Thermal Degradation Kinetics of Polyamide 6,6 Cable Ties by Thermogravimetric Analysis

Nabil N. Rammo

Dept. of Physics/ College of Education Scientific Departments/ University of Salahaddin

Hind A. M. Mahdi

Dept. of Physics/College of Education for Pure Science(Ibn Al-Haitham/ University of Baghdad

Abstract

The thermal degradation of cable ties of polyamide (PA6,6) neat and UV stabilized was investigated by thermogravimetry (TG) and its derivative (DTG) at several heating rates between 5 and 80 ^{o}C min^{-1} in helium atmosphere. High heating rates signal novel peaks in the DTG curves that indicate melting temperature of PA6,6. The kinetic parameters calculated via isoconversion and nonisothermal data using the Flynn-Wall-Ozawa, Kissinger and Coats-Redfern methods showed comparable activation energy values. Exposure of the ties to outdoor environment causes pre-mature stress cracking and brittle failure due to prevalence of crosslinking reaction occurring in the polymer chains.

المجلد 26 (العدد 3)عام 2013

Ibn Al-Haitham Jour. for Pure & Appl. Sci.

مجلة إبن الهيثم للعلوم الصرفة و التطبيقية

Vol. 26 (3) 2013

Introduction

Polyamides such as PA6 and PA6,6 possess a favorable balance of physical and chemical properties, which has been widely used as engineering material [1]. However their thermal stability is hindered by low glass transition temperature posing limit on their high temperature application [2]. Recent usage of PA6,6 in automotive industry has focused on their use for greater fuel economy and weight reduction coupled with the critical requirement of higher continuous use temperature (CUT) and resistance to thermal degradation [3]. Therefore, the knowledge of thermal degradation kinetics of PA6,6 whether photo-oxidized [4] or electron beam irradiated [5] is essential, and for this purpose thermogravimetric analysis (TGA) is widely used because of its experimental simplicity and the wealth of information obtained from a simple thermogram, such as the activation energy in addition to the understanding of thermal degradation mechanism [6]. It has been found that the main route of thermal degradation of PA6,6 is the elimination of the main organic product cyclopentanone and also some hydrocarbons, nitriles and vinyl groups [7,8]. PA6,6 can be crosslinked or degraded as the consequence of their exposure to ionizing radiation in addition that the two processes may compete in the degradation reaction [9,10].

The kinetic analysis of a decomposing material can be done using the dynamic thermogravimetric study, which can be analyzed by the isoconversional method. In this method a series of thermogravimetric curves obtained at different heating rates can be used to calculate the activation energy [11].

The present paper focuses of the thermal degradation kinetic of PA6,6 neat and UV stabilized under dynamic conditions using three methods: Kissinger and Flynn-Wall-Ozawa that utilize heating rate at different levels of conversion, and Coat-Redfern that utilizes ,conversion at different levels of heating rate, to verify the effectiveness of the kinetic analysis method and to shed a light on the thermal degradation mechanism that PA6,6 undergoes when used outdoors for tying cables and pipes. It has been noticed that outdoor use of PA6,6 cable ties fail by stress cracking under its own constant tying load.

Kinetic Methods [12]

The reaction rate in TG analysis can be defined as the change of degree of conversion (α) with time or temperature and is calculated as:

$$\alpha = m_o - m_t / m_o - m_f \qquad \ldots\ldots\ldots(1)$$

where m_0, m_t and m_f represent the initial, actual and final mass of material respectively. All kinetic studies assume that the isothermal rate of conversion, $\frac{d\alpha}{dt}$, is a linear function of temperature and is expressed in Arrhenius form as:

$$\frac{d\alpha}{dt} = A(1-\alpha)^n \, e^{-E/RT} \qquad \cdots\cdots\cdots(2)$$

Where A, n, E, R and T are the pre-exponential factor (min^{-1}), assumed to be temperature – independent of the reaction order, the activation energy (KJ mol^{-1}), the gas constant (8.314 J mol^{-1} K^{-1}) and the absolute temperature (K) , respectively.

