

Pyrolysis kinetics of epoxy resin in a nitrogen atmosphere

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Abstract

Pyrolysis kinetics of epoxy resins are investigated under various heating conditions (2, 5, 10, and 20 K min⁻¹) in nitrogen by means of thermogravimetric measurements. Experimental initial reaction temperatures are within 531–552 K for each heating rate and the averaged apparent activation energy is 41.26 kcal mol⁻¹. The initial and final reaction temperatures, and thus the reaction range, all increase when the heating rate is increased. The overall rate equation can be modelled by an Arrhenius-type equation from which the kinetic parameters such as the activation energy, the pre-exponential factor, and the reaction order are determined by using the Friedman method. The results will be useful in developing pyrolysis or starved-air incineration systems for thermosetting plastic waste.

Keywords: Pyrolysis kinetics; Epoxy resin; Thermogravimetric analysis; Arrhenius equation; Thermosetting plastic waste

1. Introduction

Thermal treatment of solid wastes and materials by pyrolysis or incineration has received considerable attention in recent years due to fast-growing municipal and industrial wastes regionally or worldwide. A recent report [1] indicated that there were about 20 million tons of municipal solid wastes produced in 1991 in Taiwan, of which plastic materials contributed about 20 percent. Since plastic materials are essentially non-biodegradable, they are not suitable either for composting or land-filling. Accordingly, thermal treatment of these materials by pyrolysis or incineration is becoming attractive.

A properly functioning thermal-treatment system can not only solve disposal prob-

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lems, but can also make energy or fuel from the wastes [2–4]. However, as described by Dellinger et al. [5], Lee [6] and Chen et al. [7] in order to provide more detailed thermal and flow analysis and more accurate performance evaluation of an incinerator, the rate of thermal decomposition of solid wastes must be known; that eventually relies on kinetic studies of solid wastes under conditions of pyrolysis or burning.

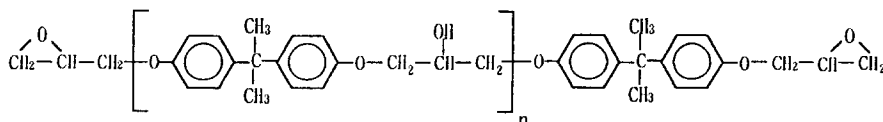
Extensive research has been performed on the pyrolysis kinetics and gaseous products of thermoplastic materials such as polyethylene, polypropylene, polystyrene, poly(vinyl chloride), and acrylonitrile–butadiene–styrene plastics [8–12] in vacuum or inert gas (nitrogen or helium). Some investigations have also been given on the reaction mechanisms and product yields of thermosetting plastics such as cured epoxy resins [13], and the activation energy of cured and uncured epoxy resin [14]. Epoxy resins have been widely used for: surface coatings on household appliances and gas storage tanks; adhesive for composites and for metals, glass, and ceramics; casting metal-forming tools and dies; encapsulation of electrical parts; floor surfacing and wall panels; and so on [15]. That is, epoxy resins are almost always present in municipal or industrial wastes in various forms, and ultimately have a dominant impact on those pyrolysis or incineration systems. Because pyrolysis is not only an independent process, but is also a first step in the gasification or combustion process, the kinetics of pyrolysis of epoxy resin in an inert atmosphere, to which there are few literature references, deserve more investigation.

In this paper, pyrolysis kinetics of epoxy resin under non-isothermal conditions are investigated by thermogravimetric measurement. The experiments were carried out for various heating rates (2, 5, 10, and 20 K min⁻¹) with nitrogen as the carrier gas. The apparent kinetic parameters such as the activation energy, the pre-exponential factor, and the reaction order of unreacted material, and thus the overall rate equations of pyrolysis reaction are determined. The results should be useful for the rational design or operation of pyrolysis or starved-air incineration systems in which thermosetting plastic wastes are involved.

