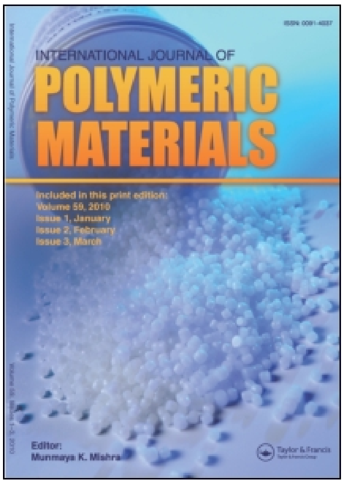

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A Chemiluminescence Study of the Thermo-oxidative Degradation of Copolymers

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The in situ thermo-oxidative degradation of ABS-copolymers, initiated by di-benzoyl peroxide (BP) has been followed by chemiluminescence (CL) measurements. When conducted in the presence of an antioxidant it turns to a quick mean of antioxidant efficiency evaluation. ABS-copolymer containing antioxidants of various classes such as Irganox 1076, Irganox 565, trisnonylphenyl phosphite and di-alkyl-thio-dipropionate was tested. The study has been carried out on the CL signal of the hydroperoxides in the SAN phase produced by BP initiated oxidation or processing. The best protecting efficiency was found for Irganox 565 and trisnonylphenyl phosphite. The results were confirmed by impact strength testing. The conditions for a correct antioxidant efficiency evaluation are discussed.

KEY WORDS Chemiluminescence, thermo-oxidative degradation, ABS-copolymer, antioxidant efficiency.

INTRODUCTION

Acrylonitrile-butadiene-styrene (ABS) copolymer is known to undergo oxidation in the most labile phase- poly-butadiene particles[1] under various oxidizing conditions, including processing.[2]

During processing under air both thermo-oxidative and thermo-mechanical degradation processes are effective. According to the common opinion the limited amount of air available under such conditions restrict the extent of thermo-oxidative degradation. However, our chemiluminescence (CL) studies on processed ABS-copolymer have revealed non-negligible hydroperoxide (HP) concentration (10^{-6} mol —OOH/kg) after processing in ordinary conditions.[3] The following picture regarding the participation of the ABS-copolymer phases has been revealed by CL studies. A significant concentration of HP in the styrene-acrylonitrile (SAN) phase accumulates upon processing. These HP give a CL signal with a peak at 200°C. They are apparently attached to the acrylonitrile (AN) units neighbouring the azomethinic structures (Species I, Scheme I). HP of type II are formed originally and they probably coexist with HP of type I. CL method cannot account for type II HP as they do not generate luminescence.

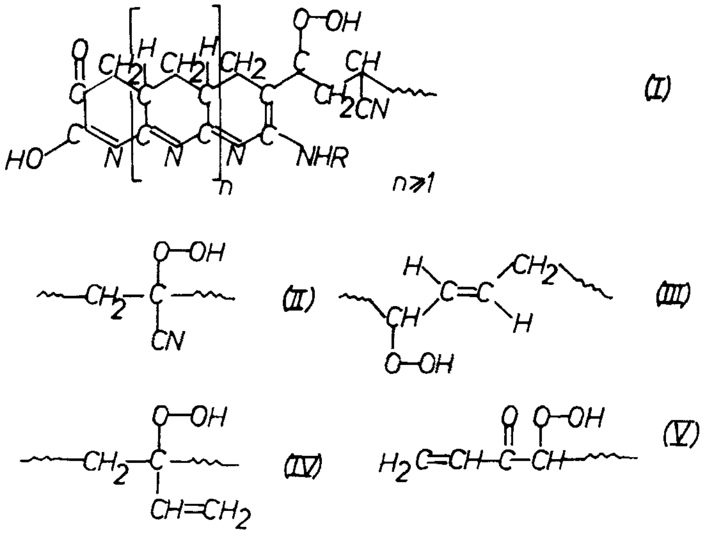
Small amounts of HP in the polybutadiene phase could be also evidenced in

ABS-copolymer after processing. They belong to the 1,4 trans units (Species III, Scheme I) and give a CL peak at 320°C. Polybutadiene can also produce HP of type IV in the 1,2 units. These ones make it possible for type V HP to appear. Type V HP give a CL peak at 180°C but they do not survive processing which normally occurs at 220°C. To sum up, the HP that can be evidenced in ABS-copolymer after processing are in the SAN phase and become manifest through their CL peak at 200°C.

