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Review

THE OXYLUMINESCENCE OF POLYMERS. A REVIEW

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ABSTRACT

A review of the oxyluminescence of polymers is presented here. When polymers are heated in an air or oxygen atmosphere, they exhibit a low-level light emission called oxyluminescence (OL). This new phenomenon has been used to study the oxidative degradation of polymers as well as to evaluate stabilizer concentration and behavior. This review consists of the following: (a), OL intensity and spectral distribution; (b), mechanism of the OL process; (c), kinetics of OL; (d), OL in polymer stabilizer studies; (e), instrumentation; and (f), polymers studied by OL.

INTRODUCTION

When many polymers are heated in air or oxygen in the temperature range 150–300°C, they exhibit a low-level emission of light that is called oxyluminescence (OL). This phenomenon was first detected by Ashby [1] in 1961 who heated polypropylene in an oxygen atmosphere. It was noted that (1) oxygen must be present for light emission to occur, (2) the intensity of the light was proportional to the concentration of oxygen in contact with the polymer surface, and (3) the presence of stabilizers decreased the intensity of the light. Thus, a new tool was discovered which would provide invaluable insight into the study of the oxidative degradation of polymers as well as to elucidate the effects of stabilizers on the polymer oxidation process. This technique is not widely used at the present time although numerous investigations have elucidated much of the fundamental nature of the process, as well as its kinetics and other physical parameters. It has been found that OL is a general phenomenon which applies to many other organic compounds as well as to polymeric materials [2]. In view of this, it was felt that a brief review of OL would be of interest to a wide audience composed of polymer chemists as well as to thermal analysts in general.

There is little agreement on the name for this phenomenon. Ashby [1] and others used the term oxyluminescence, Barker et al. [3] called it thermochemiluminescence (TCL), David [4] used photothermal analysis (PTA), and

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Wynne and Wendlandt [5] called it light emission (LE). The term employed here will by oxyluminescence (OL) although thermooxyluminescence would probably be just as appropriate.

For convenience in this discussion, the OL of polymers will be divided into the following sections: (a), OL intensity and spectral distribution; (b), mechanism of the OL process; (c), kinetics of OL; (d), OL in polymer stabilizer studies; (e), instrumentation; and (f), polymers studied by OL.

INTENSITY AND SPECTRAL DISTRIBUTION

The emitted light in the OL of most polymers is fairly low level in that it requires a sensitive photomultiplier tube (PMT) and photometer circuit to detect it. Ashby [1] used a PMT and photometer in which the light emission was expressed in A of anode current. It was estimated that 1 lm generated 10 A of anode current for the PMT employed. The OL intensities, using this system, ranged from 10^{-10} to 10^{-8} lm for all of the polymers investigated. Nylon had the most intense OL in that at 200°C, it emitted enough light to be seen by the human eye in the dark. Schard and Russell [6] employed a PMT and photometer system with a luminous sensitivity of ~ 80 A lm^{-1} in the region 400 ± 50 nm. The OL intensities, as described previously [1], were expressed in anode current from 10^{-11} to 10^{-8} A. Barker et al. [3] stated that the OL of a Lexan resin and polypropylene at 250°C in air could be seen with the human eye in the dark. Wynne and Wendlandt [5] used a sensitive photon counter; the OL was expressed in CPM in the range 10^1–10^5. The PMT and photometer used by David [4] had a sensitivity of 2000 A lm^{-1} in the spectral range 200–600 nm.

The spectral distribution of the emitted light has been determined by a wavelength filter method. Ashby [1] found that the PMT anode current was attenuated about 50% by interposing a filter that absorbed light of wavelengths shorter than 420 nm between the polymer and the PMT. No current could be detected if, instead, a filter was interposed that absorbed light of wavelengths shorter than 515 nm. It was concluded that in OL, 50% of the light emission had wavelengths between 420–515 nm and 50% between 300–420 nm. Barker et al. [3] also employed filters to determine the spectral distribution of the emitted light. Using a set of Corning filters, the spectrum of the OL of Lexan PC in air at 220–230°C was determined. If the overall response of the PMT and filters is F_i (i = a, b, c, ..., g), the PMT signal should be

$$I_i = K\int_0^{\infty} F_i W_\lambda d_\lambda$$

where W_λ is the radiant power density of the OL and K a proportionality factor which depends upon the sensor area and geometry. The filter output "areas" (I vs. λ)

$$A_i = \int_0^\infty F_i d_\lambda$$

were determined graphically and the OL spectrum, W_λ, was estimated by application of the mean value theorem in the form

$$\text{relative OL signal} \approx K \langle W_\lambda \rangle_{\text{av}} = I_i / A_i$$

The resulting spectrum consisted of a broad peak from 400 to 610 nm with a maximum at about 540 nm. A shoulder peak was observed at about 475 nm. Also, using wavelength filters, de Kock and Hol [7] obtained the OL spectrum of dicumyl peroxide in polypropylene: the OL curve extended from 360 to ~ 500 nm with a peak maximum at 420 nm. It was very similar to the phosphorescence spectrum of acetophenone dissolved in poly(methyl methacrylate); in fact, the peak maxima were exactly the same.

