Thermochimica Acta, 99 (1986) 43–47
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE KINETICS OF OXYLUMINESCENCE OF SELECTED POLYMERS

C.H. HSUEH and W.W. WENDLANDT

Department of Chemistry, University of Houston, University Park, Houston, TX 77004 (U.S.A.)

(Received 14 August 1985)

ABSTRACT

The oxyluminescence (OL) curves of polyethylene, poly(vinyl stearate), and Nylon 6/9, obtained at various heating rates, were used to evaluate E and A of the light emission process. The Kissinger and Murray–White equations were used to evaluate the OL curves and thus obtain the kinetic parameters. A graphical method was used to calculate the theoretical E and A values for these three polymers using T_{max} experimental data. Good agreement was found between the experimental and theoretical E and A values.

INTRODUCTION

The oxyluminescence (OL) of polypropylene, when heated isothermally in an oxygen atmosphere, was first observed by Ashby [1]. Soon after this discovery, the kinetics of the OL process for numerous polymers were reported by many investigators [1–5]. We wish to report here a non-isothermal method that can be used to evaluate the kinetics of the OL process from simple heating rate data. The method was used to evaluate the kinetic parameters, E and A, for the polymers polyethylene, poly(vinyl stearate), and Nylon 6/9.

EXPERIMENTAL

The OL apparatus was the same as previously described [6–8]. It consisted of a furnace assembly, a temperature programmer, an atmosphere control enclosure, and a Bascom-Turner Model 8110-4 data center recorder. The recorder permitted data storage on an 8-in. floppy disk with resultant mathematical manipulation [8] of the experimental data. Background furnace emission was subtracted from all of the OL curves giving a corrected OL curve, I_c, versus temperature. Sample sizes ranged in mass from 3 to 7 mg. Four furnace heating rates were employed, 2.5, 5, 7.5 and 10°C min^{-1}. An oxygen gas flow rate of 40 ml min^{-1} was used in all of the experiments.

0040-6031/86/$03.50

The polymer samples were obtained from Scientific Polymer Products, Inc., Webster, New York, in powdered or film form. Particle sizes of the powdered forms ranged from 10 to 30 mesh.

RESULTS AND DISCUSSION

As reported previously [2,5], it is usually assumed that the instantaneous value of I_c is directly proportional to the OL process rate and that a single-step OL reaction obeys a first-order state equation. Therefore, Kissinger's equation [9,10]

$$\frac{\mathrm{d}\left(\ln\frac{\phi}{T_{\max}}\right)}{\mathrm{d}\left(\frac{1}{T_{\max}}\right)} = -\frac{E}{R} \tag{1}$$

where ϕ is the heating rate, $T_{\max}$ is the peak maximum temperature, and E the activation energy, was used for calculation of the apparent E values. Also, the Murray–White [11] equation

$$\frac{E}{RT_{\max}^2} = \frac{A}{\phi}\exp\left(\frac{-E}{RT_{\max}}\right) \tag{2}$$

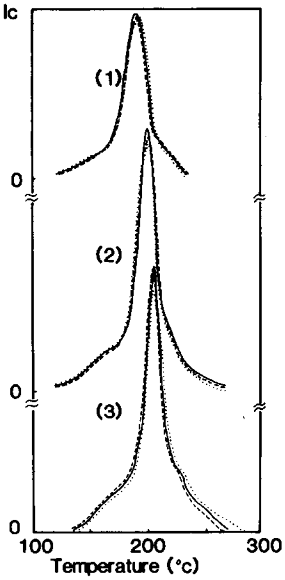

Fig. 1. OL curves of Nylon 6/9 with particle size of 10–30 mesh. Heating rates of: (1) 2.5; (2) 5; and (3) 10°C min^{-1}. Three independent curves are indicated by (———), (······), and (- - - - - -).

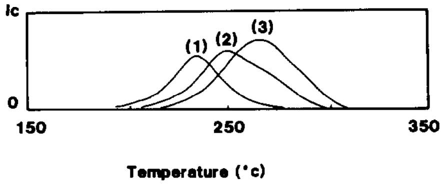

Fig. 2. OL curves of polyethylene. Heating rates of: (1) 2.5; (2) 5; and (3) 10°C min^{-1}.

can be rearranged to

$$A = \frac{\phi E \exp\left(\frac{-E}{RT_{\max}}\right)}{RT_{\max}^2} \tag{3}$$

or

$$\phi = \frac{RAT_{\max}^2}{E \exp\left(\frac{-E}{RT_{\max}}\right)} \tag{4}$$

so that if E is known, A can be calculated. Substituting the values of E and A into eqn. (2), as well as setting $f(T) = RAT^2/E \exp(-E/RT)$ and $g(T) = \phi$, the theoretical values of $T_{\max}$ can be found graphically, using the intersection of the $f(T)$ and $g(T)$ curves.

The OL curves of Nylon 6/9 and polyethylene are given in Figs. 1 and 2, respectively, while the peak maxima temperatures are tabulated in Table 1.

