

Thermal Decomposition Kinetics of Photooxidized Nylon 66

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Abstract: The thermoanalytical method offers a convenient means for testing a starting material before the end application. Differences in the kinetic parameters between neat and irradiated nylon 66 samples were estimated in the temperature range of 25°C–800°C by thermogravimetric analysis (TGA) and in the range of 25°C–300°C by differential scanning calorimetry (DSC). Under nitrogen flux the average activation energy for decomposition was in the range of 12.2–26.9 kcal/mol for the neat sample and 15.7–33.1 kcal/

mol for the irradiated sample (250 h). Activation energy is affected by the process of bond breaking at the C–N bonds, which is the rate-determining step of the decomposition in nylon 66. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2146–2150, 2003

Key words: nylon 66; photoirradiation; thermal decomposition; kinetics

INTRODUCTION

Degradation is a crucial factor and causes deterioration of the useful properties of polymeric materials. Several polymers tend to decompose during the fabrication process; therefore, a thermal decomposition study is also necessary. In the last decade several investigators^{1–4} have studied the degradation of nylon 66. The kinetics of photoaging of nylon 66 has been widely studied,^{5,6} but to improve all aspects polymer stability, a fundamental understanding of the photoas well as the thermal-degradation process involved is essential; therefore, in the present study we investigated the thermal decomposition kinetics of neat and UV-irradiated nylon 66 and correlate the results using different kinetic equations.

EXPERIMENTAL

Materials

The nylon 66 commercial samples (Zytel I01 L NC 10) used in this study were received from E. I. Dupont de Nemours (Spruance, VA) and used after purification in order to remove the additives. These samples were then subjected to polychromatic irradiation ($\lambda \geq 290$ nm) in an accelerated weathering chamber (SEPAP 12/24) with (4 × 400 W) medium-pressure mercury vapor lamps at 60°C for different time intervals.

Experimental procedure

The commercial nylon 66 was processed into thin film in a Carver press at 270°C by applying ≈ 14 kg/cm² pressure for 2 min. The thermogravimetric studies were carried out with a Perkin Elmer TGA-7 model with closed pan. The sample weight taken for analysis was kept almost identical for all experiments (approximately 9.0 mg). The percentage weight loss versus temperature of neat and photooxidized samples was measured at five heating rates—5°C min⁻¹, 10°C min⁻¹, 20°C min⁻¹, 30°C min⁻¹, and 40°C min⁻¹ in the nitrogen flux in the temperature range of 25°C–800°C. A Perkin Elmer DSC-7 (differential scanning calorimeter) was used to determine the melting point, T_m ; crystallization temperature, T_c ; enthalpy, ΔH ; and entropy, ΔS in the heating and cooling runs in the nitrogen atmosphere from 25°C to 300°C at a heating rate of 5°C min⁻¹, 10°C min⁻¹, 20°C min⁻¹, 30°C min⁻¹, and 40°C min⁻¹. The baseline was calibrated with an empty pan for each heating rate. The FTIR was taken using a Perkin Elmer 16 PC spectrophotometer.

RESULTS

The onset of degradation temperature (IDT), maximum decomposition temperature (T_{max}), and 10%–50% weight loss at various temperatures were read from the TGA plots, and those data are summarized in Table I. The integral procedural decomposition temperatures (IPDT) were calculated from the normalized curve (with respect to the residual weight) using Doyle's equation⁷:

$$T^* = 875A^* + 25 \quad (1)$$

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TABLE I
Thermal Decomposition Kinetics of Neat and Photooxidized Nylon 66