MECHANISM OF THE OL PROCESS

The origin of the OL process in polymers has been the subject of numerous investigations, with little agreement as to the mechanism of the light emitting process. Ashby [1] found that for every photon of light emitted, 10^4 carbonyl groups were formed. This estimate indicated that the chemical reaction(s) involved in OL occur infrequently when compared to the reaction leading to carbonyl formation. Schard and Russell [6] indicated that as the number of tertiary hydrogen atoms increased, the OL increased. They stated that OL may be useful as a method for determining chain branching. It was also noted that the species responsible for OL increased more rapidly in the case of nylon than in polypropylene and reached an equilibrium or steady state condition much sooner. The rapid increase in luminosity, on changing from nitrogen to oxygen atmospheres, indicated that the OL process occurred principally on the surface of the polymer. There were no significant differences in the OL of polymers when the thickness of the sample varied from 7 to 70 mm. Barker et al. [3] calculated that for a 0.1-g sample of polypropylene, about 2×10^{-11} photons/reaction site were obtained. They postulated that the process may be similar to that proposed by Vassilev [8] to explain the chemilumescence of substituted anthracenes in hydrocarbon solutions. This process consisted of the reactions

$$\text{hydrocarbon} + \text{oxidizing agent} \rightarrow {}^3\text{P}' + \text{other products}$$

$${}^3\text{P}' + {}^1\text{A} \xrightarrow{k_{\text{PA}}} {}^1\text{P} + {}^1\text{A}'$$

$${}^1\text{A}' \xrightarrow{k_{1,1}} {}^1\text{A} + h\nu_{\text{f}} \xrightarrow{k_{1,3}} {}^3\text{A}' \xrightarrow{k_{3,1}} {}^1\text{A} + h\nu_{\text{P}}$$

where the superscripts 1 and 3 denote singlet and triplet states, respectively, and the primes denote electronic excitation. Thus, the observed OL may be due to the fluorescence, ν_f, and/or phosphorescence, ν_p, of the acceptor materials. Spin orbit coupling is the mechanism leading to a measurable intermolecular energy transfer rate, k_{PA}.

de Kock and Hol [7,9] argued that since the reaction of polypropylene with oxygen was too complicated to be used for verifying the origin of OL, a model system composed of dicumyl peroxide mixed with polypropylene could be employed. Heating this mixture in a nitrogen atmosphere would be expected to give rise to OL and at the same time the nature of the reaction products could be ascertained. From the spectrum of the model system, which was almost identical to that of the phosphorescence spectrum of acetophenone (a decomposition product), it was stated that the observed OL of the former may result from the phosphorescence of the reaction product, acetophenone. Methyl radicals split off from a number of the cumyl radicals and the remaining compound may be an excited acetophenone molecule, which, via a phosphorescence process, deactivate to the electronic ground state. It was concluded that the OL reaction of polypropylene may possibly be interpreted as the phosphorescence of a carbonyl-group containing reaction product. Wynne and Wendlandt [5] suggested that the OL process involved polymer peroxy radicals, $PO_2^{\cdot}$, such as are involved in the thermal degradation of polymers [10]. In the presence of oxygen, the polymer-free radicals, $P^{\cdot}$, formed hydroperoxide radicals, $PO_2^{\cdot}$, or molecules, PO_2H, giving the following termination steps

$$2P^{\cdot} \rightarrow \text{products} \tag{1}$$

$$PO_2^{\cdot} + P \rightarrow \text{products} \tag{2}$$

$$2PO_2^{\cdot} \rightarrow \text{products} + O_2 \tag{3}$$

At high oxygen concentration, step (3), thought to involve ketonic intermediates, is the most significant while at low oxygen concentrations, step (1) predominates. OL accompanies all three termination steps; however, that associated with steps (2) and (3) is considerably more intense than that arising from step (1). Wynne and Wendlandt [5] called the light emission from step (1) "chemilumescence" since it occurred in a nitrogen atmosphere and "oxyluminescence" from steps (2) and (3), which occurred in air or oxygen atmospheres.

