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## Study of the thermal stability and kinetic parameters of polyamide 56

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**Abstract**

The kinetics of the thermal degradation of polyamide 56 (PA56) have been investigated by dynamic thermo-gravimetric analysis (TGA) at different heating rates in flowing nitrogen. Thermal degradation of PA56 could be accomplished by one step. The corresponding kinetic parameters of the degradation process, including the activation energy  $E_a$ , the reaction order  $n$ , and pre-exponential factor are determined by using Kissinger and Flynn–Wall–Ozawa methods. Coats–Redfern method is also used to explain the probable degradation mechanism of the PA56. The results showed that the activation energy obtained from Kissinger method is in a good agreement with the value obtained by using Flynn–Wall–Ozawa method. The solid-state degradation mechanism of the PA56 is a decelerated  $R_1$  type (Phase boundary controlled reaction one-dimensional movement).

**Keywords:** polyamide 56, thermal degradation, kinetic analysis, activation energy, thermo gravimetric

**Introduction**

Aliphatic polyamide (PAs) has excellent properties such as high modulus, good strength and toughness, and excellent chemical and abrasion resistance; so they widely used in many applications (Kohan, 1995) <sup>[10]</sup>. The thermal properties are one of the most important properties for polymeric materials. Thus, the thermal stability and thermal degradation kinetics, understanding its mechanism of degradation and associated factors, are of great significant for the production and industrial applications (Meng, Huang, Yu, & Lv, 2007) <sup>[13]</sup>. Thermo-gravimetric analysis (TGA) has been widely used to determine the kinetic parameters of the degradation process of polymer materials (Samanta *et al.*, 2013; Wang, Fang, Yao, & Wu, 2011) <sup>[17, 21]</sup> such as activation energies ( $E$ ) and reaction orders ( $n$ ), etc. The kinetic analysis of decomposing material can be done using two different techniques: the dynamic and isothermal thermo-gravimetric studies. In this article, the thermal stability and degradation kinetics of PA56 were studied by combination of dynamic thermo-gravimetric analysis (TGA) and derivative thermo-gravimetric analysis (DTG) measurements under nitrogen at different heating rates. The thermal degradation and the kinetic parameters of PA56 were studied by different kinetic methods through non-isothermal TG thermo-grams. The dependences of the thermal degradation and kinetic parameters on the heating rates and calculating methods are discussed in detail.

**Material and Methods**
**Material**

Polyamide 56 (PA56) pellets with an intrinsic viscosity 0.68 dl/g were kindly supplied from Guangdong Xinhui Media Nylon Co. Ltd China, with a molecular weight of 18,000.

**TG and DTG measurements**

Thermo-gravimetric analysis (TG) and derivative thermo-gravimetric analysis (DTG) of the polyamide 56 (PA56) pellets were conducted on NETZSCH TG 209 F1 Iris thermo-gravimetric analyzer instrument (NETZSCH instrument manufacturing company, Germany). The measurements were performed in the scanning mode of TG and DTG from 30°C to 900°C under nitrogen flow, using heating rates of 10°C/min, 15°C/min, 20°C/min,

and 30°C/min, respectively. Each sample size was approximately about 5-10 mg.

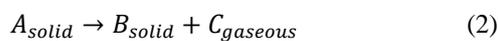
### Thermal degradation kinetics theory

Generally for polymer degradation, it is assumed that the rates of conversion ( $\alpha$ ) are proportional to the concentration of reacted material. For thermo-gravimetric analysis (TGA), the degree of conversion ( $\alpha$ ) is defined as the ratio of weight loss at time  $t$  to the total weight loss at complete decomposition temperature as shown in Eq. (1):

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

Where,  $W_0$  is the initial weight of the sample;  $W_t$  is the weight of the sample at certain time  $t$  during the reaction;  $W_f$  is the weight of the sample at the end of the reaction.

Assuming PA56 follows the simple model of thermal degradation reaction of a solid polymer, which may be represented by the process (Herrera, Matuschek, & Kettrup, 2001) [8]:



Where,  $A$  represents the original solid polymer;  $B$  represents a solid residue after the decomposition of solid and  $C$  gas generated by gas species.