2. Experiments and data analysis

2.1. Test material

The samples of epoxy resins used in this study were commercial grade material (NPES-903G, # 233B201), produced and supplied by a local company, with the following chemical structure (equivalent to D.E.R. 669, the Dow Chemical Company):



They were epoxyated bisphenol-A solid resins. The initial mass W_0 of the sample was 6.76–9.44 mg. No special sample preparation procedures were adopted, the sample simply being cut from the centre of the batch. The basic properties of the sample

Table 1
Properties of epoxy resin

Proximate analysis (wt%)		Lower heating value (cal g ⁻¹)	Elemental analysis (wt%)	
Water	0.18	7618	C	75.1
Combustible	99.79	–	H	7.1
Ash	0.03	–	O	17.8

obtained by elemental analysis and heating value test are listed in Table 1, which shows that the sample mainly consists of carbon (75.1%), oxygen (17.8%) and hydrogen (7.1%) with lower heating value of 7618 cal g⁻¹.

2.2. Test apparatus

The thermogravimetric system (Shimadzu TGA-50) for pyrolysis studies is shown schematically in Fig. 1. It consists of an electrically heated reaction tube 18 mm in inner diameter and 165 mm in length. A known weight of sample of about 8.5 mg is placed in a quartz cell 6 mm in diameter. The cell is then put on a platinum crucible that is hung by a 155-mm-long suspension wire and connected to the thermobalance. The temperature of reaction tube in the range 373 ~ 1273 K is controlled by a type-K chromel–alumel thermocouple wire placed about 1 ~ 2 mm below the platinum crucible. The heating rate to the reaction tube can be pre-set manually in the range of 0–99 K min⁻¹. In this study, heating rates, β , of 2, 5, 10, and 20 K min⁻¹ were chosen.

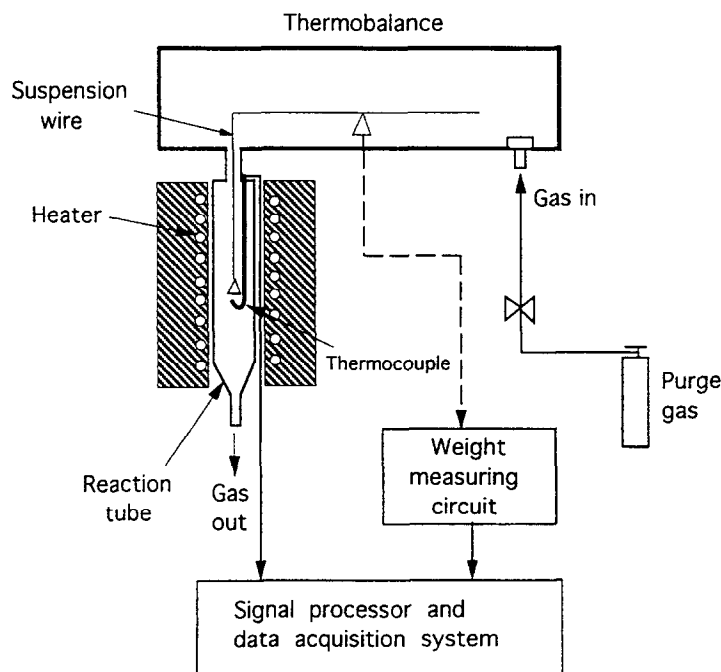


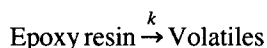
Fig. 1. Schematic diagram of thermogravimetric apparatus.

The carrier gas, nitrogen (99.99%), was supplied from a gas bottle and regulated by a mass-flow meter. It passed through the reaction tube from top to bottom and volatile products were collected by a water trap. For all tests conducted in this study, the mass flow rate of the carrier gas was fixed at 50 mL min^{-1} .

Mass variation of the sample with reaction temperature is detected by the photoelectric element and weight-measuring circuits in the thermobalance. The signals are then transmitted to the personal computer through the A/D converter for subsequent data storage, analysis and plotting. The experiments started after all control units had been set ready, and the mass of the sample (the TG curve) and the derivative of the mass-change with respect to reaction temperature (the DTG curve) were recorded every one or two seconds. The readability and the accuracy of the thermobalance are 0.01 mg and $\pm 1\%$, respectively. When the experiment was finished, the furnace power was turned off but the carrier gas was kept flowing until the reactor temperature had cooled below 100°C .

