Thermochimica Acta, 71 (1983) 129–137
Elsevier Science Publishers B V., Amsterdam – Printed in The Netherlands

THE OXYLUMINESCENCE AND KINETICS OF OXYLUMINESCENCE OF SELECTED POLYMERS

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(Received 13 June 1983)

ABSTRACT

The oxyluminescence (OL) curves of 19 polymers are presented These curves may be employed as a means of characterization and/or identification of the polymer A new method for determining the kinetics of the OL is described The E_a values of 6 different polymers ranged from 60 to 135 kJ mole^{-1} The method is only applicable to single-step OL processes

INTRODUCTION

When polymers are heated to moderate temperatures in air or oxygen, they may exhibit a low-level light emission called oxyluminescence (OL). This phenomenon was first described by Ashby [1] for polypropylene in 1961 and has subsequently been studied for a wide variety of polymeric materials by numerous workers [2–11]. The technique has been employed as a powerful tool for determining the oxidative stability of polymers and the efficiency of antioxidants. A survey of these has recently been presented by Collins and Wendlandt [12].

The origin of the oxyluminescence phenomena has been investigated by various workers. OL takes place only at elevated temperatures and is generally thought to proceed via the intermediate formation and subsequent degradation of peroxides, peroxy- or oxy-radicals [5]. Since the oxidation of polymers such as polypropylene is very complicated, De Kock and Hol [5] studied the OL of dicumyl peroxide mixed with this polymer. They concluded that the observed OL of this mixture may be due to the phosphorescence of one of the decomposition products, acetophenone. Part of the cumyloxy radical splits off methyl radicals; the remaining compound may be an excited acetophenone molecule, which, via a phosphorescence process, deactivates to its ground state. Ashby [1] also noted the formation of carbonyl groups in the polypropylene samples he studied. Barker et al. [4] developed a model which indicated that the OL should be due to fluorescence and/or phosphorescence of acceptor materials formed during the

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oxidation reaction. Wynne and Wendlandt [9] proposed that the OL of a polymer such as polyethylene was due to the decomposition of $PO_2^{\bullet}$ radicals that are formed during the degradation of the polymer (P) in oxygen or air.

We would like to extend our studies in this area by characterizing selected polymers according to their OL curves and the development of a kinetics method for single step OL reactions.

EXPERIMENTAL

The OL curves were obtained using the apparatus previously described [13,14]. The outputs from the photometer and temperature sensor were recorded on a Bascom–Turner Model 8110-4 data center recorder [15]. This recording system permitted floppy disk storage of the raw data and then mathematical manipulation to obtain the corrected OL data (I_c), which is presented in the figures. Sample sizes ranged in mass from 5 to 20 mg; a furnace heating rate of 12°C min^{-1}, and an oxygen flow rate of 40 ml min^{-1}, were employed.

The polymer samples were commercially available samples obtained from Scientific Polymer Products, Inc., Webster, NY. The samples were in pellet or powder form.

RESULTS AND DISCUSSION

As discussed previously [10,11], OL can be used to characterize polymers by virtue of their unique light emission curves. Each curve is slightly different and may be used to identify or characterize that particular polymer. This applies even to polyethylene polymers containing various amounts of chlorine. The OL curve peaks are generally found in the 200–300°C temperature range, although some peaks are present in the curves at temperatures approaching 400°C, the limit of the apparatus employed. All of the curves are plots of the corrected intensity, I_c, versus temperature, with the background radiation being subtracted out by the recording system.

The OL curves for the vinyl polymers are given in Figs. 1–3. All of the OL curves, except poly(vinyl formal) (Fig. 1A), consist of multiple peak curves generally in the 150–400°C temperature range. The presence of these peaks suggests sequential reactions that are light-emitting processes; however, their origin and resolution are beyond the scope of this investigation. A particularly interesting OL curve is that for poly(vinyl pyrrolidine) (Fig. 1B) which contains four main peak maxima with several smaller shoulder peaks. Poly(vinyl butyral) (Fig. 3B) contains two sharp maxima in its OL curve as well as two shoulder peaks. Ignition of the sample occurred in only one of the polymers, poly(vinyl stearate) (Fig. 3A). The OL curve consisted of a