According to the reaction theory, a kinetic study is generally started with the following basic equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (3)$$

Where,  $da/dt$  is the decomposition rate of the weight loss, and  $k(T)$  and  $f(\alpha)$  are functions of temperature and conversion, respectively.

The temperature dependence of the rate constant  $k(T)$ , for the process is assumed to follow the Arrhenius equation:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (4)$$

Where  $A$  and  $E$  are kinetic parameters, the pre-exponential factor and the activation energy, respectively;  $T$  is the absolute temperature and  $R$  is the universal gas constant, its value is 8.31 J/(mol.K) (Sengupta, Sabharwal, Bhowmick, & Chaki, 2006) [18].

$f(\alpha)$ , which depends on the specific degradation mechanism, can be expressed by:

$$f(\alpha) = (1 - \alpha)^n \quad (5)$$

Where  $n$  is the reaction order, a combination of equations (4) and (5) in equation (3), we obtain the kinetic equation in the following form:

$$\frac{d\alpha}{dt} = (1 - \alpha)^n A \exp\left(-\frac{E}{RT}\right) \quad (6)$$

For non-isothermal conditions, when the temperature is raised with time at a constant heating rate,  $\beta = dT/dt$ , equation 6 is represented as follows:

$$\frac{d\alpha}{dt} = \frac{A}{\beta} f(\alpha) \exp\left(-\frac{E}{RT}\right) \quad (7)$$

Therefore, Eq. (7) is the fundamental relation to determine kinetic parameters on the basis of TG data. The integrated formal of equation (6) can be written as:

$$g(\alpha) = \frac{AE}{\beta R} P(u) \quad (8)$$

$$P(u) = \int_{\infty}^u \frac{\exp(-u)}{u^2} du \quad , \quad u = \frac{E}{RT}$$

Wherein,

Based on the degree of conversion measurement, ( $\alpha$ ), and on the heating rate,  $\beta$ , there are several methods available for the calculations of the apparent activation energy. Hence, the determinations of the kinetic parameters for the degradation from the TGA data are strongly depended on the method of calculation. There are several methods to determine the apparent activation energy based on one or multiple heating rates of TGA curves such as Kissinger method, Friedman method, Flynn-Wall-Ozawa method, Kissinger-Akahira-Sunose (KAS) method and Coats-Redfern method (Vyazovkin *et al.*, 2011; Zeng, Li, Li, Wang, & Yang, 2009) [20, 22]. Polyamide 56 (PA56) as a new material, the apparent activation energies were calculated by using Kissinger and Flynn-Wall-Ozawa methods, and then we are applied the Coats-Redfern method to determine possible degradation mechanism.

## Results and Discussions

### Thermal degradation process of PA56

TGA is widely used technique for evaluating the thermal stability of polymers because it requires a small sample and the entire study was over in a few hours. Figure 1 and 2 show the TG and DTG thermal degradation curves of PA56 obtained at different heating rates of (10°C/min, 15°C/min, 20°C/min, and 30°C/min), respectively, under nitrogen atmosphere. The TG curves of the thermal decomposition of PA56 at different heating rates are shown in Fig. 1. From the figure, it can be observed that all curves are approximately in the same shape and indicated that the mass loss is independent of the heating rate. DTG curves of PA56 at different heating rate are shown in Fig. 2. DTG curve of a single peak, indicating that the PA56 degradation in nitrogen is a single reaction. The PA56 stable up approximately 400°C, which illustrated that PA56, had excellent thermal stability. The greatest weight loss of PA56 take places in the range 400~600°C, the weight loss rate is close to 100%. Obviously, by increasing the heating rates, the initial degradation temperature of the PA56 gradually increased, the peak temperature of DTG curve, i.e. the temperature corresponding to the maximum rate of degradation is increased successively, and the corresponding maximum degradation rate is also gradually increase. According to thermal degradation mechanism of Polyamide 6 (Levchik, Weil, & Lewin, 1999) [11], we can roughly

understand the mechanism of the thermal degradation of PA56: when the temperature reaches a certain temperature, degradation start, the cleavage of the weakest C-N bonds between the amide groups to form an amide and its eventual transformation to nitrile by dehydration reactions. With continuous rise in temperature, the carbonyl C=O is removal, and carboxyl groups react with the CO<sub>2</sub>. When the temperature reaches near the maximum decomposition temperature, a large number of C-C bond breaks.