2.3. Analysis of kinetic parameters from TG data

It is known that when polymers are subject to heating or burning conditions, complicated reaction mechanisms such as random-chain scission, end-chain scission, chain stripping, cross-linking and coke formation take place. There is no intention in this work to describe the fundamental pyrolysis mechanisms of epoxy resin, nor to analyse its volatile products. Rather, the paper focuses on the determination of apparent kinetic parameters useful for large chemical reactors. As such, a global and simple reaction is assumed as follows:



Further, the overall rate equation of conversion α is expressed in the Arrhenius relationship in the form:

$$\frac{d\alpha}{dt} = A \cdot \exp(-E/RT) \cdot (-\alpha)^n \quad (1a)$$

$$\alpha = \frac{W_0 - W}{W_0 - W_f} \quad (1b)$$

where t is the time (min), A is the pre-exponential factor (min^{-1}), E is the activation energy (cal mol^{-1}), T is the reaction temperature (K), R is the universal gas constant ($= 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$), W (mg) is the mass of the sample at time t , and W_0 (mg) and W_f (mg) are the initial and final (or residual) masses of the sample, respectively; the n th order is assumed for the unreacted material. That is, the rate equation for conversion in terms of the reaction rate constant k is:

$$\frac{d\alpha}{dt} = k \cdot (1 - \alpha)^n \quad (2)$$

$$k = A \cdot \exp(-E/RT) \quad (3a)$$

or

$$\ln k = \ln A - E/(R \cdot T) \quad (3b)$$

In this study the Friedman method [16] is employed to evaluate the apparent kinetic parameters E , A and n from the TG data; this has been shown one of the best methods for analysing the kinetic parameters from thermogravimetric data (see Cooney et al. [17], and Petrovic and Zavargo [18]).

3. Results and discussion

3.1. Effect of heating rate

Fig. 2 shows the variations of fractional mass (TG curves) and derivative of mass-change (DTG curves) with respect to reaction temperature T at various heating rates. It shows that each TG curve is smooth with one inflection point during reaction, and that there is just one peak in each DTG curve for which only one kind of reaction is involved under pure nitrogen atmosphere. Further, the reaction zone shifts to the high-temperature region and peak height increases when the heating rate increases. Table 2 summarizes the reaction characteristics of epoxy resin, which shows that both

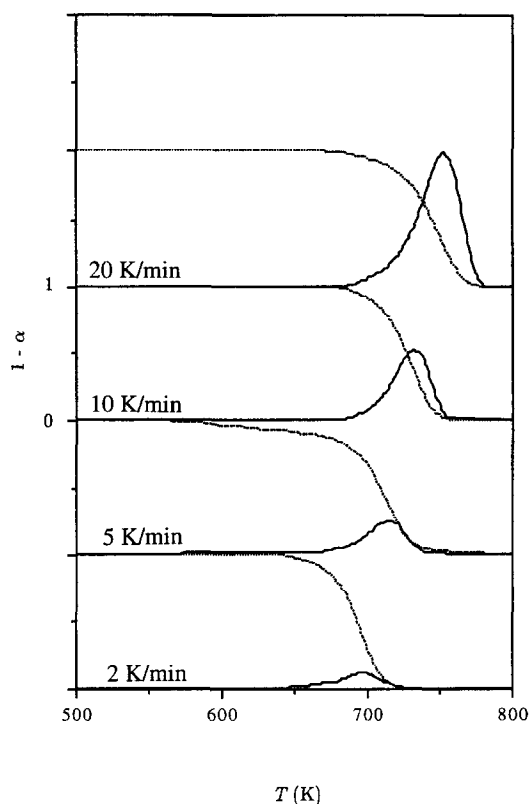


Fig. 2. Typical TG (dashed) and DTG (solid) curves for various heating rates in nitrogen atmosphere. TG curves are drawn to scale, but DTG curves are not.