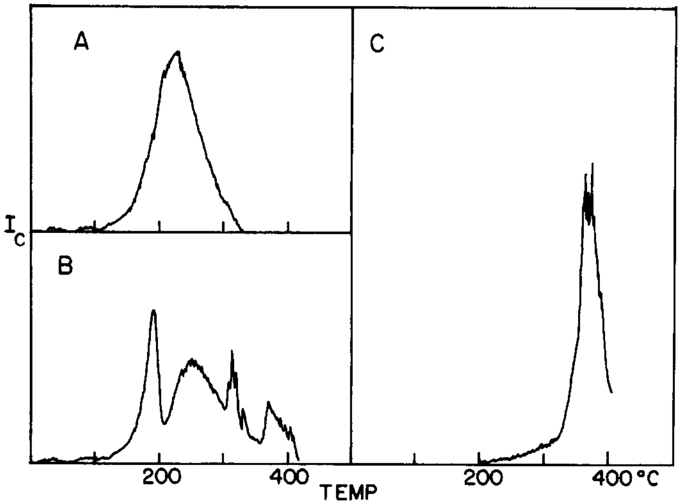

Fig 1. OL curves of selected polymers A, Poly(vinyl formal), B, poly(vinyl pyrrolidine), C, poly(vinylidene fluoride).

narrow peak with a maximum at 260°C followed by the ignition reaction starting at about 320°C.

The OL curves of polyethylene chlorinated with various amounts of chlorine are given in Fig. 4. The chlorine contents ranged from 25 to 48%; all of the curves are plots in which the I_c values are multiplied by a factor of four. The low chlorine content polymer (Fig. 4A) consists of a rather broad peak in the curve from 150 to 325°C. On increasing the chlorine content, a

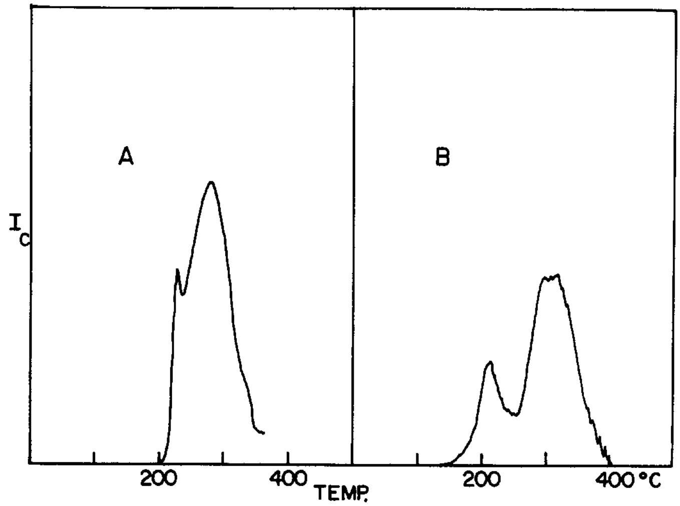

Fig 2 OL curves of selected polymers A, Poly(vinyl fluoride), B, poly(vinyl alcohol), 100% hydrolyzed.

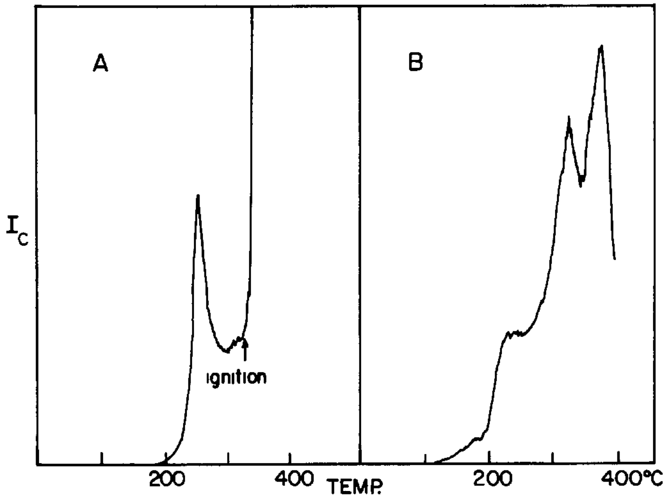

Fig 3 OL curves of selected polymers. A, Poly(vinyl stearate); B, poly(vinyl butyral)

narrow peak appears in the OL curves with a peak maxima at about 210°C. This peak is followed by a shoulder peak on the high temperature side except for the 48% Cl polymer (Fig. 4D). The latter contained only a single narrow peak.

