

Thermal Decomposition Kinetics of an Epoxy Resin with Rubber-Modified Curing Agent

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ABSTRACT: Thermal decomposition kinetics of diglycidyl ether of bisphenol A (DGEBA)/4,4'-methylene dianiline (MDA) system with rubber-modified MDA was studied by the methods of Ozawa, Kissinger, and Friedman, and the kinetic parameters were compared. The thermal decomposition data of the cured epoxy resin were analyzed by thermogravimetric analysis (TGA) at different heating rates. TG curves showed that the thermal decomposition of the epoxy system occurred in one stage regardless of rubber-modified MDA content. The apparent activation energies for the DGEBA/MDA system with 10 phr of rubber-modified MDA, as determined by the Ozawa, Kissinger, and Friedman methods, are 184, 182, and 222 kJ/mol, respectively. The thermal stability of the epoxy system increased with the increasing content of rubber-modified MDA, which has four benzene rings with high thermal resistance due to the resonance structure. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 479–485, 2001

Key words: thermal decomposition; epoxy; Ozawa equation; Kissinger equation; Friedman equation

INTRODUCTION

Epoxy resins have been widely used as high performance materials in many fields, such as adhesive, coating, laminating, capsulation, electrical insulation, and composite applications.^{1–3} However, the toughness of the epoxy resin cured with aromatic amine is poor. So, many methods have been proposed to enhance the fracture toughness, and one of the most well known is to incorporate various amounts of reactive liquid rubber.^{4–7} When epoxy resin together with liquid rubber is cured, the rubber-rich domains are separated from the epoxy-rich matrix because of the incompatibility between

epoxy resin and liquid rubber, and the rubber domain improves the toughness by absorbing the impact energy.^{6,7} Various reactive liquid rubbers, such as carboxyl-terminated butadiene acrylonitrile (CTBN), amine-terminated butadiene acrylonitrile (ATBN), epoxy-terminated butadiene acrylonitrile (ETBN), or hydroxyl-terminated butadiene acrylonitrile (HTBN), etc., are incorporated. However, the toughness improvement is generally obtained by sacrificing the tensile, thermal, or other properties. Therefore, the appropriate amount of rubber compound should be chosen to avoid the severe decrements of other properties.

In this study, CTBN-modified 4,4'-methylene dianiline (MDA) was introduced to epoxy resin and the thermal decomposition characteristics were studied to estimate the properties to use as high performance and heat-resistance matrix.

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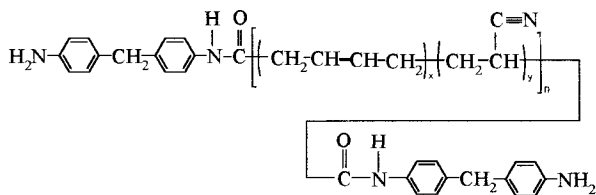
Thermogravimetric analysis (TGA) was employed to measure the weight loss and the derivative weight loss of the cured epoxy resin by heat. The TGA data were then introduced to many expressions, such as Ozawa, Kissinger, and Friedman equations, to investigate the thermal decomposition kinetics.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A (DGEBA; Epon 828 grade; MW, 385; functionality, 2), supplied by Shell Company, was used as a base resin, and 4,4'-methylene dianiline (MDA; MW, 198.3; T_m , 90°C), from Fluka Chemie AG Company, was used as a curing agent. Carboxyl-terminated butadiene acrylonitrile copolymer (CTBN), manufactured by B. F. Goodrich Company under the trade name of Hycar 1300×8 was used as a toughener.

To obtain better compatibility between epoxy resin and CTBN, CTBN was capped with MDA at 160 °C for 1h, and the following molecular formula was found by Fourier transform infrared spectroscopy (FT-IR; new peak of amide group at 1690 and 1630 cm^{-1}).