The efficiency of antioxidants is usually determined by induction period measurements in processes such as: O_2 uptake, enthalpy variation during oxidation as followed by DSC and lately, CL emitted by recombination of peroxy radicals.[4] The depreciation of a mechanical property such as impact strength is also an indication of the extent of degradation taking place. All these methods require enough time for sample preparation and/or measurement. With the above mentioned analytical methods except CL, there is also the trouble of film preparation with a thickness that avoid the O_2 diffusion control and makes the comparison reliable. It is the aim of this paper to put forward a CL alternative that enables a quick estimation of the antioxidant efficiency. Accordingly, the *in situ* polymer oxidation initiated by a radical initiator is followed during the CL run. The presence of an antioxidant results in the CL intensity suppression, the extent of which is a measure of antioxidant efficiency providing that:

1. There is no misleading effects arising from luminescence quenching by the antioxidant or the species derived by its activity.
2. There is no reaction between the radical initiator and the antioxidant, either luminescent or not.

The above described method was conceived to give rapid information about the anti-oxidative protection exerted by various antioxidants during ABS-copolymer



SCHEME I Hydroperoxide species formed in oxidized ABS-copolymer processing. Naturally, it does not offer any indication about the effectiveness of the antioxidant as a scavenger of the alkyl radicals produced in appreciable concentration by thermo-mechanical stresses.

EXPERIMENTAL

The ABS-copolymer was obtained by emulsion graft-copolymerization of freshly distilled AN and styrene in the presence of polybutadiene latex to which 0.2% $K_2S_2O_8$ as an initiator has been added. After coagulation, washing and vacuum drying, a polymer powder was obtained. Some of it was solved in CH_2Cl_2 together with di-benzoyl peroxide (BP) 2% and the antioxidant (0.2%). A film was cast and vacuum dried. The following antioxidants have been used: 2-(3,5-di-*tert*-butyl-4-hydroxyanilino)-4,6-bis(octylthio)-1,3,5-triazine (Irganox 565 from Ciba Geigy), octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate (Irganox 1076 from Ciba Geigy), trisnonylphenyl phosphite (TNPP of indigene production) and alkyl 3,3-thiodipropionate with alkyl = C_{14}–C_{18} (DATDP of indigene production).

CL was recorded on 10 mg of polymer samples in the form of powder, films or chips with a Harshaw 3000-A apparatus under an air stream of 2.5 l/min. BP signal was recorded on 0.5 mg samples. The heating rate was 4°C/s, unless otherwise mentioned.

Polymer and stabilizer powders were homogeneously mixed in a Fluid Mischer machine and then molded on a Engel injection machine at 210°C. The resulted Izod impact specimens were tested for strength according to ASTM D 236, Pt. A.

RESULTS AND DISCUSSION

1. The di-benzoyl peroxide initiated degradation of the ABS-copolymer

The ABS-copolymer powder as resulting from synthesis does not present CL emission. If containing 2% BP a strong CL signal at 200°C is recorded (Figure 1, curve 2). This signal is very close, on the temperature scale, to the one presented by BP alone which has a peak at 176°C (Figure 1, curve 1). More work has been carried out in order to isolate the signal characteristic to the ABS-copolymer (on which antioxidant efficiency is studied) from that belonging to BP alone.

If touched by hand, a certain amount of BP decomposes explosively giving an additional apparent signal at 110°C. In fact, this is not due to luminescence, but to fumes. The BP signal intensity in air is 4 times as intensely as in N_2, which proves that the origin of luminescence does not reside in BP decomposition, but in a successive reaction. Not much is known about the products of the solid state thermal degradation of BP, though some unsaturated conjugated dialdehydes resulting from phenyl oxidation[5] could be among the excited emitting products (Scheme II).