Sample	<i>n</i>	β (°C min ⁻¹)	Temperature at weight loss					IDT (°C)	<i>T</i> _{max} (°C)	IPDT (°C)	ΔE_a	ΔE_a	ΔE_a	ΔE_a
			10%	20%	30%	40%	50%				(kcal mol ⁻¹)	(kcal mol ⁻¹)	(kcal mol ⁻¹)	(kcal mol ⁻¹)
										[A]	[B]	[C]	[D]	
Neat	0.5	5	510	525	535	550	580	500	630	480	23.5	26.3	19.6	25.3
	1.0	10	515	530	540	545	580	520	610	462	12.2	14.2	15.6	16.2
	1.5	20	475	495	507	520	530	490	580	432	13.6	15.6	16.7	17.5
	2.0	30	490	500	506	510	515	485	535	428	14.1	17.8	18.9	19.8
	2.5	40	430	440	450	465	470	425	530	424	18.6	21.7	24.8	26.9
Irradiated 100 h	0.5	5	495	500	515	525	540	490	600	472	23.0	24.7	25.0	26.7
	1.0	10	485	490	510	515	520	480	55	468	19.5	20.1	22.2	23.0
	1.5	20	485	490	500	502	505	480	540	458	25.2	22.2	25.6	27.1
	2.0	30	475	490	505	515	530	470	580	454	28.6	23.4	28.6	30.5
	2.5	40	475	475	478	480	490	450	530	444	26.5	31.3	24.6	32.9
Irradiated 250 h	0.5	5	510	520	530	540	550	500	580	4321	24.2	30.3	24.4	19.7
	1.0	10	495	500	502	510	515	490	530	428	16.1	15.7	17.3	18.8
	1.5	20	485	490	500	510	515	480	580	421	21.2	25.4	18.9	19.6
	2.0	30	485	490	500	510	515	480	570	418	28.6	27.3	19.3	21.6
	2.5	40	490	460	465	470	480	435	560	410	32.3	33.1	23.3	29.3

Where [A] is Anderson–Freeman method, [B] is Ozawa method, [C] is Coats-Redfern method, and [D] is MacCallum–Tanner method.

where T^* represents IPDT and A^* is the total area under the normalized curve from 25°C to 800°C. The TGA plots (Fig. 1) of neat and irradiated samples reveal a maximum weight loss in the temperature range of 515°C–630°C.

Dynamic thermogravimetric measurements (Fig. 1) have the advantage of calculating the reaction kinetics from a single curve; the results obtained are reproducible and very consistent with the observed changes. It

also has the advantage over measurements at a constant temperature because the later part of the sample may change while the sample is still heated to the desired temperature, especially for high polymers, whose initial structural change is a rather complicated process. The use of the nonisothermal method^{8–10} for determining kinetic parameters has been widely studied:

$$-dW/dt = A \exp(-\Delta E/RT) W^n \quad (2)$$

where W is the fractional residual weight of the sample; T is the absolute temperature; R is the gas constant; t is time; and A , ΔE , and n are the preexponential factor, activation energy, and order of the reaction, respectively. Equation (2) is the differential equation, and the fraction weight is derived by integration as a function of temperature. The thermal decomposition methods are not limited kinetically with the single process but in fact depend on all the physical parameters. The Anderson and Freeman¹¹ equation was thus applied:

$$\log(-dw/dt) = n \Delta \log W_r - (\Delta E/2.303R) \Delta(1/T) \quad (3)$$

where dw/dt is the rate of the reaction, n is the order of reaction, ΔE is the activation energy, R is the gas constant, T is the absolute temperature, W_r is $W_c - \Delta W$, ΔW is the weight loss at the point where dw/dt is taken, and W_c is the total weight loss associated with the given reaction.