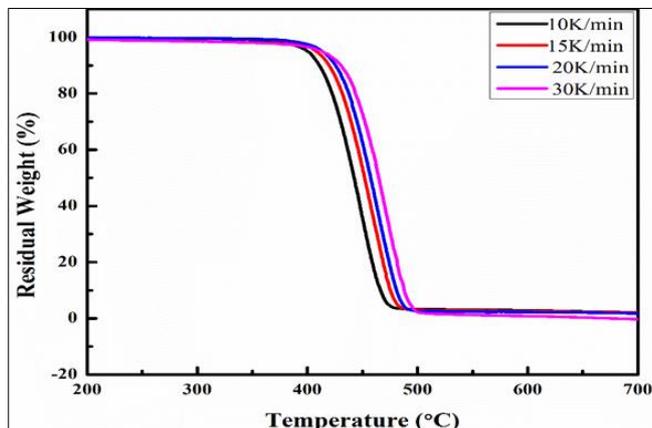


Fig 1: Typical TG curves of PA56 at different heating rates

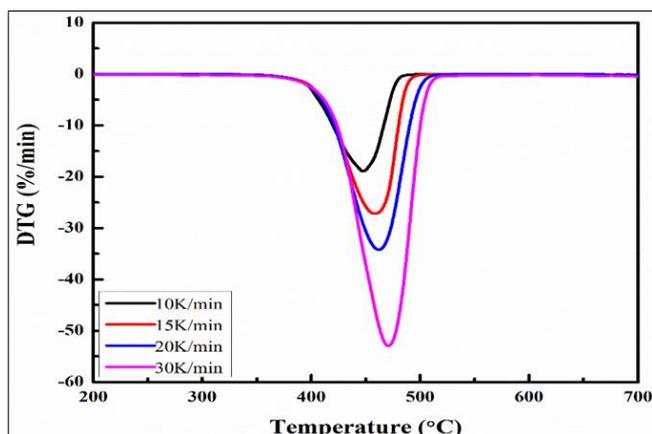


Fig 2: Typical DTG curves of PA56 at different heating rates.

**Characterization degradation temperatures of PA56**

The TGA characteristic temperatures of PA56 such as initial decomposition temperature (*T<sub>0</sub>*), the maximum weight loss rate DTG peak temperature (*T<sub>p</sub>*), and final decomposition temperature (*T<sub>f</sub>*) were obtained by extrapolation of the double tangent method as shown in Table 1. The results showed that the initial decomposition temperature, peak temperature of DTG and the final decomposition temperatures were increased gradually with the heating rates.

**Table 1:** Characteristics temperature of thermal degradation for PA56 under different heating rates

$\beta$ (°C/min)	$T_0$	$T_p$	$T_f$
10	416.0	447.7	467.4
15	420.2	458.3	477.9
20	430.0	462.0	483.6
30	438.6	470.7	491.0

**Kinetics of thermal degradation of PA56**

Generally, there are a variety of thermal degradation

kinetics methods, for instance, the thermal degradation process of PA56 was determined using three well-known methods for dynamic heating experiment i.e., the Kissinger method, Flynn-Wall-Ozawa method and Coats-Redfern method.

**1. Kissinger method (Differential method) (Kissinger, 1957)<sup>[9]</sup>**

Kissinger method calculates the activation energy (*E*) uses the maximum decomposition temperature (*T<sub>p</sub>*) at which the rate of mass loss is the highest. Because the highest rate happens when  $d(d\alpha/dt)/dt = 0$ , by incorporated equations (3), (4), and (5) to obtain:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) (1-\alpha)^n \tag{9}$$

When  $T = T_p$ ,  $\frac{d}{dt} \left[ \frac{d\alpha}{dt} \right] = 0$ , Equation (9) on both sides of the differential was re-simplification:

$$\frac{E}{RT_p^2} \frac{dT}{dt} = \frac{E\beta}{RT_p^2} = An(1-\alpha_p)^{n-1} \exp\left(-\frac{E}{RT_p}\right) \tag{10}$$