Thermogravimetric Analysis

TGA was performed with a Chan 121 instrument. DGEBA, MDA (30 phr), and rubber-modified MDA (0, 10, and 20 phr) were well mixed at 80 °C and cured at 150 °C for 1 h after curing at 80 °C for 1.5 h (phr means parts per one hundred base resin). Three to five milligrams of the cured sample was placed on the balance located in the furnace of the TG analyzer, and heat was applied in the temperature range 30–600 °C at the heating rates of 5, 10, 15, and 20 °C/min. Five TGA curves were obtained for each sample, and the standard deviations of weight loss in the experimental temperature range were within 2%. Nitrogen gas flowed into the furnace at 40 mL/min to prevent the oxidation or other reactions of the sample.

RESULTS AND DISCUSSION

All kinetic studies can start with the basic equation that relates the rate of weight loss at a constant temperature to the fractional decomposition:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

where $d\alpha/dt$ is the rate of weight loss, α is the fractional decomposition at any time, and k is rate constant. The term $f(\alpha)$ is a function form of α ; namely,

$$f(\alpha) = (1 - \alpha)^n \quad (2)$$

The rate constant, is dependent on the reaction temperature according to the Arrhenius expression:

$$k = A \exp\left(\frac{-E_d}{RT}\right) \quad (3)$$

where E_d is the activation energy, A is a pre-exponential factor, R is the gas constant, and T is the reaction temperature. Combining eqs. 1–3,

$$\frac{d\alpha}{dt} = A(1 - \alpha)^n \exp\left(\frac{-E_d}{RT}\right) \quad (4)$$

Because $d\alpha/dt = (d\alpha/dT)(dT/dt) = \beta(d\alpha/dT)$, the integrated form of eq. 4 can be expressed as

$$F(\alpha) = \int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E_d}{RT}\right) dT \quad (5)$$

where β is the heating rate. The temperature-dependent part of eq. 5 cannot be solved analytically, so many good approximation methods are proposed by using TG and derivative thermogravimetry (DTG) data.

Figure 1 shows the representative TG and DTG curves for the DGEBA/MDA system with 10 phr of rubber-modified MDA at four different heating rates. All curves show that the thermal decomposition took place in one stage and the curves shift to the right-hand side with the increasing heating rate. The same trends were found in all systems regardless of rubber-modified MDA content. The decomposition temperatures,

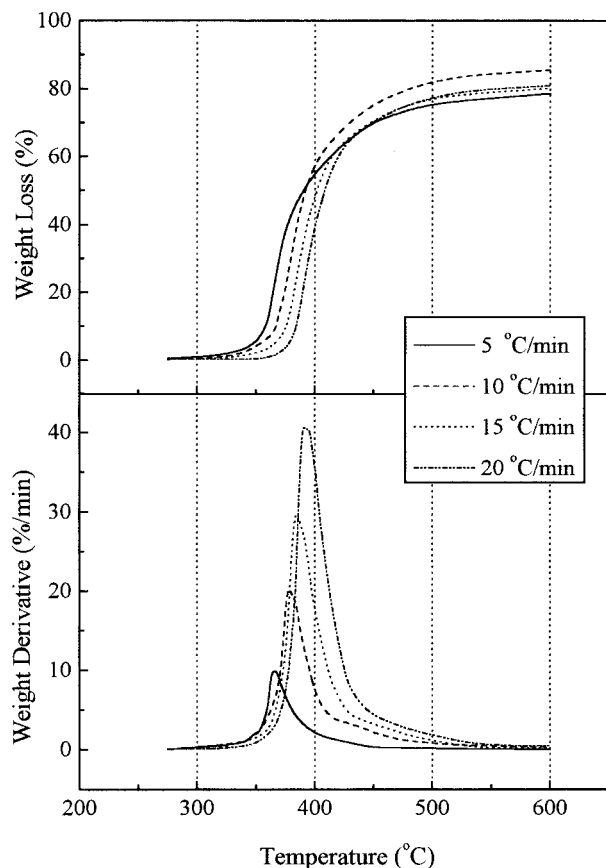


Figure 1 TG and DTG curves for DGEBA/MDA system with rubber-modified MDA (10 phr) at four different heating rates.