At constant heating rate $\beta = dT/dt$, Eq. (2) may be written as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}(1-\alpha)^n \, e^{-E/RT} \qquad \cdots\cdots\cdots(3)$$

Kissinger's method [13]

Kissinger's method is one of the differential methods that has been utilized to calculate the activation energy from plots of the logarithm of the heating rate versus the inverse of the temperature at the maximum reaction rate in constant heating rate experiments. The beauty of this method is that even without a precise knowledge of the reaction mechanism, the activation energy can be determined after taking the logarithm in Eq. (3):

$$\text{Log}(\beta/T^2_{max}) = \{\log AR/E + \log[n(1-\alpha_{max})^{n-1}]\} - E/2.303RT_{max} \quad \cdots\cdots\cdots (4)$$

مجلة إبن الهيثم للعلوم الصرفة و التطبيقية | المجلد 26 (العدد 3) عام 2013

Ibn Al-Haitham Jour. for Pure & Appl. Sci.　　　*Vol. 26 (3) 2013*

where β, A, R, E, n have their usual significance, T_{max} is the temperature indicating the inflection point of the thermal degradation curves which corresponds to maximum rate and α_{max} is the maximum conversion .

From the plot of $\log(\beta/T^2_{max})$ versus $1/T_{max}$ and fitting to a straight line, E can be computed from the slope.

Flynn - Wall - Ozawa method

This isoconversional integral method is suggested independently by Ozawa [14] and Flynn and Wall [15] uses Doyle approximation [16] of the temperature integral. From Eq. (3) after taking logarithm is:

$$\text{Log } \beta = \log (AE/(1-\alpha)^n R) - 2.315 - E/2.303RT \quad \ldots\ldots\ldots(5)$$

Thus for α = constant, the plot of logβ versus 1/T gives a straight line with the slope determining the activation energy. Using this method, one can determine the activation energy at different levels of conversion.

Coats – Redfern [17]

Coats – Redfern method has been used by researchers to determine the activation energy of solid state reactions from plots of the logarithm of conversion versus 1/T. Thus Eq. (3) after integration becomes:

$$\log (- \log (1-\alpha) /T^2) = \log (AR/\beta E) – E/2.303RT \quad \ldots\ldots\ldots (6)$$

Here α is the fraction of sample degradation at temperature T, where T is the derivative peak temperature obtained from DTG curve .

Thus a plot of $\log(-\log(1-\alpha)/T^2)$ versus 1/T gives a straight line with the slope determining the activation energy. Using this method one can determine the activation energy at different levels of heating rate.

Experimental

Samples of polyamide 6,6 were obtained from cable ties (colors: white and black) manufactured by Y.Y. Cable Accessories Co. Taiwan. Samples for the analysis were taken from a sealed pack. Others were outdoor tied on plastic tubes and were failed by stress cracking during one season. Brittleness was obvious on these ties.

Thermal degradation was performed on a Perkin Elmer TGA-7 thermogravimetric analyzer at the ibn Sina company / Ministry of Industry and Minerals . The samples were heated from ambient temperature to 850℃ using heating rates of 5, 10, 20, 40 and 80 ℃ min^{-1} in helium at a gas flow rate of 20 ml min^{-1} . The initial mass of the sample was 22~38 mg.

Results and Discussion

Figures 1 and 2 show the variations of the TGA and DTG curves with respect to temperature for various heating rates in helium atmosphere for neat and UV stabilized polyamide 6,6 respectively. It is seen from Figures 1 and 2 that the TG curves for neat and UV stabilized PA6,6 are displaced to higher temperature due to heat transfer lag with increased heating rate and the height of the DTG peaks also increase with the heating rate due to excesses heat flux.

These findings are in agreement with the reported similar observation for polyethylene terephthalate[18] and for styrene butadiene rubber[19]. It is also observed that the residual mass fractions in the neat PA6,6 remain constant after 700℃ and are about 0.1~0.2 for the heating rates 5-80 ℃ min^{-1} . However, for the UV stabilized PA6,6 the residual mass fractions for the high heating rates namely 40 and 80 ℃ min^{-1} remain constant after 600℃ and are about 0.2 ~ 0.3, but for the 5, 10 and 20℃ min^{-1} it remains constant after 750℃

المجلد 26 (العدد 3)عام 2013

Ibn Al-Haitham Jour. for Pure & Appl. Sci.

