Chemiluminescence and Thermo-oxidation Stability of Poly(2,6-dimethyl-p-phenylene ether) in Blends with Polystyrene and Polybutadiene

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SYNOPSIS

It has been ascertained that chemiluminescence–time curves for samples of poly(2,6-dimethyl-p-phenylene ether) blended with high-impact polystyrene containing polybutadiene yield a very reproducible pattern even at a temperature of 190°C. The chemiluminescence light emission has been associated with consumption of double bonds in polybutadiene, and a corresponding rate constant and activation energies of chemiluminescence decay from both the isothermal and nonisothermal parts of chemiluminescence–time curves have been determined. As demonstrated by these curves, an attempt to stabilize the blends toward thermooxidation by the peroxide decomposer and stabilizer led to retardation of the oxidation process only and further investigation searching for an optimum stabilizing system is required. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Following reports of Ashby,[1] Schard and Russell,[2] Billingham et al.,[3] Mendenhall,[4] Audouin-Jiráčková and Verdu,[5] Zlatkevich,[6] and George,[7] it becomes clear that polymers which produce the most intensive light emission during their oxidation are those containing aliphatic hydrocarbon chains such as polyolefins, polyamides, or various copolymers and blends of these.

Light emission originates from free-radical processes taking place during polymer oxidation, and several alternative interpretations of this phenomenon exist. At a given temperature, the development of light intensity in the first stages of the oxidation process usually matches the kinetics of the oxidation. Declinations result from the surface contraction during sample melting, filtration, and quenching effects on light emitted due to additives and from the variety of populations of excited states that can be formed during free radical oxidation of various polymers.

Because of these complicating factors, it is difficult to compare the oxidizability of different polymers according to the intensity of light emitted, and until now, the method is used mainly to estimate the antioxidative efficiency of various kinds of thermooxidation stabilizers in a given polymer.[8,9]

Poly(2,6-dimethyl-p-phenylene ether) (PPE) belongs to the class of amorphous polymers having a high transition temperature (215°C). For the pure PPE, the required processing temperature is so high ($\approx$ 360°C) that degradation accompanied with an unintentional deterioration of the polymer properties may occur. To reduce T_g and enable the processing, poly(phenylene oxide) is blended with high-impact polystyrene (HIPS) containing about 20% butadiene units. The application of PPO/HIPS blends is, however, hindered by a rather poor thermooxidative stability of the system.[10] It is assumed that the presence of carbon–carbon double bonds in the elastomeric component of a blend increases greatly the susceptibility of the system toward thermooxidation, and a system of additives are being sought to suppress it.

The still high T_g of the PPE/HIPS blend matrix ensures a constant sample surface at temperatures around 200°C. This is a good prerequisite for reliable

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utilization of chemiluminescence for the investigation of thermooxidation of such a system; temperatures well above 150°C can be used.

In the present article, the chemiluminescence of chemically modified PPE and PPE/HIPS blends is described. The kinetic analysis of the dependence of chemiluminescence intensity vs. time was used to reach more sophisticated evaluation of the results in searching for the optimum stabilization system for such a polymer blend.

EXPERIMENTAL

Six different samples were examined, namely, that of (1) poly(phenylene ether); (2) poly(phenylene ether) with the end hydroxyl groups capped by benzyl, both free of additives; (3) the blend of PPE/HIPS 1 : 1, free of additives; (4) the same blend containing stabilizing system (aromatic phosphite and inorganic sulfide) or (5) copper decomposer, final Cu concentration 10 ppm; or (6) the mixture of both, stabilizer and copper decomposer.

All materials were provided by General Electric Plastics, Bergen op Zoom. Samples (1) and (2) were supplied as fine powders; the other samples [(3)-(6)] were prepared by milling the granules of a polymer in a laboratory mill.

Chemiluminescence measurements were performed on a spectrometer PU SNK 7M with an analogous output, photomultiplier FEU-38 working at a high voltage of 1400 V. A sample mass of 100 mg was used for thermooxidation in each experiment. Temperature for the measurements was at 190°C; the flow of oxygen above the sample was at 4 dm^3/h. The chemiluminescence intensity is expressed in multiples of the photocurrent of 1.6 $\times 10^{-13}$ A at a circuit resistance 1×10^{11} ohm (au).