Table 2
Reaction characteristics of epoxy resin

Carrier gas	β (K/min)	T_i (K)	T_m (K)	T_f (K)	W_f/W_0 (%)	ΔT (K)
100%N ₂	2	531.5	689.5	731.5	17.9	200
	5	538.2	712.3	786.3	15.4	248.1
	10	543.2	732.3	824.1	15.1	280.9
	20	552.3	754.6	863.3	12.1	311

initial T_i and final T_f reaction temperatures increase when the heating rate is increased. Thus, the reaction range $\Delta T (= T_f - T_i)$ also increases with increasing heating rate. It should be noticed that T_i and T_f were determined from the original, not normalized, DTG curve. This was done by inspecting the original DTG data in such a way that T_i was determined when the DTG value changed from 0.00 to 0.01. Likewise, T_f was determined when the DTG value changed from 0.01 to 0.00. Table 2 also shows that the initial reaction temperature is about 531–552 K (258–279°C). The peak temperature T_m at which conversion rate is maximum (i.e., $d\alpha/dT = 0$) is about 698–755 K (425–482°C), which is in good agreement with Lee's result [13] that the peak endothermic reaction is about 420°C. It is also seen from Table 2 that the fractional residual W_f/W_0 of epoxy resin for heating temperatures up to 900°C ranges from 12.1% to 17.9%, decreasing with increasing heating rate.

Fig. 3 shows the activation energy versus conversion. It is seen from Fig. 3 that the activation energy is about 36–41 kcal mol⁻¹ for $0 < \alpha \leq 0.6$, and is about 42–51 kcal mol⁻¹ for $0.7 \leq \alpha \leq 1.0$; the average value is 41.26 kcal mol⁻¹ (Table 3). The reaction characteristics of epoxy resin in nitrogen are summarized in Table 3, which shows that the pre-exponential factor A is 5.35×10^{14} (min⁻¹) and the reaction order n of unreacted material is 0.4.

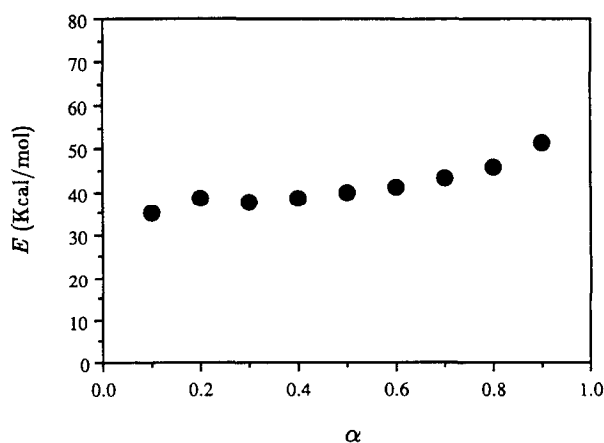


Fig. 3. Plot of activation energy versus conversion factor.

Table 3
Kinetic parameters of epoxy resin

Carrier gas	E (cal mol^{-1})	n	A (min^{-1})
100% N_2	41 260	0.4	5.35×10^{14}

3.2. The overall rate equation

When the values of the kinetic parameters listed in Table 3 are substituted into Eq. (2), the overall rate equation in nitrogen (100% N_2) atmosphere is found to be:

$$\frac{d\alpha}{dt} = 5.350 \times 10^{14} \cdot \exp\left(-\frac{41\,260}{RT}\right) \cdot (1-\alpha)^{0.4} \quad (4)$$

Fig. 4 shows the DTG data and computed values from Eq. (5), which shows very good agreement.

The equation of the reaction rate constant (Eq. (3b)) can be obtained in a similar way, and is:

$$\ln k = 33.913 - \frac{41\,260}{RT} \quad (5)$$

The corresponding Arrhenius plot of k versus $1000/T$ is shown in Fig. 5. It is seen that the derived equation fits the data fairly well. It is worth mentioning because the reaction temperature is related to the heating rate, β , by:

$$\frac{dT}{dt} = \beta \quad (6)$$

Hence, the conversion, α , or the fractional mass, $(1-\alpha)$, of the reaction can be

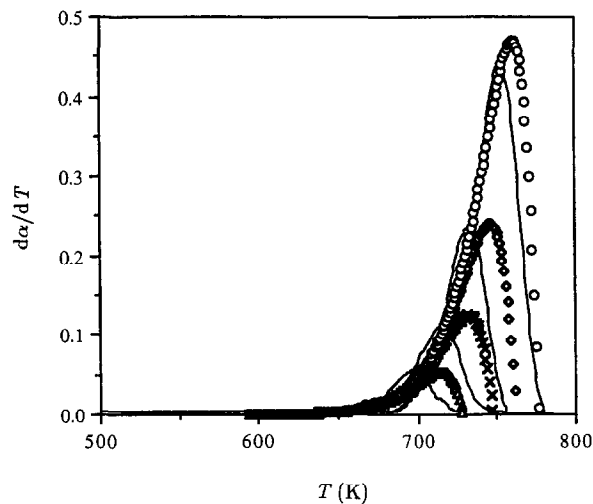


Fig. 4. Comparison between the DTG data (O) and computed values (solid line) from the rate equation.