مجلة إبن الهيثم للعلوم الصرفة و التطبيقية

Vol. 26 (3) 2013

for the same residual mass fractions. It is also noticed from the DTG curves in both figures 1(b) and 2(b) the appearance of two peaks near the melting temperature of PA6,6 at the heating rates of 40 and 80 ℃ min^{-1} (see Table 1). This can be seen as a way of monitoring melting behavior by adapting high heating rate thermogravimetry.

Figure 3 shows the plots of 1/T versus $\log\beta$ and log (β / T^{2}max) for neat and UV stabilized PA6,6 from which the activation energy is computed for different conversion levels by Flynn-Wall-Ozawa and Kissinger methods.

The activation energy values deduced from the plots in Figure 3 by Flynn-Wall-Ozawa and Kissinger methods are shown in Table 2.

Figure 4 shows the plots of log(-log (1-α)/T^2) versus 1/T for neat and UV stabilized PA6,6 from which the activation energy is computed for different heating rates by Coats – Redfern method.

The activation energy values deduced from the plots of Figure 4 by Coats-Redfern method are shown in Table 3.

The results in Tables 2 and 3 indicated that the activation energy obtained from nonisothermal data (Flynn-Wall-Ozawa and Kissinger methods) are comparable with the isoconversion data (Coats-Redfern method) in the low to moderate heating rate range (5 to 20 ℃ min^{-1}). It is also noted that the activation energy varies with both kinetic parameters i.e. heating rate and conversion in similar fashion, an indication that the kinetic analysis using the various methods show consistent variations. Table 4 shows the comparison of the activation energy results obtained in this work with the corresponding values reported in the literature for PA6,6 (neat).

Effect of environment on degradation

The TG and DTG curves of the outdoors used and failed samples of neat PA6,6 show significant changes in the TG curve at the beginning and at the end of the heating cycle. For low conversion of 2.5%, the outdoor sample degrade faster than the unused sample by a wide margin of temperature 230 ^{o}C relative to 355 ^{o}C. The reason is that exposure to environment has caused pre-mature chain scission reaction especially when the molecular chain endure constant load, which triggers lower temperature degradation. For high conversion of 99.2%, the remaining residue is sustained up to a temperature of 780 ^{o}C in the outdoor samples in comparison with 675 ^{o}C for the unused samples indicating appreciable build up of crosslinking network in the outdoor samples. This is manifested by the mechanical brittleness endured by the outdoor used samples. The activation energy deduced from Coats-Redfren method for the outdoor samples show an increase relative to the unused samples. A summary of temperatures and activation energy deduced from the TG curves are shown in Table 5.

Conclusions

Thermal degradation of PA6,6 was studied by dynamic thermogravimetry and the kinetic parameters were analyzed by three analytical methods. Although the route of calculating the activation energy is different within the three methods, comparable results of activation energy were obtained. High heating rates with the conjunction of DTG curves can be useful in monitoring the adaptation of polymer molecules at the boundaries of melting before degradation occurs. Cable ties of PA6,6 exposed in moderate to sever outdoor atmosphere are likely to end up with failure from stress cracking condition by the effect of crosslinking reaction in the polymeric chain. Such observation are likely to be taken for further detail investigation.

مجلة إبن الهيثم للعلوم الصرفة و التطبيقية | المجلد 26 (العدد 3) عام 2013

Ibn Al-Haitham Jour. for Pure & Appl. Sci.   Vol. 26 (3) 2013

References

1. Domininghaus, H. (1993) Plastics for engineers, Munich: Hanser Publishers, 363-401.

2. Gu, H. , He, J.M. ; Hu J. and Huang, Y.u. (2012) Thermal degradation kinetics of semi-aromatic polyamide containing benzoxazole unit, J. Therm. Anal. Calorim., 107(3) : 1251- 1257.

3. Wang, X.L. ; Yang, K.K. ; Wang, Y.Z. ; Wn, B. ; Lin ,Y. and Yang, B. (2003) Thermogravimetric analysis of the decomposition of poly (1,4-dioxan- 2-one) / starch blends, Polym. Degrad. Stab., 81 : 415-421.

4. Singh, R.P. ; Desai, S.M. and Pathak, G. (2003) Thermal decomposition kinetics of photo-oxidized nylon 6,6 , J Appl. Polym. Sci., 87 : 2146-2150.