Kissinger was on both sides of the equation in logarithmic form (Tiptakorn, Damrongsakkul, Ando, Hemvichian, & Rimdusit, 2007)<sup>[19]</sup>

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{nRA(1-\alpha_p)^{n-1}}{E}\right) - \frac{E}{RT_p} \tag{11}$$

Kissinger assumed that the degradation product,  $n(1-\alpha_p)^{n-1}$  is independent of  $\beta$ , which is approximately equal to the value of 1. In such a case the equation (11) can be written as:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln \frac{AR}{E} - \frac{E}{RT_p} \tag{12}$$

Which, *T<sub>p</sub>* and  $\alpha_p$  are the absolute temperature and the maximum rate of conversion, respectively. The activation energy can be calculated from the slope of the plots of  $\ln(\beta/T_p^2)$  versus  $1/T_p$  (*T<sub>p</sub>* is the temperature at the maximum weight loss rate) for various heating rate. Figure 3 shows the relationship between the  $\ln(\beta/T_p^2)$  versus  $1/T_p$ . The calculated values are summarized in Table 2. The obtained value of activation energy (*E*) is 202.79kJ/mol. The advantage of the Kissinger model is that the activation energy can be obtained without the knowledge of any thermal degradation mechanism in advance (Gu, He, Hu, & Huang, 2012)<sup>[7]</sup>. From the literature (Criado & Ortega, 1986)<sup>[3]</sup>, the Kissinger’s method was reported to obtain highly reliable values of *E* with an error of less than 5% independent of reaction mechanism, provided that  $E/RT > 10$ .

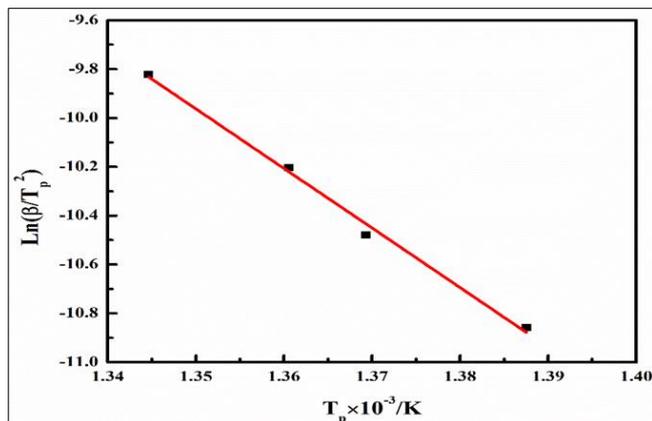


Fig 3: Plot of  $\ln(\beta/T_p^2)$  versus  $1/T$  according to Kissinger method

Table 2: Activation energy ( $E$ ) calculated by Kissinger method and correlation coefficient ( $R$ )

$\beta/(K/min)$	$T_p/K$	$E/(kJ/mol)$	$\ln A$	$R$
10	720.7	202.79	22.97	0.993
15	731.3			
20	735.0			
30	743.7			

**2. Flynn-wall-ozawa method**

Flynn-Wall-Ozawa method (Joseph H. Flynn & Wall, 1966; Ozawa, 1965) [6, 15] is one of the integral methods for obtaining activation energies from weight loss against temperature at different heating rates. The main advantage of this method is that the calculation of activation energy ( $E$ ) had no relationship with real degradation process, and also the reaction order was not necessary. This method was used to determine activation energy ( $E$ ) by plotting of the logarithm of the heating rate as a function of the inverse of the temperature at different conversion (Gu *et al.*, 2012) [7]. From Eq. (7), it can be integrated using the Doyle approximation (Doyle, 1961; J. H. Flynn, 1997) [4-5]. The result of the integration after taking logarithm is:

$$\log \beta = \log \left( \frac{AE}{Rg(\alpha)} \right) - 2.315 - 0.4567 \frac{E}{RT} \tag{13}$$

The activation energy ( $E$ ) of the thermal degradation process of PA56 could be determined from the slope of the straight line of the plot of  $\log \beta$  vs.  $(1000/T)$ . The values of the activation energies ( $E$ ) were obtained under different conversion rate ( $\alpha$ ), based on the slope of a straight lines.