The ABS-copolymer containing 2% BP gives a much more intense signal than the one produced by the amount of BP contained in the polymer (Figure 1, curve 3). In order to obtain a better separation of the two signals, their displacement on

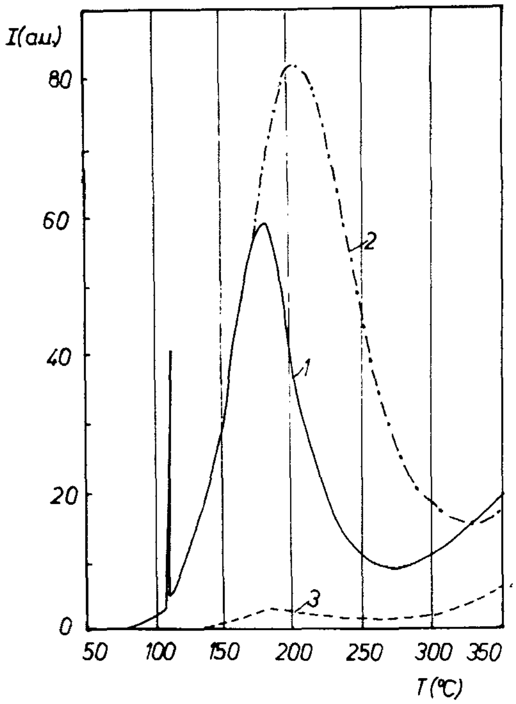
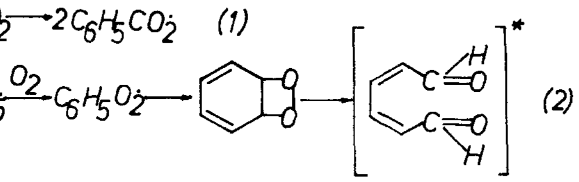


FIGURE 1 The chemiluminescence signal (intensity versus temperature) emitted by 1-di-benzoyl peroxide (-), 10 times amplified, 2-the ABS-copolymer containing 2% di-benzoyl peroxide (- · -), 3-the amount of BP contained in the polymer sample (- - -).



SCHEME II Possible mechanism for excited species formation in di-benzoyl peroxide degradation

the temperature scale with the heating rate was used. Successive runs for BP and ABS-copolymer with 2% BP at 0.2°C/s heating rate brought the separation between the two signals (Figure 2). A 30:70 mixture of ABS-copolymer:BP heated at 0.2°C/s allowed simultaneous recording of the two distinct signals, the one due to BP and the other due to BP initiated ABS-copolymer degradation. At 4°C/s a non-differentiated envelope was obtained.

The CL signal recorded with BP initiated thermo-oxidative degradation of the ABS-copolymer is identical to that found after processing and it has been attributed to the hydroperoxides of type I formed in the SAN phase of the copolymer.[4] The HP of type I appear after the creation of the azomethinic structures through a process initiated by HP of type II. Therefore, the concentration of HP of type I, as expressed by CL intensity, is an indication of the extent of the oxidative processes taking place in the polymer.

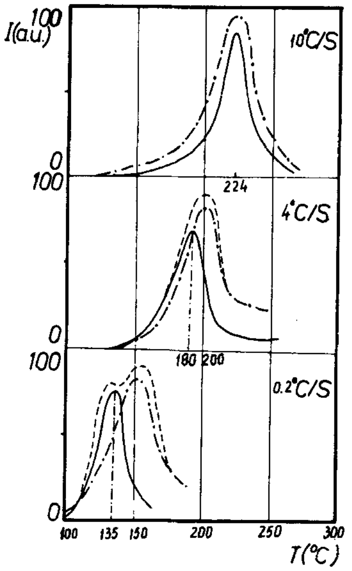


FIGURE 2 The CL signals obtained at different heating rates for: di-benzoyl peroxide (–), ABS-copolymer + 2% di-benzoyl peroxide (-··-) and a 30:70 mixture of polymer:di-benzoyl peroxide (- - -).

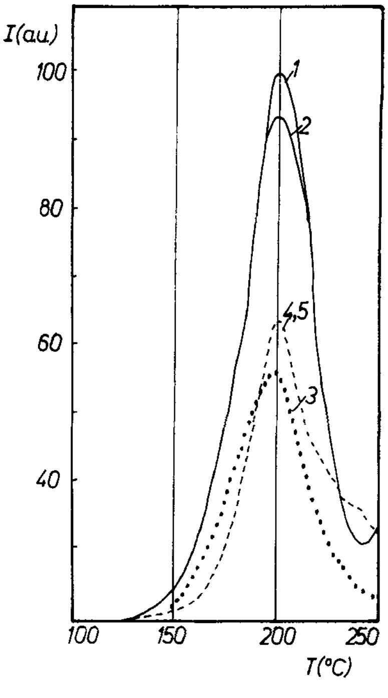


FIGURE 3 The CL signal of the di-benzoyl peroxide initiated degradation of ABS-copolymer. Curves: 1-antioxidant free, 2-Irganox 1076, 3-Irganox 565, 4-TNPP, 5-TNPP + DATDP added.