The OL curves for the remaining selected polymers are given in Figs. 5 and 6. With this series of polymers, the OL curve peaks are found at

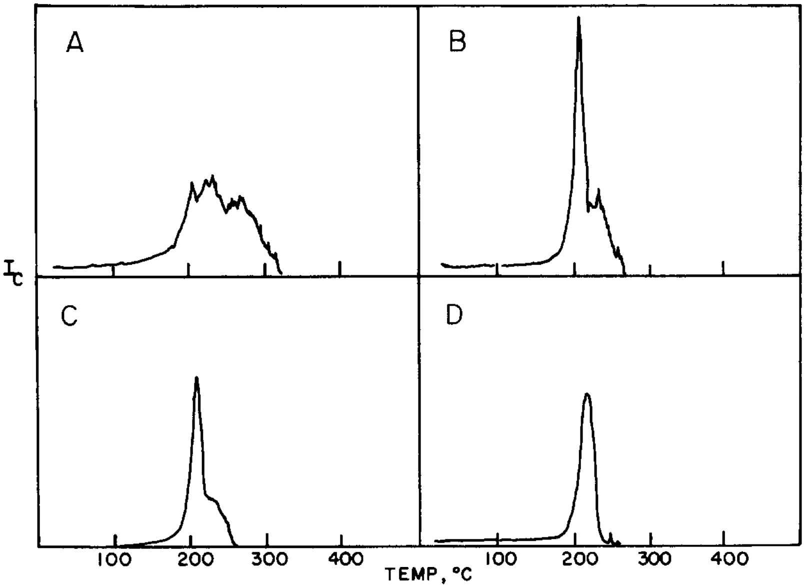

Fig. 4 OL curves of chlorinated polyethylene containing various amounts of chlorine. A, 25% Cl ($I_c \times 4$); B, 36% Cl ($I_c \times 4$); D, 42% Cl ($I_c \times 4$); D, 48% Cl ($I_c \times 4$).

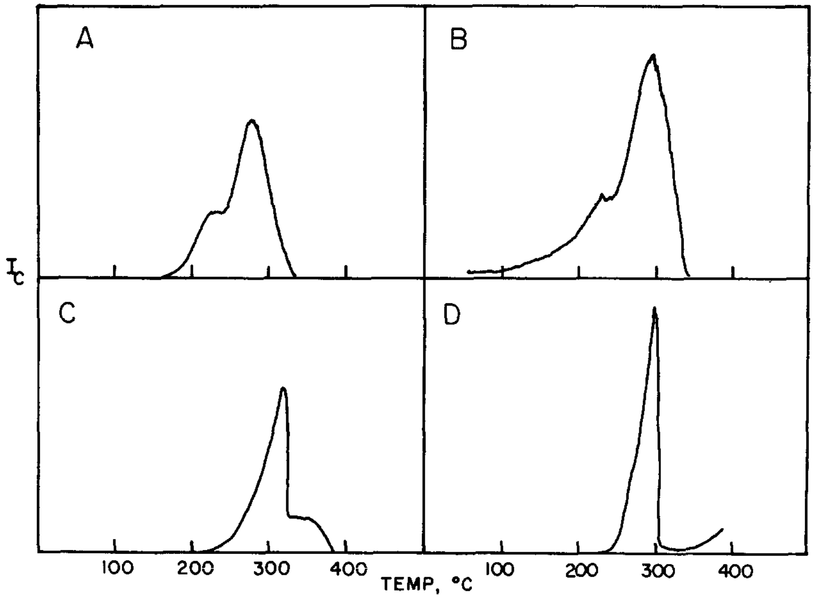

Fig 5 OL curves of selected polymers. A, Poly(diallyl isophthalate) ($I_c \times 4$); B, poly(diallyl phthalate) ($I_c \times 4$); C, polycaprolactone; D, poly(acetal) ($I_c \times 3$)