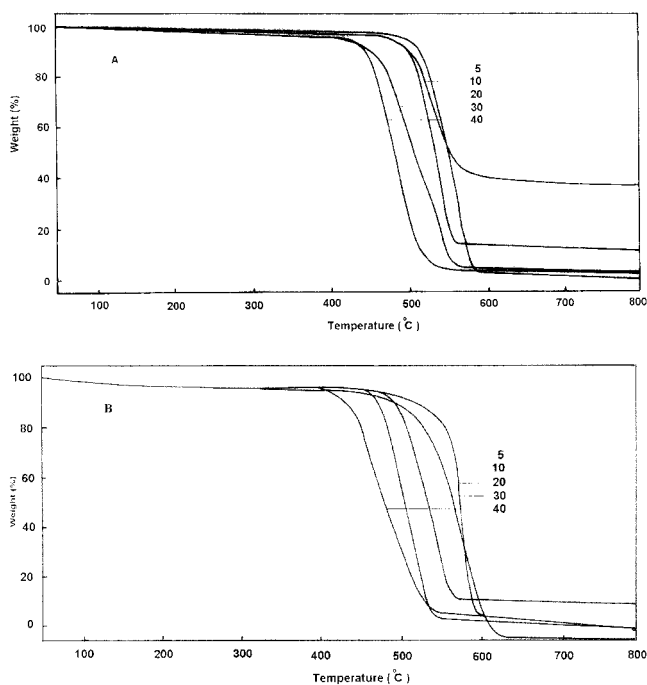


Figure 1 TGA thermograms of nylon 66: (a) neat, (b) photoirradiated for 250 h at a heating rate of 10°C min⁻¹.

The slope of the plots $\Delta \log(dw/dt)$ versus $\Delta \log W$ gives n , and the intercept on the ordinate gives ΔE when $1/T$ is kept constant. The calculated activation energy profile is summarized in Table I.

There has been disagreement about the validity of the kinetic parameters from a single nonisothermal curve; therefore, we applied the desired temperature range to three additional models:

- Coats–Redfern equation¹²

$$\ln \left(\frac{g^\alpha}{T^2} \right) = \ln AR/\phi E_a (1-2RT/E_a) - E_a/RT \quad (4)$$

- MacCallum–Tanner equation¹³:

$$\begin{aligned} \text{Log}(\alpha) = \text{log} [AE_a/\phi R] - 0.485E_a^{0.435} \\ - (0.449 + 0.217) \times 10^3 \end{aligned} \quad (5)$$

where α is the fraction decomposition, ϕ is the heating rate, n is the order of parameter, T is the absolute temperature (K), A is the preexponential factor, E_a is the activation energy, and R is the gas constant.

Weight loss (%) in the range of $\alpha = 0.1$ – 0.9 showed linear plots of LHS against $1/T$ (K) for value of $n = 0.5, 1.0, 1.5, 2.0,$ and 2.5 at heating rates of, respectively, 5°C – 40°C . The validity of the thermal decomposition was also checked by calculating the correlation coefficient (r):

$$r = \sum xy / \sqrt{\sum x^2 y^2} \quad (6)$$

where x is the average value at the X axis and y is the average value at the Y axis.

The calculated values of E_a for the Coats–Redfern and MacCallum–Tanner equations [eqs. (4) and (5)] are reported in Table I.

Ozawa^{14–16} also has proposed a relationship for considering a heating rate as a prime tool toward learning the kinetics of thermal decomposition. We calculated the activation energy for this process by thermogravimetric analysis at several heating rates using the well-known Ozawa's equation :

$$\begin{aligned} \text{log} F(\alpha) = \text{log} AE/R - \text{log} \beta \\ - 2.315 - 0.4567(E_a/RT) \end{aligned} \quad (7)$$

The DSC thermograms are shown in Figure 2(a,b). The rate constant for the overall decomposition was calculated¹⁷ from eq. (8):