It was found that the peak temperatures ($T_{\max}$) at a given heating rate were reproducible to about $\pm 1\%$ of each other. For poly(vinyl stearate) and Nylon 6/9, three values of the peak temperature were taken as $T_{\max}$. These data for the three polymers, polypropylene, poly(vinyl stearate) and Nylon

TABLE 1

$T_{\max}$ values obtained for three polymers

Polymer	$T_{\max}$ (K)			
	(°C min^{-1}) $\phi = 2.5$	5	7.5	10
Nylon 6/9	465	473	478	
	464	473	478	
	466	474	478	
Poly(vinyl stearate)	491	505		520
	491	506		520
	491	505		520
Polyethylene	508	522		538

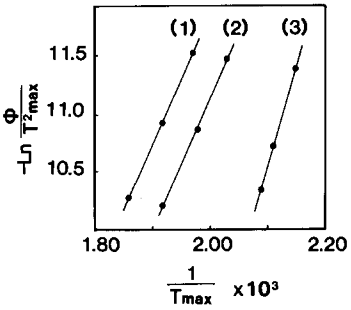

Fig. 3. Kissinger plots of: (1) polypropylene; (2) poly(vinyl stearate); and (3) Nylon 6/9.

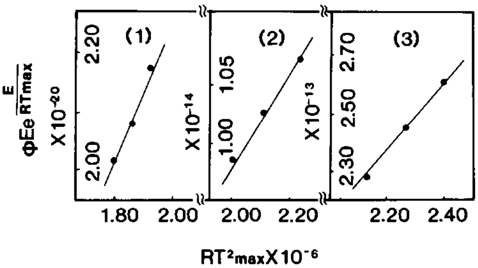

Fig. 4. Murray–White plots to obtain values of A. (1) Nylon 6/9; (2) poly(vinyl stearate); and (3) polyethylene.

6/9, are plotted using Kissinger's equation in Fig. 3. By substituting the values of E, obtained from Fig. 3, into eqn. (1), the curves in Fig. 4 were obtained. Values of A were calculated from the slopes of the curves in Fig. 4. The values of E and A thus calculated are tabulated in Table 2.

Plotting f(T) and g(T) versus the peak maximum temperature gave the theoretical values of T_{max}, as shown in Fig. 5. The theoretical T_{max} values were in very good agreement with the experimental values, thus indicating that the Kissinger equation can be used to calculate E for the OL process. Of course, the basic assumption of a first-order reaction must be implied in order to use this method. Although Nylon 6/9 gives a far larger E value than the other two polymers studied, it also has a much larger A. This

TABLE 2

Values of E and A found for three polymers

Kinetics parameter	Polymer [a]		
	A	B	C
E (kJ mol^{-1})	147	98	95
A (s^{-1})	1.1×10^{14}	4.8×10^{7}	1.1×10^{7}

[a] A = Nylon 6/9; B = poly(vinyl stearate); C = polyethylene.

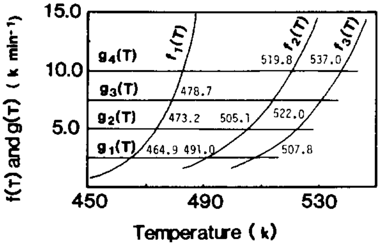

Fig. 5. Change of experimental T_{max} with f(T) and g(T). $f_1(T)$ = Nylon 6/9; $f_2(T)$ = poly(vinyl stearate); and $f_3(T)$ = polyethylene.

indicates that Nylon 6/9 has a much higher concentration of active sites, which are responsible for the light emission, and that they are properly oriented for effective reaction with oxygen in the furnace atmosphere. It is also possible that Nylon 6/9 has a different OL mechanism than the other two polymers.

ACKNOWLEDGMENT

The financial support of this work by the Robert A. Welch Foundation of Houston, Texas, is gratefully acknowledged.

REFERENCES

1 G.E. Ashby, J. Polym. Sci., 50 (1961) 99.
2 M.P. Schard and C.A. Russell, J. Appl. Polym. Sci., 8 (1964) 997.
3 R.E. Barker, J.H. Daane and P.M. Rentzepis, J. Polym. Sci., Part A, 3 (1965) 2033.
4 A.M. Wynne and W.W. Wendlandt, Thermochim. Acta, 14 (1976) 61.
5 W.W. Wendlandt, Thermochim. Acta, 71 (1983) 129.
6 W.W. Wendlandt, Thermochim. Acta, 39 (1980) 313.
7 W.W. Wendlandt, Thermochim. Acta, 35 (1980) 255.
8 W.W. Wendlandt, Thermochim. Acta, 50 (1981) 7.
9 H.E. Kissinger, J. Res. Natl. Bur. Stand., 57 (1956) 217.
10 H.E. Kissinger, Anal. Chem., 29 (1957) 1702.
11 P. Murray and J. White, Trans. Br. Ceram. Soc., 54 (1955) 204.