2. The ABS-copolymer oxidation in the presence of an antioxidant

Antioxidants of different classes have been used: chain terminators (Irganox 1076), hydroperoxide deactivators (DATDP and TNPP) and one of a complex type cumulating both functions (Irganox 565). Figure 3 presents the effect of these antioxidants on the CL intensity emitted during the BP initiated oxidation of the ABS-copolymer.

From the direct comparison of the CL intensity suppression in the presence of antioxidants the following observations can be formulated: Irganox 1076 is not effective in ABS-copolymer protection, nor DATDP is effective in HP nonradicular decomposition. Conversely, Irganox 565 is most effective in antioxidative protection and so is TNPP. It should be remembered that this conclusion refers to the SAN phase of the ABS-copolymer. The order of effectiveness presented in Figure 3 is confirmed by impact strength testing of the processed samples (Table I) and also by CL peak area measurement of these samples.

The Irganox 565 effectiveness is understandable in view of its multiple functions to which the protecting action of its reaction products is adding up.[6] Similar results regarding the best protection toward ABS-copolymer being exerted by Irganox 565 have been previously reported on the basis of DSC measurements.[7]

Regarding Irganox 1076, its low activity can be partly explained by the reinitiating action of its oxidated form AOO·:

$$\mathrm{ROOH} + \mathrm{AH} \rightarrow \mathrm{ROOH} + \mathrm{A\cdot} \qquad (3)$$

$$\mathrm{A\cdot} + \mathrm{O_2} \rightarrow \mathrm{AOO\cdot} \qquad (4)$$

$$\mathrm{AOO\cdot} + \mathrm{RH} \rightarrow \mathrm{AOOH} + \mathrm{R\cdot} \qquad (5)$$

$$\mathrm{R\cdot} + \mathrm{O_2} \rightarrow \mathrm{ROO\cdot} \qquad (6)$$

where AH stands for the antioxidant. The above allegation is supported by the variation of the CL intensity with increasing Irganox 1076 concentration (Figure 4). There is a decrease in CL intensity for the Irganox 1076 concentration of 0.3%, a levelling off in the 0.3–0.6% range, followed by an increase at concentrations higher than 0.6%. This trend is also illustrated by impact strength testing of oven aged (180°C) specimens (Table II). As it can be seen, the impact strength of the

TABLE I

Impact strength and CL peak area of the processed ABS-copolymer samples

Antioxidant	% Impact strength retention after 3 injection moldings	CL peak area (μC)
—	82	260
Irganox 1076	93	179
Irganox 565	100	65
TNPP	98	126
TNPP + DATDP	96	139

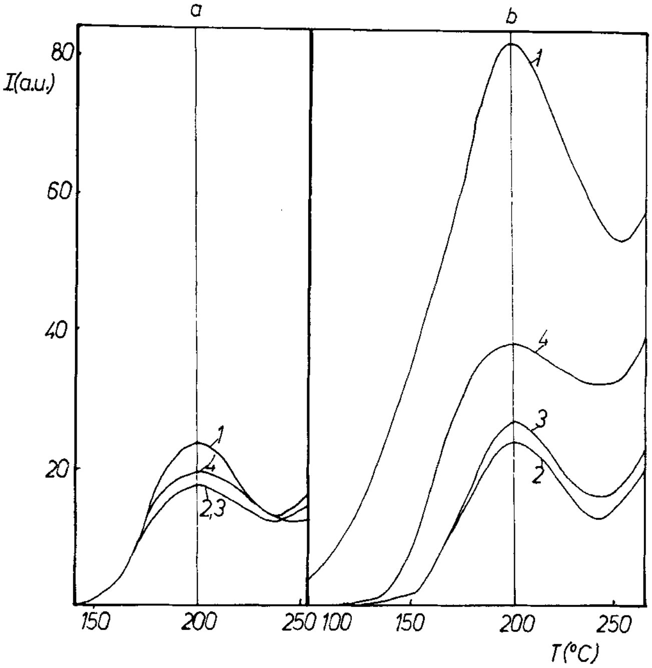


FIGURE 4 The CL signal of the ABS-copolymer: untreated control and with 2–0.3, 3–0.6, and 4–0.9% Irganox 1076. a) Unprocessed; b) Injection molded.