KINETICS OF OXYLUMINESCENCE

The kinetics of the OL process in polymers has been fairly extensively studied by several investigators. Schard and Russell [11] were the first to calculate apparent activation energies, E_a, for the OL reactions using Arrhenius plots of the light intensities measured at various temperatures

They found no relationship between E_a and the intensity of light emission. Polypropylene required a higher E_a (97.5 kJ mol^{-1}) than polyethylene (82.4 kJ mol^{-1}) but the former had a greater intensity of light emission. Poly (methyl methacrylate) showed a sharp change in slope (for the log OL vs. $1/T$ curve) and hence different values for E_a were obtained. The average value of 97.5 kJ mol^{-1} found for unstabilized polypropylene was reasonably close to the 109–113 kJ mol^{-1} for the oxidation of both isotactic and amorphous polypropylenes found by other techniques. It is even closer to the value of 100–105 kJ mol^{-1} that Manyasek et al. [12] found for the E_a of peroxide formation in atactic polypropylene. They reported a value for E_a of 113 kJ mol^{-1} which could be interpreted as supporting the theory that light is emitted by the reaction of $RO_2^{\bullet}$ radicals. Nylon 6, which undergoes an autoretardant reaction [6], had a lower E_a value than do polyolefins.

Barker et al. [3] calculated an apparent E_a for polypropylene from Ashby's data [1]. The E_a values ranged from 23.4 to 73.6 kJ mol^{-1} depending upon the oxygen concentration. They reported that OL obtained in static atmosphere systems always tends to be low; thus, the flow replacement of the boundary layer gases is important. Comparing the OL E_a for polypropylene ($E_a = 172$ kJ mol^{-1}) with the E_a for oxidation by O_2 absorption (121 kJ mol^{-1}), IR (130 kJ mol^{-1}) and TG in vacuum (243 kJ mol^{-1}), it was found that the former was larger than the average value obtained by the other three methods. The E_a for Lexan consisted of three values; ~ 42 kJ mol^{-1} at lower temperatures, ~ 138 kJ mol^{-1} for intermediate temperature, and ~ 251 kJ mol^{-1} for the higher temperature region. These values are in reasonable agreement with TG results. Cycling data indicated that ln OL was approximately a decreasing linear function of the number of cycles, n, of heating and cooling. Results obtained in a CO atmosphere gave E_a values of about the same magnitude as in O_2. The Williams–Eyring [13] method that was developed for thermoluminescence (TL) was applied to the OL process giving an E_a for polypropylene of ~ 155 kJ mol^{-1}.

Wynne and Wendlandt [5] found a linear relationship between OL and the rate of reaction using

$$(R - R_b) = \alpha\phi(\mathrm{d}n/\mathrm{d}t)$$

where $R - R_b$ is the PMT response (photon counter), α is a constant, and ϕ the quantum efficiency. For Alathon 1 (polyethylene), $E_a \approx 80$ kJ mol^{-1} in air, oxygen and nitrogen atmospheres, between 385 and 460 K.

Chen [14,15] described a general kinetics equation which was applied to a thermoluminescence "glow" curve but could possibly be employed for an OL curve as well. The basic equation is

$$I = -\mathrm{d}n/\mathrm{d}t = S'n^b \exp(-E/kT)$$

where b is the kinetic order and S' the pre-exponential factor in s^{-1} $cm^{3(b-1)}$. The general theory of the TL process was also reviewed.

Wendlandt [16] described a method for evaluating the kinetics of OL employing a method developed by McCarter [17] for evolved gas detection (EGA). Using the corrected light emission curve, the rate of OL was given by

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

where k is the specific rate constant in min^{-1}, a is the area of the curve peak up to temperature T (or time, t) and A is the total area minus a. The Arrhenius equation was then used to calculate E_a. A value for E_a of 100 kJ mol^{-1} was calculated for poly(vinyl formal) using this method.

The OL E_a values obtained for selected polymers are listed in Table 1.