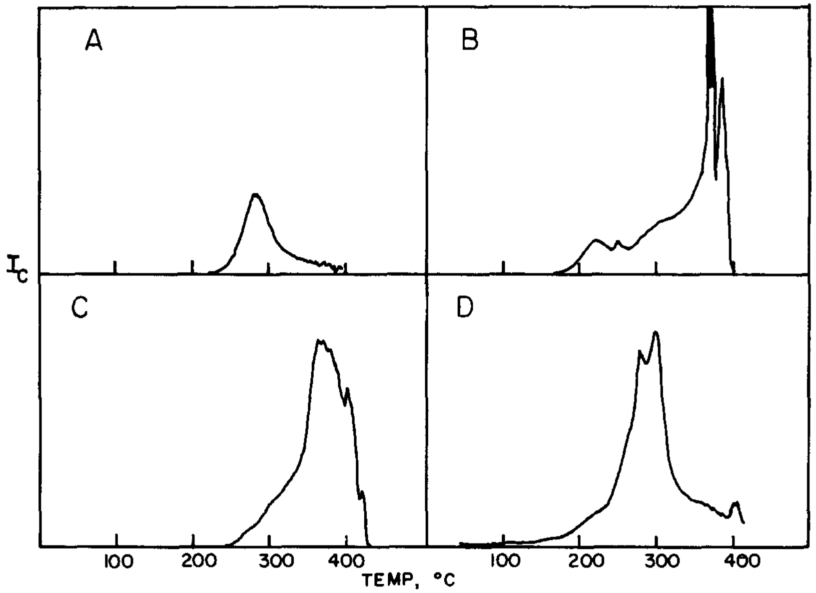

Fig. 6. OL curves for selected polymers. A, Polyacrylamide ($I_c \times 2$); B, poly(1,4-cyclohexanedimethylene terephthalate) ($I_c \times 2$), C, poly(1,4-butylene terephthalate) ($I_c \times 2$); D, poly(butyl methacrylate).

somewhat higher temperatures in that most of the peak maxima are found in the 250–400°C temperature range. With the exception of poly(acetal) and polyacrylamide, the curves contain multiple peaks or a main peak preceded or followed by a shoulder peak(s). This would again suggest multiple or consecutive reactions for the light-emission processes. Each curve, with the exception of the polydiallyl polymers, is unique with reference to the curve peaks and could possibly be used to characterize these polymers.

General

The OL of the polymers presented here consist of very low level light emission and cannot be seen by the human eye. In many cases, the recorded light intensity has been amplified by use of the recording system, although in one case it has been decreased by a factor of two [poly(acetal)]. The spectra of the OL has not been determined in this study, although it has been obtained for dicumyl peroxide in polypropylene [5] and Lexan [4] using optical filters. For the former, the spectrum consists of a single broad peak from 360 to 500 nm with a peak maximum at about 420 nm. Since the phosphorescence spectrum of acetophenone in poly(methyl methacrylate) was similar, it was concluded that the OL may possibly be interpreted as phosphorescence of carbonyl group containing reaction products.

Kinetics of oxyluminescence

The kinetics of the oxyluminescence process of numerous polymers has been studied by various investigators [1,3,4,9]. On measuring the temperature dependence of OL, the activation energies, E_a, were obtained, assuming a

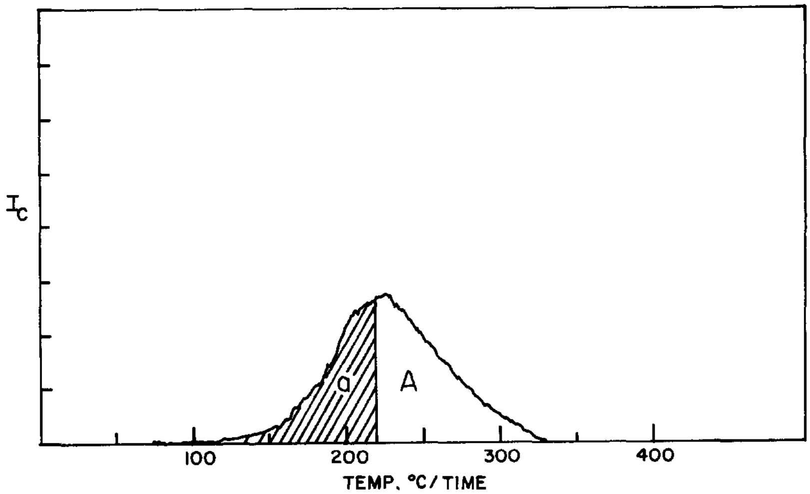

Fig. 7 OL curve of poly(vinyl formal)