Figure 4 shows that the fitting straight lines are nearly parallel to each other, which indicates that this method is applicable to our system in the conversion range studied. Using Flynn-Wall-Ozawa method, the  $E$  values corresponding to the different conversions are listed in Table 3. The calculated values of activation energy vary with the conversion rate, indicating that the degradation of PA56 in nitrogen atmosphere is a single reaction mechanism mode (Meng *et al.*, 2007; Núñez, Fraga, Núñez, & Villanueva, 2000) [13-14]. The mean value of the activation energy is 207.43kJ/mol compared with the activation energy calculated by Kissinger method ( $E = 202.79$ kJ/mol) the difference between the two is small. It could be concluded from the activation energy ( $E$ ) obtained by the two methods that the results are close to each other. Therefore, it means that the determination of activation energy ( $E$ ) from

Kissinger method and Flynn-Wall-Ozawa method is reliable.

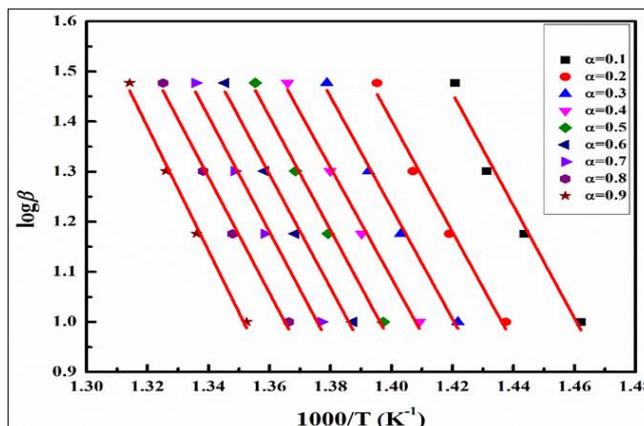


Fig 4: Plot of the  $\log \beta$  vs.  $1/T$  according to Flynn-Wall-Ozawa method

Table 3: Activation energies ( $E$ ) obtained by using Flynn-Wall-Ozawa method.

Conversion ( $\alpha$ )	Slope $\times 10^3$	$E(kJ/mol)$	Average value
0.1	-11.23	204.44	207.43
0.2	-11.12	202.43	
0.3	-11.09	201.89	
0.4	-11.03	200.80	
0.5	-11.31	205.89	
0.6	-11.34	206.44	
0.7	-11.51	209.53	
0.8	-11.57	210.63	
0.9	-12.35	224.83	

**3. Coats-redfern method**

The method of Coats-Redfern is one of the most widely used methods involving the thermal degradation mechanism. In the initial reaction, at a lower temperature  $T_0$ , the reaction rate is negligible,

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \approx \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \tag{14}$$

The integral of the right hand side of Eq. 14, named the Arrhenius integral, can be expressed in the form:

$$\int_0^T \exp\left(-\frac{E}{RT}\right) dT = \frac{E}{R} P_{FK(u)} = \frac{E}{R} \frac{e^{-u}}{u^2} = \frac{RT^2}{E} \exp\left(-\frac{E}{RT}\right) \tag{15}$$

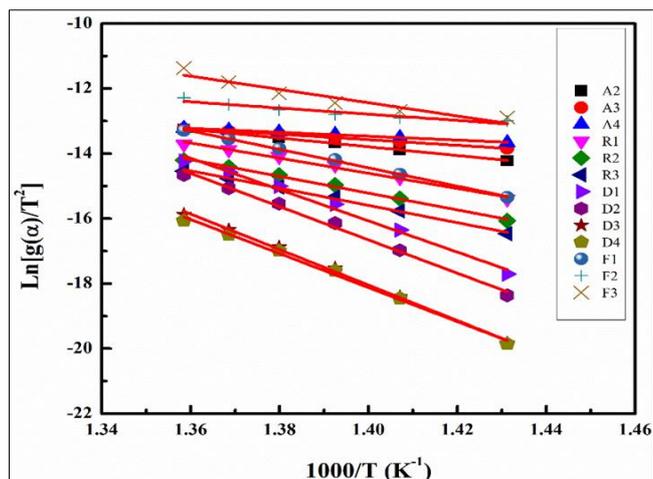
The Coats-Redfern integral (Coats & Redfern, 1964; Pérez-Maqueda & Criado, 2000) [1, 16]:

$$\ln \left[ \frac{g(\alpha)}{T^2} \right] = \ln \left( \frac{AR}{\beta E} \right) - \frac{E}{RT} \tag{16}$$