T_d , were obtained from the point where weight loss abruptly increased, and the values are 350.4, 361.2, 371.6, and 377.8 °C at the heating rates of 5, 10, 15, and 20 °C/min, respectively.

Ozawa Method

The Ozawa method^{8–10} essentially assumes that A , $(1 - \alpha)^n$, and E_d are independent of T , whereas A and E_d are independent of α . By separating and integrating eq. 5, the resulting Ozawa equation is

$$\log F(\alpha) = \log(AE_d/R) - \log \beta + p(E_d/RT) \quad (6)$$

Using Doyle's approximation for $\log(E_d/RT)$ at $20 < E_d/RT < 60$, then eq. 6 becomes

$$\log F(\alpha) = \log(AE_d/R) - \log \beta - 2.315 - 0.4567E_d/RT \quad (7)$$

Then, eq. 7 can be rewritten at a fixed conversion as follows:

$$E_d = -\frac{R}{0.4567} \frac{d(\log \beta)}{d(1/T)} \quad (8)$$

The straight lines of $\log \beta$ against $1/T$ are plotted in Figure 2, and the activation energies of thermal decomposition are determined from the slopes because the slope is given by $-0.4567E_d/R$. The nearly same slopes over the α range 0.1–0.4 indicate that the same reaction mechanism is acting on the decomposition of the crosslinked chains with a constant activation energy. However, the slope of the line at $\alpha = 0.05$ is clearly distinguished from the other lines, which means the thermal decomposition is affected by other reaction mechanisms. The determined activation energies are listed in Table I, and the average value at $\alpha = 0.1$ –0.4 is 189 kJ/mol. However, the average activation energy of $\alpha = 0.05$ is 152 kJ/mol because of the volatilization of unreacted molecules or moisture. The values of activation energies for other systems are also listed in Table I, and similar tendencies are found.

The derived E_d can be used to calculate the value of A from the y-intercept; however, another variable n is also contained in the y-intercept. So, one of them should be determined beforehand to calculate the other. Firstly, the mean value of A at

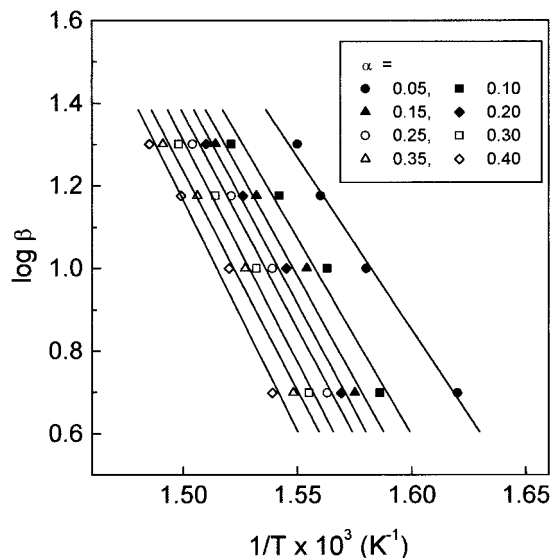


Figure 2 Plots of the Ozawa method for DGEBA/MDA system with rubber-modified MDA (10 phr) at various fixed conversions.

Table I Activation Energies, E_d , Pre-exponential Factors, A , and Reaction Orders, n , Determined by the Ozawa Method

Rubber-Modified MDA Content (phr)	α	E_d (kJ/mol)	A (min ⁻¹)	n
0	0.05	129	4.0×10^{13}	1.3
	0.10	162	8.3×10^{14}	1.4
	0.15	180	2.0×10^{16}	1.5
	0.20	180	1.8×10^{16}	1.3
	0.25	177	8.0×10^{15}	1.4
	0.30	180	1.4×10^{16}	1.4
	0.35	184	2.3×10^{16}	1.5
	0.40	180	1.0×10^{16}	1.5
10	0.05	152	1.6×10^{14}	1.2
	0.10	173	6.4×10^{15}	1.3
	0.15	182	2.7×10^{16}	1.3
	0.20	188	6.8×10^{16}	1.4
	0.25	189	8.6×10^{16}	1.3
	0.30	196	2.3×10^{16}	1.6
	0.35	194	1.3×10^{17}	1.4
	0.40	202	5.5×10^{17}	1.5
20	0.05	150	1.1×10^{14}	1.2
	0.10	209	5.8×10^{18}	1.3
	0.15	204	1.8×10^{18}	1.4
	0.20	209	3.7×10^{18}	1.3
	0.25	212	4.9×10^{18}	1.3
	0.30	202	7.0×10^{17}	1.3
	0.35	217	8.7×10^{18}	1.4
	0.40	233	1.5×10^{20}	1.5