TABLE II

Notched Izod impact strength of 180°C oven aged ABS-copolymer containing Irganox 1076

Irganox 1076 concn. (%)	Impact strength (kJ/m^2), at aging times		
	0 min	30 min	60 min
0.3	16.4	10.7	9.8
0.6	17.2	12.5	10.5
0.7	19.5	14.4	12.7
0.9	13.3	8.0	6.7

unaged specimens (which had already underwent an injection molding) as well as that of aged specimens exhibit an increase up to 0.7% Irganox 1076 followed by a decrease for higher concentrations.

The fact that the CL signal in Figure 4 preserves its form and the peak temperature regardless of the antioxidant concentration shows that the CL intensity increase is due to an increased ROOH concentration and not to AOOH. This conclusion is based on data showing that AOOH form of BHT antioxidant emits CL.[8]

The above efficiency considerations derived on the basis of CL experiments are valid if conditions 1 and 2 in the introductory section are fulfilled. Quenching effects are judged less probable for the structures resulting from Irganox 1076, improbable for amines,[9] but more probable for nitroxyl radicals and conjugated

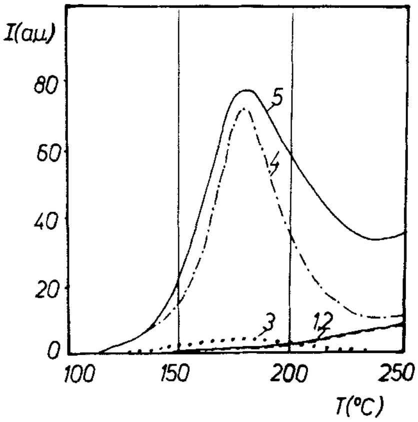


FIGURE 5 The CL signal of the 70:30 di-benzoyl peroxide:antioxidant mixtures with the following antioxidants: 1,2-Irganox 1076, 2-Irganox 565, 3-TNPP, 4-DATDP. Curve 5- pure BP in the equivalent amount.

triazine structures resulting from Irganox 565.[9] However, kinetic studies on the reaction order for the luminescence decay in the presence of these antioxidants have shown that this is not the case.[10]

As for a possible reaction between BP and antioxidants in the present conditions, considerations are presented below.

3. Chemiluminescence study of antioxidant-di-butyl peroxide reaction

1:1 (weight ratio) mixtures of BP:antioxidant were tested for CL. This ratio allowed the direct recording of the BP signal if no reaction occurred. Figure 5 shows the CL signal recorded for these mixtures. It can be seen that with the exception of DATDP, the other antioxidants totally suppress the BP signal. If one admits that HP are being formed during BP degradation, once again DATDP proves its low efficiency compared to TNPP.

It was proved above that additional luminescence from $C_6H_5CO_2\cdot$ scavenging by the antioxidant does not appear. At the same time, it is important that such scavenging do not take place in considerable extent during efficiency evaluation i.e., $^kC_6H_5CO_2\cdot + RH[RH] > {}^kC_6H_5CO_2\cdot + AH[AH]$. The corresponding rate constants were not available, but since [RH] >> [AH], $C_6H_5CO_2\cdot$ scavenging by AH could be unimportant. Resuming the experiment in Figure 3 with 0.2% BP instead of 2%, when direct scavenging is minimized, results in the same efficiency order. Instead, the lower CL intensity as a result of a less intense polymer oxidation renders the comparison more difficult.

CONCLUSIONS

The chemiluminescence emitted during ABS-copolymer oxidation in the SAN phase, initiated by a radical initiator has been used to estimate antioxidant efficiency.

Irganox 565 and trisnonylphenyl phosphite have been found to be most efficient. Irganox 1076 was found to increase the hydroperoxide content of the polymer due to the reinitiating action of its products.

The in situ oxidation of a polymer initiated by a radical initiator and conducted in the presence of an antioxidant is a quick and sensitive way of appreciating the protective efficiency, providing no interference from secondary reactions such as luminescence quenching or scavenging of the initiating radicals occur.

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