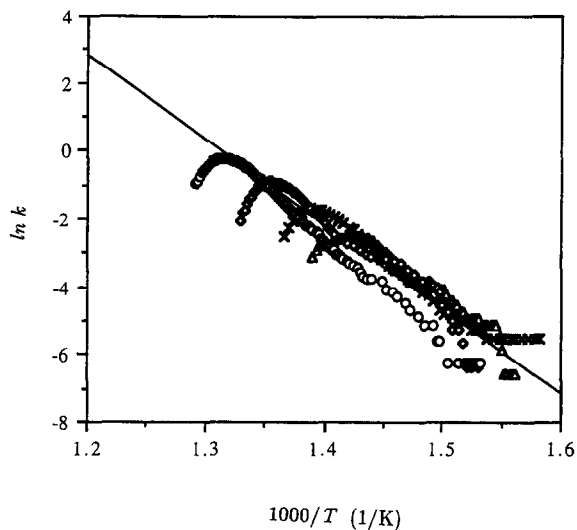


Fig. 5. Arrhenius plot of epoxy resin in nitrogen. Symbols are the data and the solid line is the plot of the rate equation. Heating rate (K min $^{-1}$): Δ -2; \times -5; \diamond -10; \circ -20.

computed by integrating Eqs. (4) and (6) simultaneously. Fig. 6 shows the TG data and computed values obtained by using the Runge–Kutta numerical integration scheme. It can be seen from Fig. 6 that the data can be recovered fairly well for large heating rates. However, there are some over-estimates for small heating rates (e.g., $\beta = 2$ or 5 K min $^{-1}$). This may be due to the fact that the initial reaction temperatures are somewhat over-estimated.

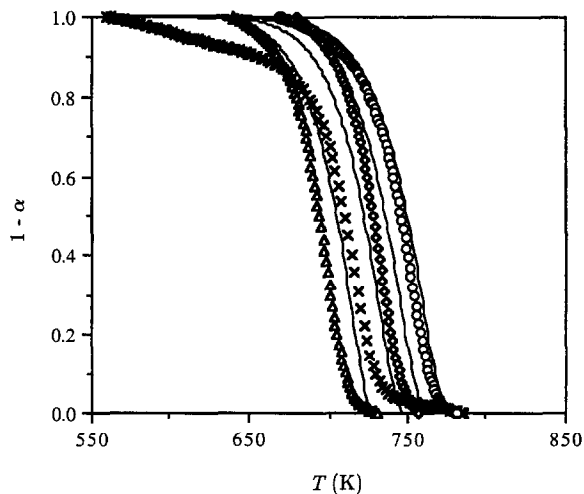


Fig. 6. Comparison of TG data (symbols) and computed values (solid lines) from numerical integration of rate equation in nitrogen. Heating rate (K min $^{-1}$): Δ -2; \times -5; \diamond -10; \circ -20.

4. Conclusions

Pyrolysis kinetics of epoxy resin in nitrogen are investigated by thermogravimetric measurement for the heating conditions of 2, 5, 10 and 20 K min⁻¹. Results show that there is only one reaction stage. The average activation energy is 41.26 kcal mol⁻¹ with reaction order 0.4. The initial reaction temperature in the range of 531–552 K (258–279°C) and reaction range both increase when heating rate is increased.

The overall rate equation can be modelled by an Arrhenius-type equation, from which kinetic parameters such as the activation energy, the pre-exponential factor and reaction order are determined using the Friedman method. Very good agreement is achieved between the measured data and predicted values. The results should be useful for the rational design and operation of pyrolysis or incineration systems in which thermosetting plastic wastes are involved.

Acknowledgements

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