each heating rate can be calculated from the following expression:¹¹

$$\log A = \log \beta + \log E_d + 0.434 \frac{E_d}{RT} - \log R - 2 \log T \quad (9)$$

The value of n can be determined by substituting the following equations for $F(\alpha)$ into the y-intercept:

$$F(\alpha) = -\ln(1 - \alpha) \quad \text{for } n = 1 \quad (10)$$

$$F(\alpha) = \frac{1 - (1 - \alpha)^{1-n}}{1 - n} \quad \text{for } n \neq 1 \quad (11)$$

The calculated pre-exponential factors and reaction orders at every conversion for all systems are also given in Table I.

Kissinger Method

Kissinger^{8,9,12} derived a useful expression that allows the calculation of activation energy by the temperature, T_m at the maxima of the first weight derivative curves at different heating rates, as shown in Figure 1. Because the maximum rate occurs when $d^2\alpha/dt^2 = 0$, differentiation of eq. 4 gives

$$\frac{E_d \beta}{RT_m^2} = An(1 - \alpha)_m^{n-1} \exp\left(\frac{-E_d}{RT_m}\right) \quad (12)$$

Kissinger assumes that the product $n(1 - \alpha)_m^{n-1}$ is independent of β . So, the following expression is derived:

$$\frac{d[\ln(\beta/T_m^2)]}{d(1/T_m)} = -\frac{E_d}{R} \quad (13)$$

Then, a plot of $\ln(\beta/T_m^2)$ as a function of $1/T$ is given in Figure 3, and the activation energy of 182.1 kJ/mol is calculated from the slope.

The values of n are determined from the following expressions, and the pre-exponential factor A can be determined by combining eqs. 14 or 15 with eq. 12:

$$-\ln(1 - \alpha)_m \cong 1 - \frac{2RT_m}{E_d} \quad \text{for } n = 1 \quad (14)$$

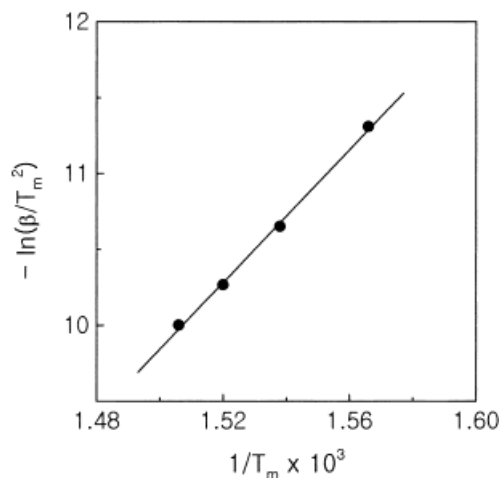


Figure 3 Plot of the Kissinger method for DGEBA/MDA system with rubber-modified MDA (10 phr).