5. Sengupta, R. ; Sabharwal, S. ; Bhowmick ,A.K. and Chaki T.K. (2006) Thermogravimetric studies on polyamide 6,6 modified by electron beam irradiation and by nanofillers, Polym. Degrade. Stab., 91 : 1311-1318.

6. Park, J.W. ; Oh, S.C. ; Lee, H.T. and Yoo, K.O. (2000) A kinetic analysis of thermal degradation of polymer using dynamic model, Polym. Degrad. Stab., 67 : 535-540 .

7. Ballistresi, A. ; Garozzo, D. ; Giuffrida, M. and Montaudo G. (1987) Mechanism of thermal decomposition of nylon 6,6 , Macromolecules, 20: 2991-2997.

8. Levchik, S.V. ; Costa L. and Camino G. (1994) Effect of the fire – retardant , ammonium polyphosphate on the thermal decomposition of aliphatic polyamides part III- polyamide 6,6 and 6,10, Polym. Degrad. Stab.,43 : 43-54.

9. Dadbin, S. ; Frounchi, M. and Goudrazi, D. (2005) Electron beam induced crosslinking of nylon 6 with and without the presence of TAC, Polym. Degrad. Stab., 89: 436-441.

10. Zaharescu, T. ; Silva, L.G.A. ; Jipa, S. and Kappel, W. (2010) Post-irradiation thermal degradation of PA6 and PA6,6 , Radiat. Phys. Chem., 79: 388-391.

11. Herrera, M. ; Matuschek, G. and Kettrup A. (2001) Main products and kinetics of the thermal degradation of polyamides, Chemosphere, 42: 601-607.

12. Vyazoukin, S. (2000) Kinetic concepts of thermally simulated reaction in solids : a view from a historical perspective, Int. Rev. Phys. Chem., 19: 45-60.

13. Kissinger, H.E. (1957) Reaction kinetics in differential thermal analysis, J. Anal. Chem., 29 : 1702-1706.

14. Ozawa, T. (1965) A new method of analysis thermogravimetric data, Bull. Chem. Soc. Jpn,38 : 1881-1886 .

15. Flynn , J.H. and Wall, L.A. (1966) A quick direct method for the determination of activation energy from thermogravimetric data, Polym. Lett.,4 : 323-328.

16. Doyle, C.D. (1962) Estimating isothermal life from thermogravimetric data, J. Appl. Polym. Sci.,6 : 639-642.

17. Coats, A.W. and Redfern, J .P. (1964) Kinetic parameters from thermogravimetric data, Nature, 201: 68.

18. Hu, S.C. ; Lee, D.G. ; Kwak ,H. and Bae, S.Y. (2006) Combusion kinetics of polyethylene terephthalate, Korean Environ. Eng. Res., 11(5): 250-256.

19. Chen, K.S. and Ye, R.Z. (1997) Kinetics of thermal decomposition of styrene – butadiene

20. Pashaei, S. ; Siddaramaiah, S. ; Souldozi, A. , Seyed, S.U.T. and Syed, A.A. (2011) Investigation on thermal and mechanical behaviors of crysnanoclay incorporated polyamide / nanoclay composites, Int. J. Chem. Tech. Res., 3(3): 1292-1301.

المجلد 26 (العدد 3) عام 2013

Ibn Al-Haitham Jour. for Pure & Appl. Sci.

مجلة إبن الهيثم للعلوم الصرفة و التطبيقية

Vol. 26 (3) 2013

Table No. (1) : Melting and decomposition temperatures of neat and UV stabilized PA6,6 obtained from DTG curves at various heating rates

Heating rate (^oC min^1)	Melting (^oC)		Decomposition (^oC)			
	Neat	UV	Neat		UV	
			on-set	max.	on-set	max.
5	-	-	342	425	324	428
10	-	-	369	437	346	438
20	-	-	375	455	351	444
40	266	253	396	474	376	449
80	272	263	420	501	409	489

Table No.(2): Activation energy of neat and UV stabilized PA6,6 obtained using Flynn-Wall- Ozawa and Kissinger methods

Conversion (%)	Activation Energy (kJ mol^{-1})			
	Flynn-Wall-Ozawa		Kissinger	
	Neat	UV	Neat	UV
2.5	105	-	101	-
5	121	141	113	151
10	144	164	134	159
20	164	192	152	183

