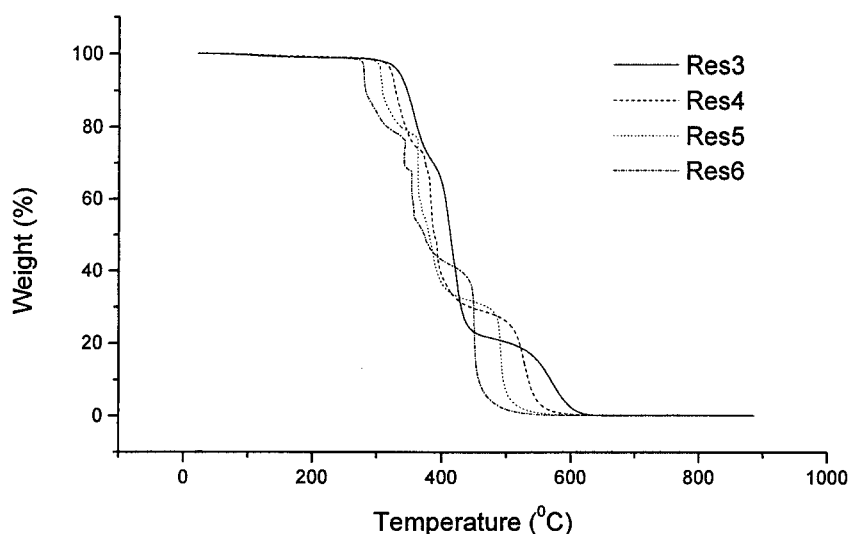


Figure 6 TGA plots of pristine epoxy in air.

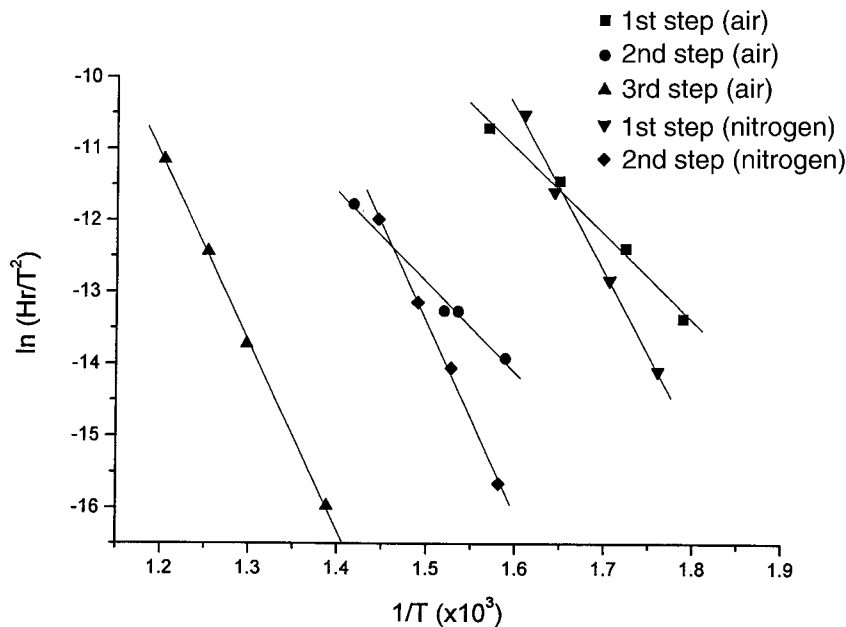


Figure 7 Plots of $\ln(Hr/T^2)$ against $1/T$ for decomposition of Ep/CTBN resin.

Plots of $\ln(Hr/T^2)$ against $1/T$ to calculate the activation energy (Ea) in eq. (1) for each degradation step are shown in Figure 7 and Figure 8. The values of Ea , n , and $\ln A$ were calculated following the approach described above and are summarized in Table IV. The Ea value of the first step (Ea_1) can be used to determine whether the initial degradation process proceeds easily or not, so it is of most interest to discuss. As can be seen from Table IV the purge gas has a great effect on Ea_1 ; the lower Ea_1 values of both resins in air reveal that the degradation reactions of both resins become easier in air,

especially for the Ep/CTBN system. For the Ep/CTBN resin, the value of Ea_1 in air is about half that in nitrogen, implying that the decomposition mechanism may be different in the two atmospheres.²² It is worth noting that, no matter whether in nitrogen or air, the Ea_1 value of Ep/CTBN was higher than that of pure epoxy resin, given that their corresponding first-reaction orders (n_1) are equal (Table IV); thus, this result implies that, in both gases, the initial degradation reaction of Ep/CTBN resin is more difficult to start than is that of pure epoxy resin and, as a result, T_i of Ep/CTBN was higher