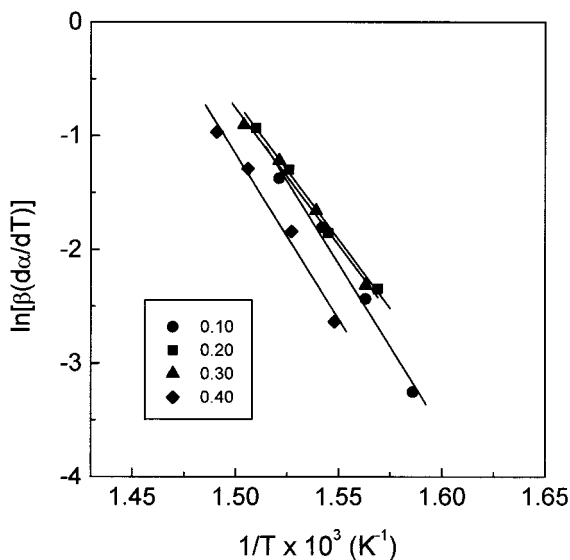
Table II Activation Energies, E_d , Pre-exponential Factors, A , and Reaction Orders, n , Determined by the Kissinger Method

Rubber-Modified MDA Content (phr)	E_d (kJ/mol)	A (min^{-1})	k at 500°C^a (min^{-1})	n
0	162	4.5×10^{12}	5.9×10^{-5}	1.0
10	182	2.2×10^{14}	2.0×10^{-5}	1.0
20	193	2.6×10^{15}	1.9×10^{-5}	1.0

^a k , Arrhenius rate constant.

$$n(1 - \alpha_m)^{n-1} = 1 + (n - 1) \frac{2RT_m}{E_d} \quad \text{for } n \neq 1 \quad (15)$$

The kinetic parameters for all systems obtained by Kissinger method are given in Table II, and the rate constants, k , at 500°C were calculated by the Arrhenius equation, $k = A \exp(-E_d/RT)$, and are also compared in Table II. The rate constants of the system with rubber-modified MDA were somewhat lower than that of the system without rubber-modified MDA. This difference implies that the thermal stability of the DGEBA/MDA system was improved by the addition of rubber-modified MDA. The reaction orders for all sys-


Figure 4 Plots of the Friedman method for DGEBA/MDA system added with rubber-modified MDA (10 phr) at various fixed conversions.

tems are equal to unity for a first-order reaction, as Kissinger argued.

Friedman Method

The Friedman method¹³ utilizes the following logarithmic differential expression derived from eq. 4:

$$\ln(d\alpha/dt) = \ln[\beta(d\alpha/dT)] \\ = \ln A + n \ln(1 - \alpha) - E_d/RT \quad (16)$$

The activation energy, E_d , over a wide range of α can be determined by plotting $\ln(d\alpha/dt)$ against $1/T$ for a constant α , as shown in Figure 4 for the DGEBA/MDA system with rubber-modified MDA (10 phr). In addition, n and A can be calculated from the plot of E_d/RT_0 against $\ln(1 - \alpha)$, where T_0 is the temperature at which $\ln(\beta d\alpha/dT) = 0$. All

Table III Activation Energies, E_d , Pre-exponential Factors, A , and Reaction Orders, n , Determined by the Friedman Method

Rubber-Modified MDA Content (phr)	α	E_d (kJ/mol)	A (min^{-1})	n	
0	0.05	197	4.1×10^{15}	1.5	
	0.10	241	1.1×10^{19}	1.8	
	0.15	227	8.9×10^{17}	1.7	
	0.20	197	3.6×10^{15}	1.5	
	0.25	188	1.1×10^{14}	1.3	
	0.30	183	3.0×10^{14}	1.4	
	0.35	200	6.7×10^{15}	1.5	
	0.40	230	1.6×10^{18}	1.7	
	10	0.05	199	2.6×10^{15}	1.4
		0.10	242	5.4×10^{18}	1.7
0.15		228	4.7×10^{17}	1.6	
0.20		202	4.9×10^{15}	1.4	
0.25		200	3.3×10^{15}	1.4	
0.30		213	3.3×10^{16}	1.5	
0.35		234	1.4×10^{18}	1.7	
0.40		256	6.4×10^{19}	1.8	
20		0.05	208	1.9×10^{16}	1.5
		0.10	238	4.0×10^{18}	1.7
	0.15	209	2.0×10^{16}	1.5	
	0.20	205	9.7×10^{15}	1.4	
	0.25	231	1.2×10^{18}	1.6	
	0.30	206	1.3×10^{16}	1.5	
	0.35	262	2.8×10^{20}	1.8	
	0.40	316	5.4×10^{24}	2.2	

the kinetic parameters determined by this method are given in Table III.