Table No.(3):Activation energy of neat and UV stabilized PA6,6 obtained using Coats-Redfern method
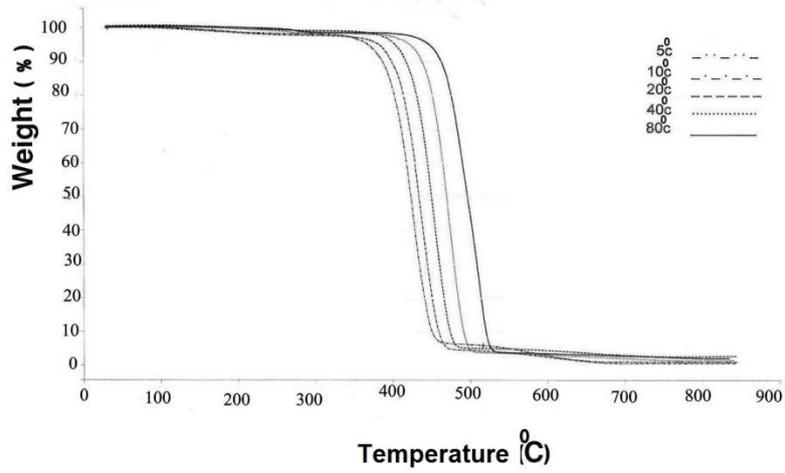
Heating rate (^oC min^{-1})	Activation Energy (kJmol^{-1})	
	Neat	UV
5	113	152
10	129	173
20	165	204
40	200	216
80	226	229

المجلد 26 (العدد 3) عام 2013

Ibn Al-Haitham Jour. for Pure & Appl. Sci.

مجلة إبن إلهيثم للعلوم الصرفة و التطبيقية

Vol. 26 (3) 2013

Table No.(4): Summary of the activation energy obtained for neat PA6,6 in this work and the ones reported in the literature by various analytical methods
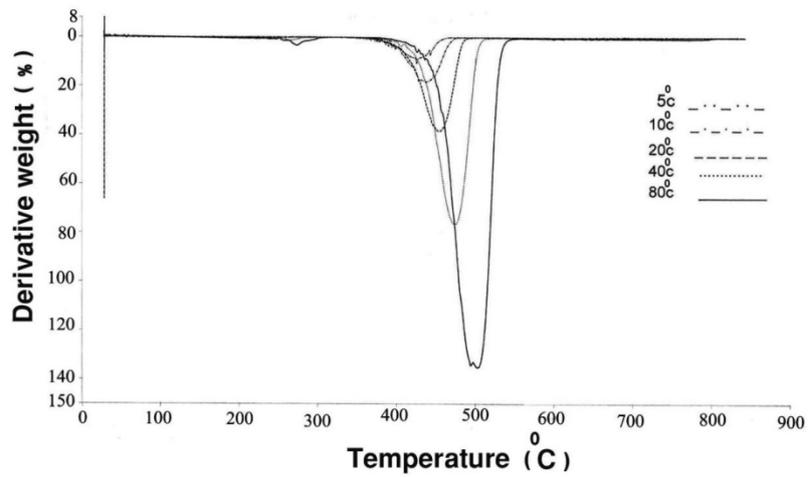
References	Range of Activation Energy (kJ mol^{-1})			
	Flynn-Wall-Ozawa	Kissinger	Coats-Redfern	Other
Gu et al. [2]	166	175	182	
Singh et al. [4]				51-112
Sengupta et al. [5]	148	180		
Herrera et al. [11]			91	
Pashaei et al. [20]			257	
This work	105-164	101-152	113-165	

Table No.(5): Comparison between thermal behavior of outdoor loaded neat PA6,6 cable ties with unused ones analyzed at β = 10 ^{o}C min^{-}

	Outdoor + loaded	Unused
Conversion α = 1%	140 ^{o}C	160 ^{o}C
α = 2.5%	230 ^{o}C	355 ^{o}C
α = 99.2%	780 ^{o}C	675 ^{o}C
Activation energy(KJmol^{-1}) (Coats-Redfern)	144	129

المجلد 26 (العدد 3) عام 2013

Ibn Al-Haitham Jour. for Pure & Appl. Sci.