first-order rate equation. For unstabilized polypropylene, Schard and Russell [3] found an E_a for the OL process of 97.5 kJ mole^{-1}, which was reasonably close to the 109–113 kJ mole^{-1} for the oxidation of both isotactic and amorphous polypropylene found by other methods. It was very close to the value of 100–105 kJ mole^{-1} found for peroxide formation in atactic polypropylene [16].

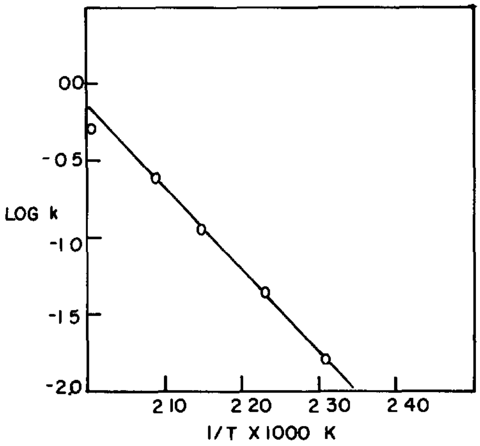

Fig. 8 Arrhenius plot for OL of poly(vinyl formal)

The kinetics of the OL processes presented here is a modification of the method described for the EGD of polymers by McCarter [17]. Using the corrected OL curve for poly(vinyl formal) shown in Fig. 7, the rate of OL is given as

$$\text{Rate} = k(a/A)$$

where k is the specific rate constant in min^{-1}, a is the area up to temperature T (time, t) and A is the total area minus a. Using five values of temperature/time, a plot of ln k versus $1/T$ is made as shown in Fig. 8. The slope of the resulting curve was found by use of a microcomputer linear least-squares fit program and E_a was calculated using the integrated Arrhenius equation

$$\ln k = \ln A - E_a/RT$$

This method is based on the assumption that the OL process is first order in oxygen concentration, a condition that appears to be justified according to Wynne and Wendlandt [9] and others [1]. It was felt that the method could only be justified for single-step OL processes, i.e. those OL curves with only one peak maximum. Hence, it was applied only to those few polymers which contained this type of OL curve.

The resultant E_a values obtained by this method and those found by others are given in Table 1. The E_a values determined here are higher, on the

TABLE 1

E_a values for the oxyluminescence of various polymers

Polymer	E_a (kJ mole^{-1})	Ref
Nylon 66	63 (to 435 K)	9
	97 (> 435 K)	9
Ivithene	41 (to 460 K)	9
	199 (> 460 K)	9
Alathon 1	80	9
Polypropylene (Profax 6701)	44 4 (< 300°C)	4
	251 (> 300°C)	4
	155 [a]	4
	97	3
	73 6 [b]	1
Polyethylene (L D)	82.4 (above transition point)	3
	31 (below transition point)	3
Nylon 6	64.4	3
Polystyrene	50.6	3
Polyurethane	46.9	3
Poly(methyl methacrylate)	85.8	3
	27 (below transition point)	3
Poly (caprolactone)	135	This work
Polyethylene, 25% Cl	60	This work
Polyethylene, 36% Cl	100	This work
Polyethylene, 42% Cl	100	This work
Polyethylene, 48% Cl	135	This work
Poly(vinyl formal)	100	This work

[a] Eyring–Williams [18].

[b] $O_2/(O_2+N_2)$ ratio = 1.0.

average, than those obtained previously. The E_a values averaged 105 kJ mole^{-1}, while earlier determinations averaged 88 kJ mole^{-1}.

ACKNOWLEDGEMENT

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

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