$$R = \frac{\Delta H^{n-1} dH/dt}{(\Delta H - H_p)^n} \quad (8)$$

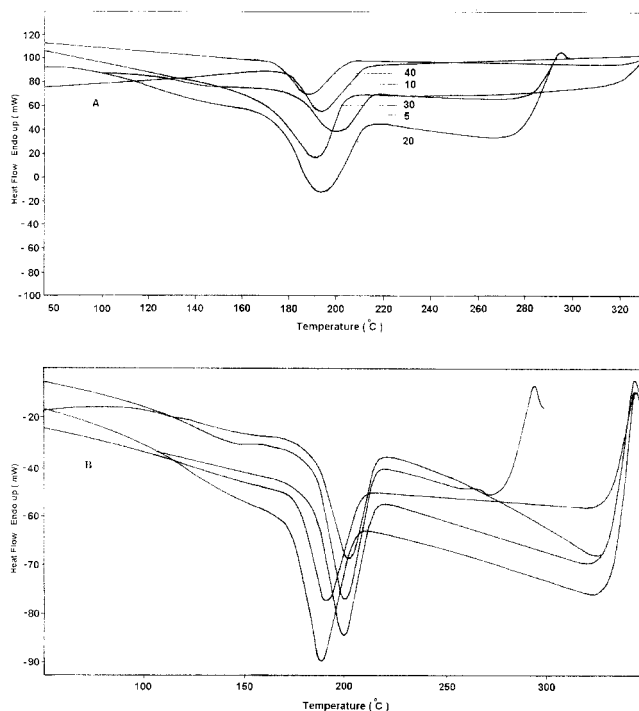


Figure 2 (a) DSC thermograms of neat nylon 66 at different heating rates (5°C min^{-1} – $40^\circ\text{C min}^{-1}$); (b) DSC thermograms of nylon 66 photoirradiated for 250 h at different heating rates (5°C – $40^\circ\text{C min}^{-1}$).

where R is the rate constant that represents the fraction of reactant decomposed per unit time at constant concentration, dH/dt is the height of the ordinate at a given temperature, H_p is the partial heat change, ΔH is the net heat change, and n is the order of the reaction.

The plot of $\log k$ versus $1/T$ is linear in nature for $n = 0.5$ – 2.5 at heating rates of 5°C min^{-1} – $40^\circ\text{C min}^{-1}$. The heating and cooling thermograms provide the different values of entropy, ΔS ; enthalpy, ΔH ; activation energy, ΔE ; melting point, T_m ; crystallization temperature, T_c ; and onset and end set temperatures, which are summarized in Table II.

DISCUSSION

In the present article we have reported the results of our study of a thermal and photooxidized sample of nylon 66 irradiated for various times. The imide species generated upon photoirradiation of the nylon samples are seen in the FTIR and UV spectra shown in Figure 3(a,b), respectively. The kinetics of degradation of nylon 66 was studied by TGA and DSC in a nitrogen atmosphere, and an attempt was made to correlate the structure with the decomposition phenomenon. The rationale for our experiments can be summarized as the weight change in the sample as a function of temperature. A TGA run of the neat sample [Fig. 1(a)] exhibited weight loss corresponding to the various stages of degradation. The TGA thermogram of

TABLE II

Sample	n	β ($^{\circ}\text{C min}^{-1}$)	T_m ($^{\circ}\text{C}$)	T_c ($^{\circ}\text{C}$)	ΔH (kcal mol^{-1})	ΔS (kcal mol^{-1})	ΔE_a (kcal mol^{-1})	Onset ($^{\circ}\text{C}$)	End set ($^{\circ}\text{C}$)
Neat	0.5	5	257	189	4.1	15.2	20.7	242.0	264.6
	1.0	10	257	188	4.6	17.7	12.1	244.7	261.9
	1.5	20	259	195	4.1	15.6	13.0	246.1	264.4
	2.0	30	260	198	5.2	10.5	20.4	255.9	264.9
	2.5	40	260	202	5.1	19.7	19.7	258.9	264.6
	0.5	5	258	188	7.6	22.4	11.0	240.4	261.5
Irradiated 100 h	1.0	10	258	189	4.5	17.5	18.0	244.7	263.7
	1.5	20	260	193	3.8	14.6	14.7	251.8	265.1
	2.0	30	261	193	4.7	17.9	13.8	252.3	267.0
	2.5	40	261	199	5.8	22.1	22.6	244.2	260.0
	0.5	5	256	199	4.46	27.0	12.4	245.7	264.3
	1.0	10	257	193	2.8	16.5	11.2	242.2	264.5
Irradiated 250 h	1.5	20	259	200	4.9	19.2	17.5	250.1	264.0
	2.0	30	261	199	3.61	17.2	25.1	252.2	267.7
	2.5	40	261	200	3.80	14.5	29.0	252.7	263.6