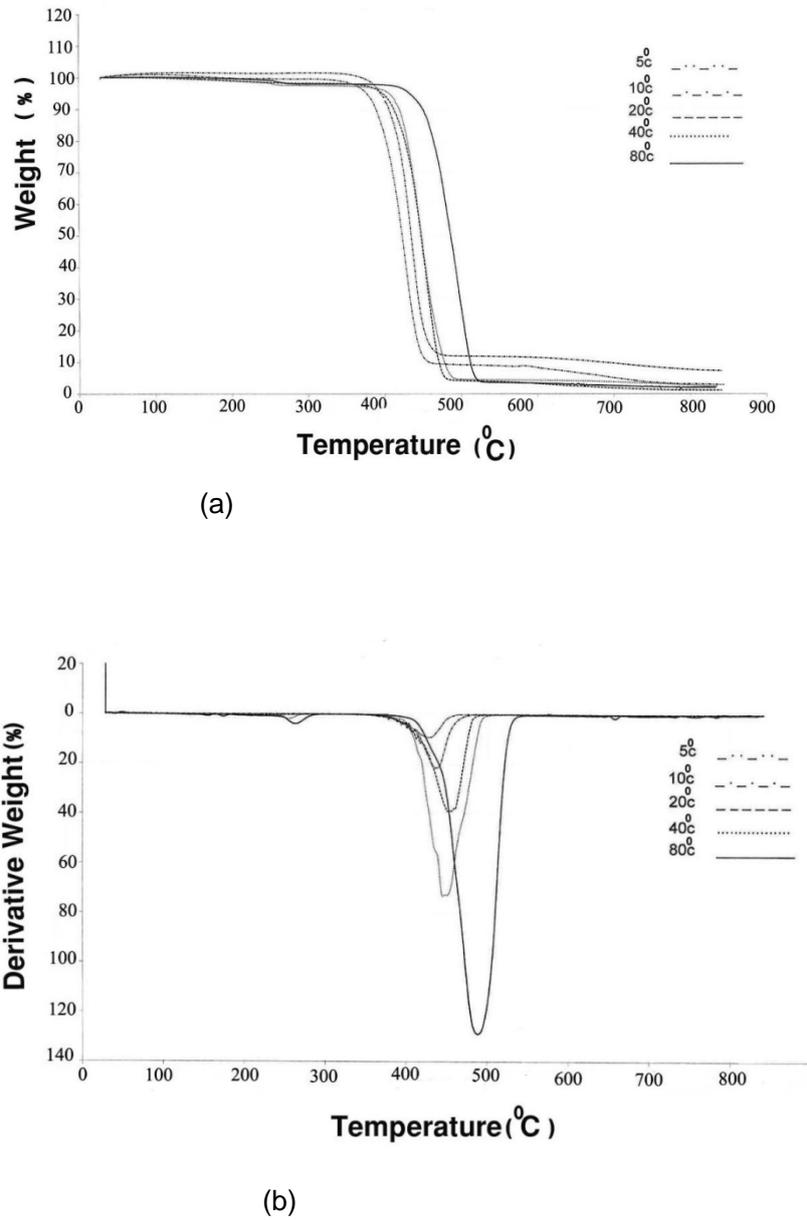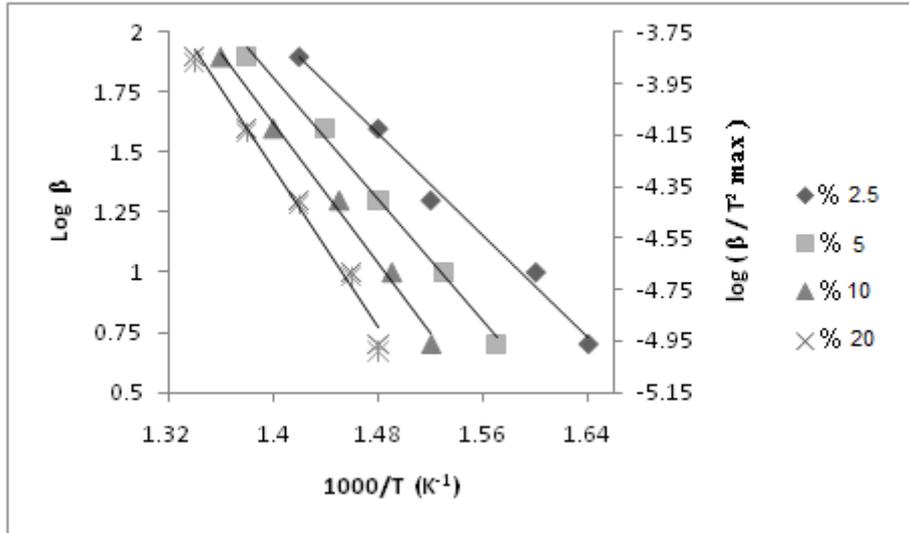مجلة إبن الهيثم للعلوم الصرفة و التطبيقية