Activation energy ( $E$ ) and  $A$  could be calculated from the plot of  $\ln[g(\alpha)/T^2]$  vs.  $(1000/T)$ , according to different degradation processes, with the theoretical function  $g(\alpha)$  being listed in Table 4. Comparing with the activation energies from Kissinger method and Flynn-Wall-Ozawa method, we can obtain the thermal reaction mechanism. Table 4 shows the most common kinetics mechanisms and their algebraic expressions (Criado, Málek, & Ortega, 1989; Ma, Hill, & Heng, 1991; Núñez *et al.*, 2000) [2, 12, 14].

**Table 4:** Algebraic expressions of the common kinetic mechanisms

Symbol	$g(\alpha)$	Solid-state processes
<b>Sigmoidal curves</b>		
A <sub>2</sub>	$[-\ln(1-\alpha)]^{1/2}$	Nucleation and growth (Avrami equation 1)
A <sub>3</sub>	$[-\ln(1-\alpha)]^{1/3}$	Nucleation and growth (Avrami equation 2)
A <sub>4</sub>	$[-\ln(1-\alpha)]^{1/4}$	Nucleation and growth (Avrami equation 3)
<b>Deceleration curves</b>		
R <sub>1</sub>	$\alpha$	Phase boundary controlled reaction (one-dimensional movement)
R <sub>2</sub>	$1-(1-\alpha)^{1/2}$	Phase boundary controlled reaction (contracting area)
R <sub>3</sub>	$1-(1-\alpha)^{1/3}$	Phase boundary controlled reaction (contracting volume)
D <sub>1</sub>	$\alpha^2$	One-dimensional diffusion
D <sub>2</sub>	$(1-\alpha)\ln(1-\alpha)+\alpha$	Two-dimensional diffusion (Valensi equation)
D <sub>3</sub>	$[1-(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion (Jander equation)
D <sub>4</sub>	$(1-2/3\alpha)-(1-\alpha)^{2/3}$	Three-dimensional diffusion (Ginstling–Brounshtein equation)
F <sub>1</sub>	$-\ln(1-\alpha)$	Random nucleation with one nucleus on the individual particle
F <sub>2</sub>	$1/(1-\alpha)$	Random nucleation with two nuclei on the individual particle
F <sub>3</sub>	$1/(1-\alpha)^2$	Random nucleation with three nuclei on the individual particle