OXYLUMINESCENCE IN POLYMER STABILIZER STUDIES

It was pointed out by Ashby [1] that in the presence of stabilizers (antioxidants), the OL of the polymer was changed. Using polypropylene

TABLE 1

Oxyluminescence E_a of selected polymers

Polymer	E_a(kJ mol^{-1})	Ref.
Nylon 66	63 (to 435 K)	5
	97 (> 435 K)	5
Ivithene	41 (to 460 K)	5
	199 (> 460 K)	5
Alathon 1	80	5
Polypropylene	44.4 (< 300°C)	3
(Profax 6701)	251 (> 300°C)	3
	155 [a]	3
	97	11
	73.6 [b]	1
Polyethylene (Low density)	82.4 (above transition point	11
	31 (below transition point)	11
Nylon 6	64.4	11
Polystyrene	50.6	11
Polyurethane	46.9	11
Poly(methyl methacrylate)	85.8	11
	27 (below transition point)	11
Poly(caprolactone)	135	16
Polyethylene, 25% Cl	60	16
Polyethylene, 36% Cl	100	16
Polyethylene, 42% Cl	100	16
Polyethylene, 48% Cl	135	16
Poly(vinyl formal)	100	16

[a] Williams–Eyring [13] method.

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

containing a 1 : 1 mixture of the stabilizer, 4,4′-thiobis(6-*tert*-butyl-*o*-cresol) with dilaurylthiopropionate, the OL intensity was greatly reduced for an initial time interval and the extent of this reduction was determined by the concentration of the stabilizer. When the stabilizer concentration was depleted, the OL returned to its original intensity. This suggested that the intensity of OL is reduced as the rate of oxidation was reduced by the stabilizer. A rapid method for determination of the concentration of the stabilizer in the polymer was also developed.

Schard and Russell [11] studied the OL change for polypropylene containing varying amounts of the stabilizer, 4,4′-thiobis(3-methyl-6-*tert*-butylphenol). The OL was delayed for a short period of time after admission of oxygen to the system to an extent depending on the stabilizer concentration. The rate of rise in the OL emission curve appeared to vary inversely as a function of stabilizer concentration. Preliminary studies showed that the effect of stabilizer upon the OL of polyethylene was quite different from that in polyethylene. The time elapsed to reach maximum intensity of OL was of little value in the former studies since, with 0.1% of stabilizer present, the maximum intensity was attained almost instantly.

Collins and Wendlandt [18] used OL to determine the stabilizer concentration in polyethylene. The initial deviation of the curve from the baseline, as well as from the peak maximum temperature, were both found to be a function of stabilizer concentration in the polymer. The method was compared to those using TG and DSC.

INSTRUMENTATION

The instrumentation used to follow the OL process in polymers is relatively simple. It generally consists of a light detection apparatus containing a sensitive photomultiplier tube and photometer; a furnace and temperature controller or programmer; an enclosed chamber surrounding the sample which is capable of a controlled static or dynamic atmosphere of oxygen or other gases; and a recording system. The output from the photometer is plotted vs. time (isothermal mode) or temperature (non-isothermal mode). Most of the early studies used the isothermal mode [1,3,6,7,11] but more recent investigations employed the non-isothermal mode [4,5,19]. Many of the early isothermal studies were carried out at a temperature of 150°C [1,3,6,7] but the non-isothermal mode has been used to study polymers up to a maximum temperature of 400°C. This is usually the upper temperature limit because of radiation effects which mask the OL emission. However, Wendlandt [20] used a data center recorder which permitted the deletion of the background radiation of the curves giving only the OL vs. temperature curves. A system for low-temperature measurements to −196°C has also been reported by Kaimin and Galeis [21].

TABLE 2

Polymers known to exhibit oxyluminescence

Polymer	Ref.
Polypropylene	1, 3, 6, 11
Polyethylene	1, 4, 6, 11, 18
Polyisobutylene	1
Polyurethane	1, 6, 11
Polychloroprene	1
Poly(methyl methacrylate)	1, 4, 6, 11
Polystyrene	1, 4, 6, 11
Poly(vinylidene chloride)	1
Polyhexamethylene adipamide (Nylon)	1
Poly(vinyl chloride)	1, 4
Polyoxymethylene	1, 6
Polyacrylonitrile	1, 19
Polytetrafluoroethylene	6
Poly(ethylene terephthalate)	6
Nylon 6/6	6, 19, 23, 25
Nylon 6	6, 11, 23, 25
Nylon 6/10	6, 23
Ethylene–propylene rubbers	9
Dicumyl peroxide in polypropylene	7
Alathon 1 (polyethylene)	5
Ivithene	19
Nalgene	19
Polycarbonate	3, 19
Poly(vinyl pyrrolidine)	16, 19
Nylon 6/9	23
Nylon 6/12	23
Nylon 6/T	23
Nylon 12	23
Poly(vinyl formal)	16
Poly(vinylidene fluoride)	16
Poly(vinyl fluoride)	16
Poly(vinyl alcohol) 100% hydrolyzed	16
Poly(vinyl stearate)	16
Poly(vinyl butyral)	16
Chlorinated polyethylenes	16
Poly(diallyl isophthalate)	16
Poly(diallyl phthalate)	16
Polycaprolactone	16
Poly(acetal)	16
Poly(acrylamide)	16
Poly(1,4-cyclo-hexanedimethylene terephthalate)	16
Poly(1,4-butylene terephthalate)	16
Poly(butyl methacrylate)	16
Cellulose acetate	24
Cellulose propionate	24
Ethyl cellulose	24
Cellulose acetate butyrate	24
Hydroxypropyl cellulose	24
Cellulose sulfate	24
Cellulose triacetate	24