Vol. 26 (3) 2013

(a)

(b)

Figure No.(1): TG (a) and DTG (b) curves of neat PA6,6 at various heating rates

المجلد 26 (العدد 3) عام 2013

مجلة إبن الهيثم للعلوم الصرفة و التطبيقية

Ibn Al-Haitham Jour. for Pure & Appl. Sci.

Vol. 26 (3) 2013

(a)

(b)

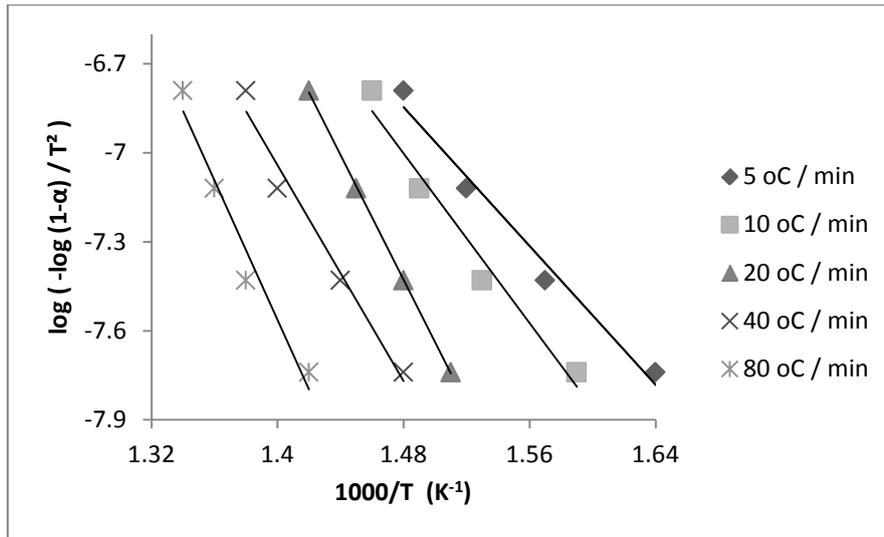**Figure No.(2): TG (a) and DTG (b) curves of UV stabilized PA6,6 at various heating rates**

مجلة إبن الهيثم للعلوم الصرفة و التطبيقية | المجلد 26 (العدد 3) عام 2013

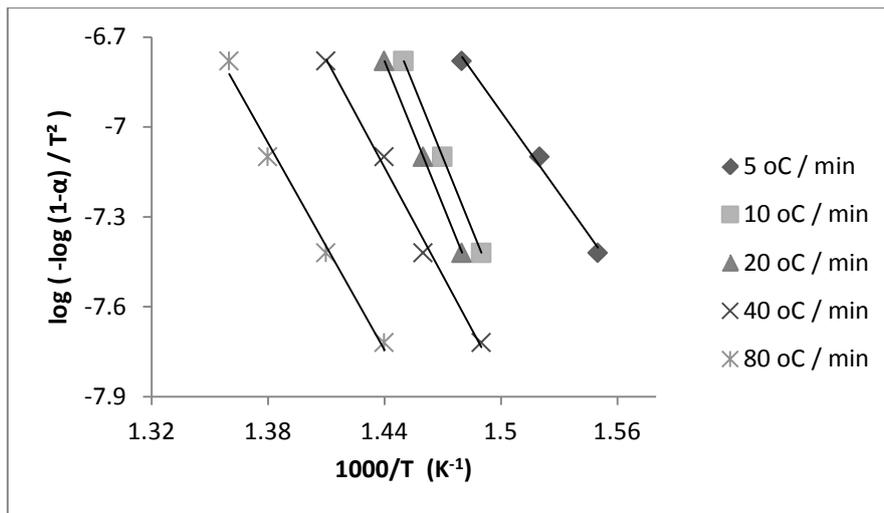*Ibn Al-Haitham Jour. for Pure & Appl. Sci.*   *Vol. 26 (3) 2013*