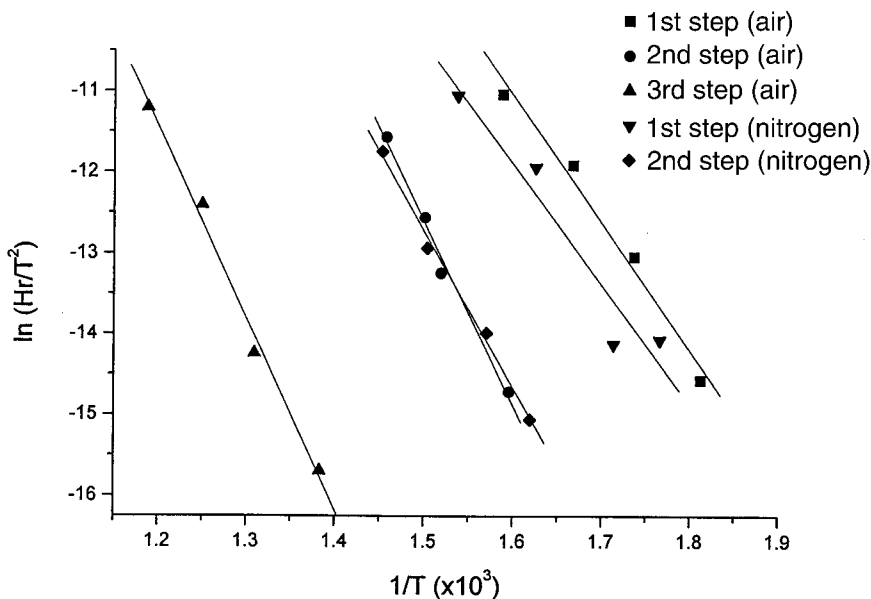


Figure 8 Plots of $\ln(Hr/T^2)$ against $1/T$ for decomposition of epoxy resin.

TABLE IV
Kinetic Parameters of Ep/CTBN in Nitrogen and Air^a

Purge gas	Ea_1 (kJ/mol)	n_1	\ln/A_1	Ea_2 (kJ/mol)	n_2	\ln/A_2	Ea_3 (kJ/mol)	n_3	\ln/A_3
N ₂	190.28	0.80	40.48	222.41	1.18	41.55	—	—	—
Air	108.20	0.48	21.79	104.51	0.82	20.02	217.33	1.18	34.43

^a n_i is the degradation reaction order of i step, $i = 1, 2$; A_i is the preexponential factor of i step, $i = 1, 2$.

TABLE V
Kinetic Parameters of Epoxy Resin in Nitrogen and Air^a

Purge gas	Ea_1 (kJ/mol)	n_1	\ln/A_1	Ea_2 (kJ/mol)	n_2	\ln/A_2	Ea_3 (kJ/mol)	n_3	\ln/A_3
N ₂	112.64	0.70	23.68	160.28	1.05	31.16	—	—	—
Air	102.74	0.32	27.94	188.48	2.19	36.09	196.69	1.77	30.69

^a n_i is the degradation reaction order of i step, $i = 1, 2, 3$; A_i is the preexponential factor of i step, $i = 1, 2, 3$.

8than that of epoxy, as discussed above. Another important result is that n_1 of both resins in nitrogen is higher than that in air: the former is about 1; the latter is about 0. Thus, during the thermal degradation processes of both resins in nitrogen, the weight loss results from monomer scission from the polymer chain end and small molecule scission from a side chain, whereas in air the weight loss results from the random scission of a main chain, according to Denq et al.¹⁹

CONCLUSIONS

Liquid rubber-modified epoxies have drawn the attention of scientists and engineers because of their strongly improved toughness. However, to date, no fundamental data have been available on their thermal and thermal-oxidative stability. A system made up of epoxy and 20-phr CTBN, Ep/CTBN, was chosen as a model resin, and a dynamic heating rate approach of high-resolution TGA was used to study the thermal degradation behavior and kinetic analyses of Ep/CTBN resin and pure epoxy resin. Calculated kinetic parameters from the experiments and initial degradation temperature reveal that Ep/CTBN has better thermal and thermal-oxidative stability than that of pure epoxy resin.

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