RESULTS AND DISCUSSION

In Figure 1 the dependence of chemiluminescence intensity on time is shown for all samples tested. Three parts can be distinguished on each curve: The first part corresponds to heating and leads to an increase of the intensity up to a maximum value. The next decrease of intensity can be explained by a fast decay of easily oxidizable sites in the polymer, as, e.g., as double bonds. After this period, the intensity decays slowly.

When comparing both the original and end-capped PPO, it is seen that the end-capping of OH groups results in reduction of intensity to less than one-half of the original value. Obviously, the end-capping has a beneficial effect on thermal stability,
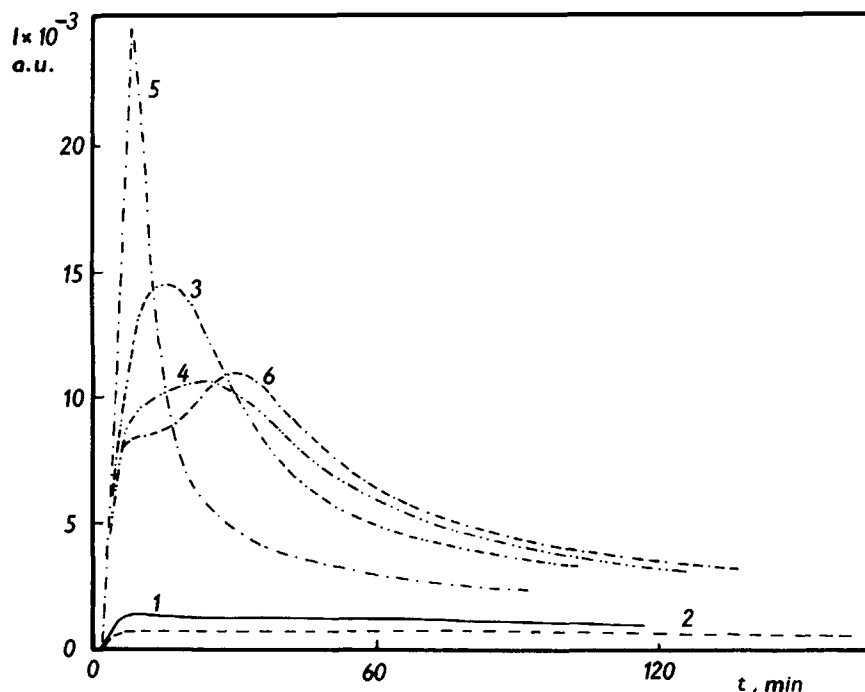

Figure 1 The dependence of chemiluminescence intensity on time for samples (1)-(6) at 190°C in oxygen.

although no induction period of oxidation was observed, the same as with the original PPE.

Blending PPE with HIPS containing butadiene units leads to a substantial increase in the intensity of light emission. Ten times higher intensity was observed with an unstabilized PPE/HIPS blend when compared to the original PPE. This can hardly be due to the presence of polystyrene, as this polymer gives a very low level of oxyluminescence.[2] The chemiluminescence burst is obviously connected with the oxidation of polybutadiene in the HIPS part of the blend. Higher segmental mobility of butadiene units contributes to the facile initiation of oxidation as well. The effect of additives on the thermooxidative stability of PPO/HIPS blends is also seen in Figure 1.

The stabilizer in sample (4) does not behave as observed, e.g., in polyolefins. In the presence of an efficient inhibitor, the termination of peroxy radicals, which is the process largely responsible for the light generation, is expected to be fully suppressed by reaction (1):

$$RO_2^{\bullet} + InH \rightarrow products \qquad (1)$$

and the light emission should be very low. As the inhibitor is consumed, the intensity should start to increase, resulting in the typical "S"-like dependence on time.

As can be seen from Figure 1, this is not the case with samples PPE + PS/PB. The stabilizers used act here as retarders of oxidation. A competition between reactions (1) and (2):

$$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow products + h\nu \qquad (2)$$
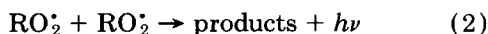
has obviously a comparable rate under given conditions, with eq. (1). This leads to a decrease of the maximum value of intensity (from 15,000 to 10,500 rel. units) and to a change of the shape of intensity of the chemiluminescence–time curve. The fact that no induction period of oxidation was observed may follow from a rather high rate of initiation of the process due to the presence of unsaturations.