(a)
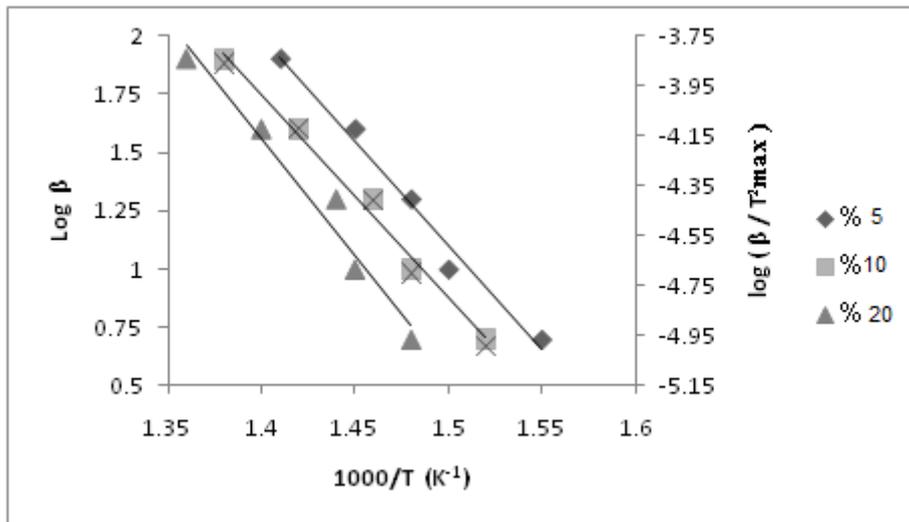
(b)

Figure No.(3): Plots of 1/T versus log β (Flynn-Wall-Ozawa) and log (β/T²max) (Kissinger) at different levels of conversions for neat (a) and UV stabilized (b)

المجلد 26 (العدد 3) عام 2013

Ibn Al-Haitham Jour. for Pure & Appl. Sci.

مجلة إبن الهيثم للعلوم الصرفة و التطبيقية

Vol. 26 (3) 2013

(a)

(b)

Figure No.(4): Plots of 1/T versus log (-log (1- α) / T²) (Coats-Redfern) at different heating rates for neat (a) and UV stabilized (b)

حركيات التفكك الحراري لرابطات الكابل نوع بولي امايد 6,6 بوساطة التحليل الحراري التفاضلي

نبيل نعيم رمو

كلية التربية ، جامعة صلاح الدين

هند عبد المجيد مهدي

قسم الفيزياء/ كلية التربية للعلوم الصر فة (ابن الهيثم) / جامعة بغداد

الخلاصة

درس التفكك الحراري لرابطات الكابل نوع بولي امايد 6,6 النظيف و المستقر للاشعة فوق البنفسجية بوساطة منحنيات التحليل الحراري الوزني TG و مشتقتها DTG عند معدلات تسخين مختلفة بين 5 – 80 ˚م لكل دقيقة في جو الهيليوم . لوحظ أن معدلات التسخين المرتفعة (40 و80 ˚م/دقيقة) تبين وجود قمم فريدة في منحنيات DTG التي تشير الى درجة انصهار البولي امايد 6,6. المعلومات الحركية المحسوبة من البيانات المتضمنة تساوي Coats and Redfern and Kissinger Flynn-Wall-Ozawa, التحويل و تباين الحرارة باستخدام طرائق تبين قيم متقارنة لطاقة التنشيط . تسبب تعرض الرابطات الى بيئة خارجية في تكسر اجهادي مسبق الاوان وفشل هش للانموذج جراء سيادة تفاعل التشابك الحاصل في سلاسل البوليمر.

الكلمات المفتاحية: بولي امايد 6,6 ، تفكك حراري ، تحليل الحركيات ، التحليل الحراري الوزني ، طاقة التنشيط ، رابطات الكابل .