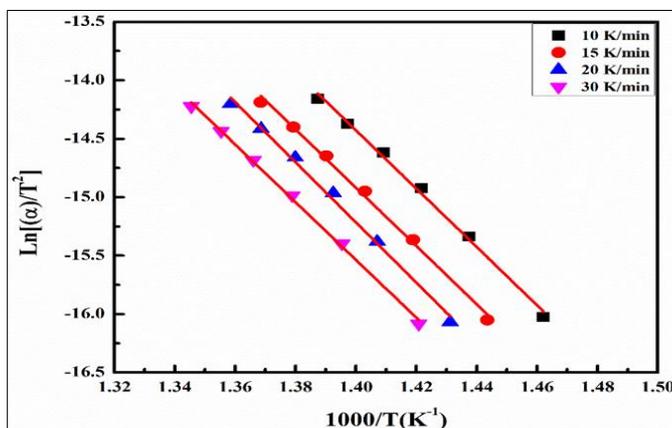


**Fig 5:** Plot of  $\ln[g(\alpha)/T^2]$  against  $1/T$  according to Coats-Redfern method

Figure 5 shows the plot of  $\ln[g(\alpha)/T^2]$  vs.  $(1/T)$  according to Coats-Redfern method, for every  $g(\alpha)$  functions listed in Table 4. (With  $\beta = 20^\circ\text{C}/\text{min}$ , for example). Table 5 shows activation energies ( $E$ ), and correlation coefficient for conversions in the range of 10-90% at constant heating rate of  $20^\circ\text{C}/\text{min}$ . It was found that the solid state thermal degradation mechanism of the PA56 is likely to be  $R_2$  type, because this mechanism presents the activation energy that is similar to the value obtained from Kissinger method and Flynn-Wall-Ozawa method. Therefore, the  $R_2$  type is probably the thermal degradation mechanism, and the rate controlling process of thermal degradation of PA56 followed by the phase boundary reaction may be cylindrical symmetry, deceleration shaped curves with the integral form  $g(\alpha) = 1-(1-\alpha)^{1/2}$ . Fitting of  $R_2$  mechanism functions into Coats-Redfern integral method, different lines of heating rates ( $\beta$ ) were obtained as shown in Figure 6, the value of  $E$  and  $A$ , values obtained are listed in Table 6. As presented in Table 6, Coats-Redfern method was applied at the heating rate of 10, 15, 20, and  $30^\circ\text{C}/\text{min}$  to determine the mean value of the  $E$ ,  $A$ , and the degradation mechanism. The average activation energy is  $208.36\text{kJ}/\text{mol}$ . The results suggest that type  $R_2$  mechanism of thermal degradation for all heating rates.

**Table 5:** Activation energies obtained by Coats-Redfern method for PA56 at a heating rate of  $20^\circ\text{C}/\text{min}$ .

Mechanism	$E(\text{kJ}/\text{mol})$	The correlation coefficient ( $R$ )
A <sub>2</sub>	111.85	0.9981
A <sub>3</sub>	70.59	0.9978
A <sub>4</sub>	49.97	0.9975
R <sub>1</sub>	193.82	0.9878
R <sub>2</sub>	213.82	0.9944
R <sub>3</sub>	220.89	0.9959
D <sub>1</sub>	399.55	0.9885
D <sub>2</sub>	425.12	0.9927
D <sub>3</sub>	453.69	0.9962
D <sub>4</sub>	434.62	0.9941
F <sub>1</sub>	235.62	0.9983
F <sub>2</sub>	78.87	0.8824
F <sub>3</sub>	169.66	0.8967



**Fig 6:** Plot of  $\ln[g(\alpha)/T^2]$  against  $1/T$  according to  $R_2$  mechanisms

**Table 6:** The apparent activation energy and the pre-exponential factor at different heating rates

$\beta(^\circ\text{C}/\text{min})$	$E(\text{kJ}/\text{mol})$	$\ln A$
10	207.34	20.50
15	207.04	19.96
20	213.82	20.81
30	205.25	19.04
Mean	208.36	20.08

**Conclusions**

The kinetics of the thermal degradation of PA56 was studied

by dynamic thermo-gravimetric analysis (TGA) at different heating rates in flowing nitrogen. TGA experiments were performed to elucidate the thermal behavior and supplied the data that characteristic the degradation. The TGA curve of PA56 under nitrogen atmosphere is smooth, DTG curve of single peak, indicating that the degradation of PA56 in nitrogen is one step reaction. As the heating rate increased, the initial degradation temperature and DTG peak temperature PA56 were gradually increased. The kinetics parameters of the thermal degradation of PA56 were investigated by using the Kissinger and Flynn-Wall-Ozawa methods. The results revealed that the activation energy ( $E$ ) obtained from Kissinger and Flynn-Wall-Ozawa methods are 202.79kJ/mol and 207.43kJ/mol, respectively. As can be seen a small difference between the two, indicating that Kissinger method and Flynn-Wall-Ozawa method are applicable to study the thermal degradation kinetic of PA56. The results from Coats-Redfern method demonstrate that the solid state process for the thermal degradation of PA56 followed by the phase boundary reaction ( $R_2$ ) may be cylindrical symmetry, deceleration shaped curves with the integral form  $g(\alpha) = 1 - (1 - \alpha)^{1/2}$ .

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