Melting point (T_m), crystallization temperature (T_c), enthalpy (ΔH), entropy (ΔS), and activation energy (ΔE_a).

the neat and 250-h irradiated samples [Fig. 1(a,b)] exhibited a sigmoid curve, indicating a single-stage decomposition process, and may have been a result of

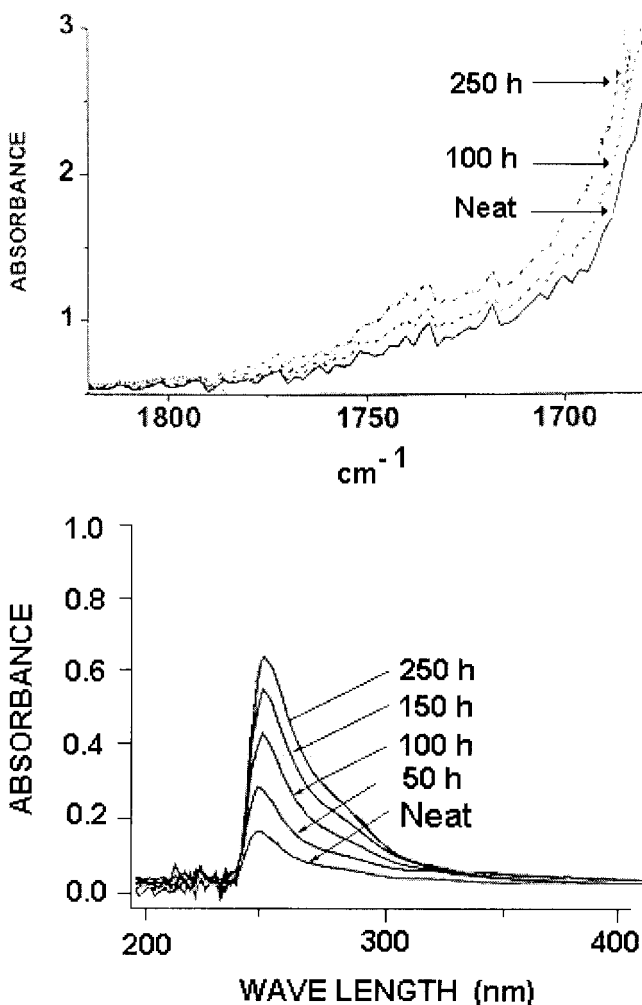


Figure 3 (a) FTIR spectra of photoirradiated nylon 66; (b) UV-vis spectra of photoirradiated nylon 66.

a random chain scission process. A shift in the peak values of onset (IDT) and end set (T_{max}) temperatures toward the lower scale [425 $^{\circ}\text{C}$ –520 $^{\circ}\text{C}$, 515 $^{\circ}\text{C}$ –630 $^{\circ}\text{C}$ (Fig. 1)] is a result of the formation of low-molecular species during irradiation. IPDT shows a descending temperature trend with an increase in irradiation time and relates to the breakdown products of low-molecular fragments of the original formulation with irradiation.

The activation energy (ΔE_a) was observed to increase with heating rate as well as with irradiation time. The activation energy of the neat sample at various heating rates (5 $^{\circ}\text{C min}^{-1}$ –40 $^{\circ}\text{C min}^{-1}$) was in the range of 12.2–26.9 kcal/mol. This increase is related to the unzipping process, which dominates at a higher heating rate, at the initial stage of decomposition and leads to an increase with the rate of depolymerization. For the irradiated sample, the ΔE_a ranged from 15.7 to 33.1 kcal/mol using the Anderson, Ozawa, Coats–Redfern, and MacCallum–Tanner kinetic models and showed a linear increasing trend (Table I) upon irradiation that may be attributable to favorable aging/crystallization at higher heating rates.