To compare the kinetic parameters, the results of the analytical methods are summarized in Table IV. Whereas Ozawa's and Friedman's calculations are the average value for all conversions, Kissinger's value comes from only one point, the point of maximum rate. The activation energies obtained from Ozawa and Kissinger methods show almost the same value; however, that of the Friedman method is somewhat higher.

The exact physical meaning of the kinetic parameters is not clear, for the exact mechanisms of the thermal decomposition for thermoset resins can't be defined. While the physical meaning of all the kinetic parameters for thermoplastics can be interpreted easily because the apparent weight loss is directly related to the mechanism of thermal decomposition, which is the emission of gaseous products after the chemical session. However, for network polymers the decomposition follows several processes, each with its own kinetic parameters. Therefore the kinetic parameters are somewhat apparent values, and there are some differences according to the various analytical methods.⁸

Figure 5 shows the comparison of DTG curves at the heating rate of 5 °C/min. The DTG curves shifted to higher temperatures and the decomposition starting temperature appeared at a higher point with increasing content of rubber-modified MDA. The DTG curves were proportional to the instant decomposition rate, and the thermal stability increased with increasing content of rubber-

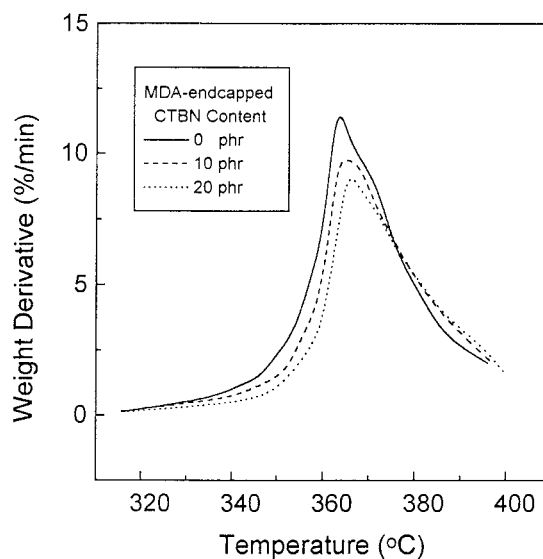


Figure 5 DTG curves for DGEBA/MDA system with various contents of rubber-modified MDA at the heating rate of 5 °C/min.

modified MDA. This result was due to the increasing content of aromatic ring in rubber-modified MDA, which has high resistance to thermal stress that is explained by the resonance structure of benzene rings.¹⁴

CONCLUSIONS

Thermal decomposition kinetics were investigated by TGA and the following conclusions are drawn. The TG curves showed that the thermal decomposition of the epoxy system occurred in one stage regardless of rubber-modified MDA content. The TG and DTG data were analyzed kinetically by three different methods, each of which gave different apparent kinetic parameters. The apparent activation energies for DGEBA/MDA system with 10 phr of rubber-modified MDA by the Ozawa, Kissinger, and Friedman methods are 184, 182, and 222 kJ/mol, respectively. The thermal stability of the epoxy system increased with the increasing content of rubber-modified MDA, which has high thermal resistance because of the resonance structure of four benzene rings.

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Table IV Summary of the Kinetic Parameters for DGEBA/MDA System with Rubber-Modified MDA

Rubber-Modified MDA Content (phr)	Method	E_d (kJ/mol)	A (min^{-1})	n
0	Ozawa	172	1.2×10^{16}	1.4
	Kissinger	162	4.5×10^{12}	1.0
	Friedman	207	2.8×10^{16}	1.6
10	Ozawa	184	1.1×10^{17}	1.4
	Kissinger	182	2.2×10^{14}	1.0
	Friedman	222	1.7×10^{17}	1.6
20	Ozawa	205	1.8×10^{18}	1.3
	Kissinger	193	2.6×10^{15}	1.0
	Friedman	234	2.7×10^{18}	1.7

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