For the sample containing Cu peroxide decomposer [sample (5), Fig. 1], the maximum intensity reached a value of about 24,000 rel. units and a very sharp decrease to the low level of light emission took place.

Our attention was paid to the kinetics of the process. Following sample heating, during which the intensity of the luminescence increases due to the

temperature elevation, a steady decrease is observed. This decaying part of the light emission was assumed to be composed of two exponentials. Description of the chemiluminescence intensity (I)–time (t) curves was attempted by nonlinear regression analysis using the following model:

$$I = H_1 \exp(-M)*\exp[A_1*\exp(-N)]$$
$$+ H_2 \exp(-M)*\exp[-A_2*\exp(-N)] \qquad (3)$$
$$M = E/R[T_e - (T_e - T_0)*\exp(-\alpha t)]$$
$$N = \int_0^t M dt$$

where E, A_1, and A_2 are activation energy and preexponential factors, of faster and slower pseudomonomolecular processes; T_e, the temperature of the experiment (463 K); T_0, the starting temperature (293 K); α, the average heat transfer coefficient of the sample and reactor; and H_1 and H_2, proportionality constants, which, in fact, represent the sum of rates of two reactions of the first order under conditions of nonisothermal regime. As the temperature of the sample approaches the temperature of the heating oven, the reaction proceeds isothermally.

Such an approach makes it possible to determine not only kinetic constants of the respective stage of chemiluminescence decay under isothermal conditions (later stages), but also yields the temperature dependence of chemiluminescence intensity I as it corresponds to the exponential heating of the sample to a given temperature of the oven. The parameters obtained in such a way are summarized in Table I.

The first process for the unstabilized sample (3) leads to the isothermal intensity of chemiluminescence of about 25,000–30,000 au extrapolated to time $t = 0$ at 190°C. The second process, which is slower, gives the isothermal intensity of luminescence at 190°C extrapolated to $t = 0$ of about 3000 au. As demonstrated for an unstabilized sample, the fit of experimental and theoretical curves is very good (Fig. 2).

The constant of chemiluminescence decay at 190°C ($k_1 = 0.04$ min^{-1}) for the faster process occurring in an unstabilized sample is reduced to 0.01 min^{-1} in the presence of the stabilizer. For the system with a Cu decomposer of the hydroperoxides, however, k_1 is several times higher (0.2 min^{-1}). A mixture of both a stabilizer and a peroxide decomposer yields a value of k_1 lower than 0.01 min^{-1}.

An apparent activation energy of about 35 kJ/mol, obtained from the rise of chemiluminescence

Table I Parameters Obtained from Chemiluminescence Measurements of PPE Samples Blended with PS and Polybutediene

Sample No.	H_1 a.u.	H_2 a.u.	A_1 min^{-1}	A_2 min^{-1}	E kJ/mol	$k_1 \cdot 10^2$ at 190° min^{-1}	$k_2 \cdot 10^2$ min^{-1}	α min^{-1}
3	25,010	3018	415	2	35	3.99	0.019	0.21
	24,862*	2685	414	0.13	35	4.15	0.001	0.21
4	24,993	2988	236	224	38	1.14	1.08	0.27
	24,988*	2985	218	222	38	1.04	1.55	0.30
5	28,261	2574	1407	77	36	17.4	0.95	0.24
	31,522*	3103	2173	118	35	22.0	1.19	0.15
6	24,990	2988	219	218	38	0.86	0.856	0.28

* Parallel runs.

intensity with temperature, is rather low for such a kind of process. This corresponds to a rate constant $k_1 = 0.04$ min^{-1} at 190°C and 0.0043 min^{-1} at 100°C, and still to the rather high value 0.00018 min^{-1} at 20°C. The half-life of chemiluminescence calculated from the value of k_1 at 100°C is about 160 min, whereas the induction period of oxidation of 1,4-polybutadiene, determined by oxygen absorption, is 165 min[11] at 100°C.

The extraordinary low values of activation energy in the study of oxyluminescence of polymers are not so rare. The value of 31 kJ/mol was reported, e.g., for oxyluminescence of LDPE in the temperature range 50–90°C.[7] Similar low activation energies were observed for polydienes oxidized with singlet oxygen, namely, 48 kJ/mol for 1,4-poly-butadiene or 40 kJ/mol for trans-polypentenamer, overall oxygen content in the samples after oxidation being 3.1 and 0.9%, respectively.