The rate of mass loss increased with an increase in temperature, and the Arrhenius plot exhibited a linear relationship when $\log k$ was plotted against $1/T$ (k). The best fit was obtained for ($n = 1$) at heating rate of 10 $^{\circ}\text{C min}^{-1}$ (Fig. 4), which is similar to the reported results. Several authors^{18–23} have studied kinetic models in different temperature ranges and estimated variation in the activation energies with interpretation of various factors to control the thermal decomposition. These values suggest that depolymerization is the only principal decomposition process and is enhanced by irradiation. Thus, the rate of monomer formation is basically controlled by segmental mobility upon irradiation.

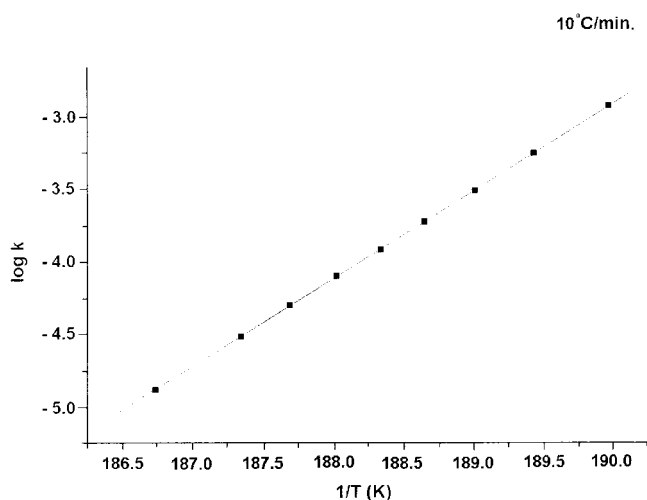


Figure 4 Arrhenius plot exhibiting a linear relationship between $\log k$ and $1/T$ at heating rate of $10^\circ\text{C min}^{-1}$.

Close observation of the results shown in Table II reveals that the melting temperature (T_m) of polyamides is almost the same. This is because of the polar nature of the amide group in the irradiated segment and its ability to form hydrogen bonding, possibly leading to almost identical T_m values.²⁴ This change reveals that during irradiation a chain of a compact and highly flexible nature is formed. This chain also effects the melting point of polyamides but enhances the crystallization temperature (T_c) and entropy (ΔS) with irradiation time. The values of ΔH are very similar throughout the reaction, from which it can be inferred that the same degradation mechanism is operating through out the system. The peak height increased continuously with increase in the exposure time, essentially a result of the formation of the imide group linkage also seen in Figure 3(a,b). Conversion at peak maximum (T_m) varied with the heating rate from 5°C min^{-1} to $40^\circ\text{C min}^{-1}$, with weight loss higher in the initial stage than in the final stage and also increasing with irradiation time. The best linear regression fit was obtained at the heating rate $10^\circ\text{C min}^{-1}$ for $n = 1$ and ΔE_a 12.2 kcal/mol, showing a strong resemblance to the TGA observation. The other feature of the DSC thermograms (Table II) indicates that the activation energy values of TGA (12.2–33.1 kcal/mol) were slightly greater than those of DSC (11.0–29.0 kcal/mol), with the only reason for this the contribution of the difference in temperature range.

CONCLUSIONS

The decomposition temperature, activation energy, and order of reaction at the initial stage of decompo-

sition corresponded to the first order, involving oxidation of the less thermally stable segments. This may be because in the initial oxidative degradation, oxygen has to diffuse into polymer, which occurs to a lesser extent. On the other hand, the second stage may consist of simultaneous thermal and oxidative degradation of polyamides segments. It was also observed that in the irradiated samples, the segments remained relatively unaffected because of the inert atmosphere, although it is possible for some scission of the N—H bond to take place. We thus conclude that the thermal decomposition of nylon 66 (neat and irradiated) samples follows a complex method and may occur because of the rapid depolymerization process.

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