OL measurements at low pressures have been taken by Barker et al. [3] who also analyzed the gaseous and condensation extractable pyrolysis products of the polymer using a gas chromatograph and mass spectrometer. To determine the OL spectral distribution, various light filters [1,7] have been employed. Simultaneous OL and DTA measurements were obtained by David [4] using a commercial DTA apparatus, while OL-DSC data were recorded by Wynne and Wendlandt [5,19], using a DuPont or a Perkin–Elmer DSC instrument. Johnson and Chiu [22] also obtained light emission measurements coupled with smoke evolution detection and TG.

POLYMERS STUDIED BY OL

A compilation of all of the polymers that are known to exhibit oxyluminescence is given in Table 2.

Most of the polymers listed were studied in the isothermal mode. This technique provided useful information concerning the effect of atmosphere, stabilizer concentration, and permitted evaluation of the kinetics of the OL process. More recent studies used the non-isothermal mode, yielding information on the OL dependency of the sample temperature. Since each OL curve appeared to be unique, it was proposed that OL be used to characterize the various polymers [16,23,24]. This would, of course, supplement other thermal analysis techniques.

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REFERENCES

1 G.E. Ashby, J. Polym. Sci., 50 (1961) 99.
2 W.W. Wendlandt, unpublished results.
3 R.E. Barker, J.H. Daane and P.M. Rentzepis, J. Polym. Sci., Part A, 3 (1965) 2033.
4 D.J. David, Thermochim. Acta, 3 (1972) 277.
5 A.M. Wynne and W.W. Wendlandt, Thermochim. Acta, 14 (1976) 61.
6 M.P. Schard and C.A. Russell, J. Appl. Poly. Sci., 8 (1964) 985.
7 R.J. de Kock and P.A.H.M. Hol, Recl. Trav. Chim. Pays–Bas, 85 (1966) 102.
8 R.F. Vassilev, Nature, 200 (1963) 773.
9 R.J. de Kock and P.A.H.M. Hol, Int. Syn. Rubber Symp., Lect., 4 (1969) 53.
10 L. Reich and S.S. Stivala, Elements of Polymer Degradation, McGraw-Hill, New York, 1971, pp. 99, 161.
11 M.P. Schard and C.A. Russell, J. Appl. Polym. Sci., 8 (1964) 997.
12 F. Manyasek, D. Berek, M. Michko, M. Lazar and Y. Pablinetz, Vysokomol. Soedin, 3 (1961) 1104.

13 F.E. Williams and H. Eyring, J. Chem. Phys., 15 (1947) 280.
14 R. Chen, J. Mater. Sci., 11 (1976) 1521.
15 R. Chen and Y. Kirsch, Analysis of Thermally Stimulated Processes, Pergamon, New York, 1981.
16 W.W. Wendlandt, Thermochim. Acta, 71 (1983) 129.
17 R.J. McCarter in O. Menis (Ed.), Status of Thermal Analysis, Natl. Bur. Stand. (U.S.) Spec. Publ., 338 (1970) 137.
18 L.W. Collins and W.W. Wendlandt, Isr. J. Chem., 22 (1982) 233.
19 A.M. Wynne and W.W. Wendlandt, Thermochim. Acta, 13 (1975) 393.
20 W.W. Wendlandt, Thermochim. Acta, in press.
21 I.F. Kaimin and Z.Z. Galeis, Vysokomol. Soedin, Ser. A, 9 (1967) 245.
22 B.B. Johnson and J. Chiu, Thermochim. Acta, 50 (1981) 57.
23 W.W. Wendlandt, Thermochim. Acta, 68 (1983) 383.
24 W.W. Wendlandt, Thermochim. Acta, 68 (1983) 387.
25 N.S. Allen, J.F. McKellar and D. Wilson, J. Photochem., 6 (1977) 337.