The reasons for such low values of activation energy were not suggested until now. It may be speculated that the process measured is either stationary
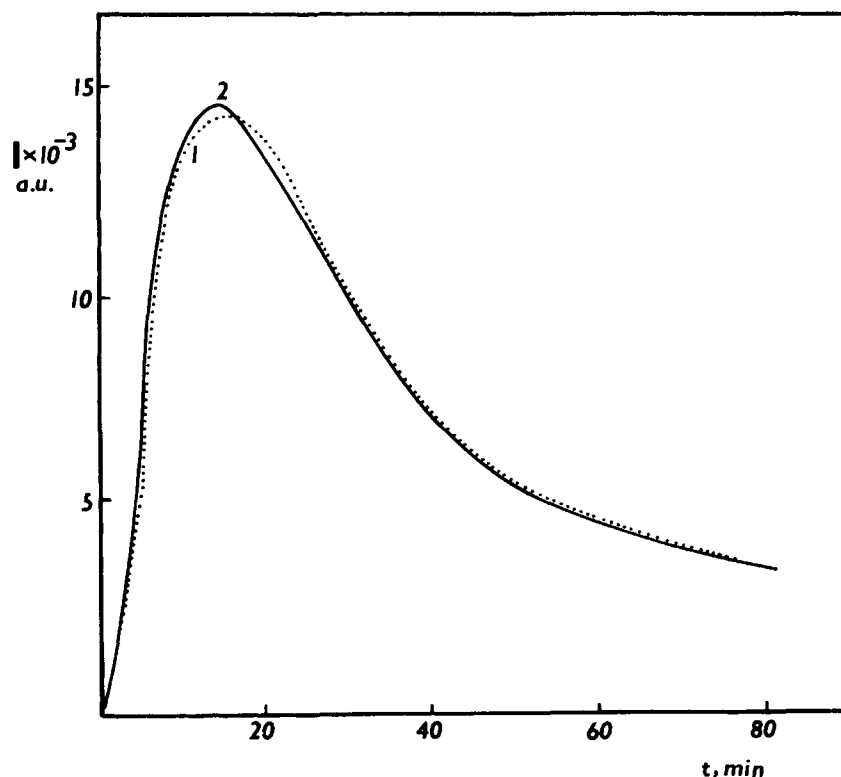

Figure 2 Comparison of (1) theoretical and (2) experimental chemiluminescence curves for sample (3) (oxygen, $T = 190$°C).

and diffusion-controlled or nonstationary and reflecting the decay of alkylperoxy radicals at an increased temperature. Such radicals may accumulate in the sample during processing and storage.

After examining the chemiluminescence–time curves of PPE/HIPS blends, we feel that the knowledge concerning the origin of chemiluminescence in polymers is not complete, especially with regard to the role of unsaturations in the overall process. Double bonds in the hydrocarbon chain are very sensitive sites of oxidation; the steady decay of chemiluminescence reflects in some way their gradual consumption.

The necessary prerequisite for the observation of the light emission is the parallel presence of hydroperoxide or peroxy radicals as the initiators of oxidation. The facts are given below, which coincide with the possible role of some level of unsaturation ($C = C$ bonds) in the initiation process and in enhancement of light emission during oxidation:

(a)Relatively strong chemiluminescence of polypropylene, in which tertiary $C - H$ bonds are the sites of the primary attack of oxygen. Tertiary peroxy radicals thus formed cannot produce luminescence in their self-decay because of energetic reasons.

(b)Nitrogen/oxygen switching experiments with polyamides and ABS copolymers.

Here, following heating the sample in nitrogen for some time, the atmosphere is switched to oxygen and the chemiluminescence bursts are observed. Intensity of these peaks increases proportionally to the time of heating in nitrogen. This corresponds rather to the accumulation of some reactive byproducts than to accumulation of alkyl radicals as it was assumed until now.[12]

The presence of double bonds and highly reactive

allylic hydrogens associated to them ensures a very high rate of initiation of oxidation, which may apparently coincide with presumed alkylperoxy radicals decay used for interpretation of the observation in the paper.[12]

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