Polymer Bulletin 57, 545–552 (2006)
DOI 10.1007/s00289-006-0600-9

Polymer Bulletin

Chemiluminescence study on HALS antioxidant activity in LDPE

Silviu Jipa[1,2], **Traian Zaharescu**[2] (✉), **Radu Setnescu**[1,2], **Laura Monica Gorghiu**[1], **Crinela Dumitrescu**[1], **Călin Oros**[1]

[1]Faculty of Science, University VALACHIA Targoviste, 2 Carol Av, 0200, Romania
[2]Advanced Research Institute for Electrical Engineering, 313 Splaiul Unirii, Bucharest 030138, Romania

e-mail: traian@gw-chimie.math.unibuc.ro; fax: 0040-1-346-8299

Received: 3 August 2005 / Revised version: 4 May 2006 / Accepted: 11 May 2006

Summary

The kinetic study on thermal degradation of stabilised low density polyethylene by chemiluminescence investigations was performed. Four hindered amine light stabilisers, additive compounds, were used as thermal protector on polymer substrate. The experiments were carried out on the samples consisting of polyetylene and 0.25 % (w/w) of hindered amine. Three temperatures (180, 190 and 200^{0}C) were selected for this assay allowing the calculation of the activation energy required for thermal oxidation of polyethylene matrix. A discussion on mechanistic aspects concerning the antioxidant efficiency of studied compounds is also presented.

Introduction

The majority of polymer-made products are subjected to various energetic damaging processes, when the scission of macromolecules takes place on the first step. The thermal-oxidative action suggestively called material ageing, progresses at different rates that are influenced by polymer structure, manufacture composition and technology, item history. The presence of stabilising compounds in the material formulation on early stage confers certain increased stability that depends on the protection efficiency of additive. The real advantage of this formulation is the long-term preservation of native characteristics.

Several categories of oxidation inhibitors are available on the market, some of them being largely used in the production of plastics. The efficiency features of all antioxidative protectors are determined by the ability of compound to provide radicals, which will be coupled with the radicals formed by molecular scission. Suitable stabilisation systems modify the rate ratio that characterises the competition between oxidative degradation and inhibition of oxidation, i. e. the main simultaneous processes in which free radicals are involved. The major route followed in the oxidation of polymers, especially polyolefins, involves a radical chain mechanism [1].

Thermal energy is generally accepted as the most habitual agent that causes the depreciation of polymer performances. The decrease in the functional attributes can be delayed by means of proper compound that inhibits the reactions between new-formed radicals and molecular oxygen diffusing toward the inner layers of polymer material.
A large category of Hindered Amine Stabilisers (HAS) are produced for the thermal and photo protection of polymers [2 – 4]. They are capable to act as protectors under severe thermal conditions [5]. Moreover, these amine compounds are applied successfully in the material conditioning, due to their worthwhile potential in slowing down weathering degradation [6 – 8]. These cited papers emphasise that amine moiety in some organic compounds is susceptible to play a favourable role in the improvement of long-term stability of polymers [9]. Hindered Amine Light Stabilisers (HALSs) constitute a distinctive class of antioxidants. Under special conditions involving simultaneous action of light and heat, they present satisfactory efficiency in oxidation prevention [10, 11].

The chemiluminescence technique, based on the counting of quantum emission by the deexcitation of oxygen from triplet state, which is incorporated in carbonyl unit [12 – 15], provides relevant information on the progress on oxidation, especially in the studies on polymers [16]. The monitoring oxidation stability of a large variety of polymers provides for polyolefins a sigmoidal CL curve (emission intensity vs oxidation time), whose analysis reflects the autocatalytic development of degradation, the influence of the chemistry of material, the effects of formulation and sample history [16, 17]. On this basic availability, this paper investigates the contribution of some HALSs to the improvement in oxidation resistance of LDPE relative to control material. The kinetic parameters, oxidation induction time, oxidation rate and Arrhenius characteristics – activation energy and frequency factors – were evaluated.

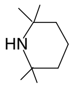
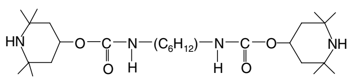
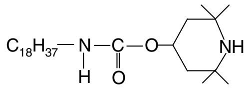
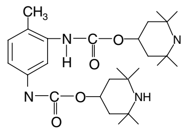
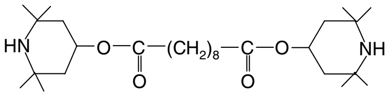
Experimental

Low density polyethylene, K 322 type (Chemical Company Brazi, Romania) was used as basic matrix. It was purified by fast precipitation and separation with methanol from hot *o*-xylene solution. After the removal of the remaining solvent by vacuum filtration, the polymer mass was dried in an oven at 30^0C for as long as the penetrant smell of *o*-xylene completely disappeared. Two compounds used as antioxidants (table 1) are commercially available products: 2,2’,6,6’-tetramethyl-piperidine (symbolised as PYP) and bis(2,2’,6,6’-tetramethyl-4-piperidyl) sebacate (TINUVIN 770, marked as HALS T). The other three stabilisers generically named HALS A, B and C.

Lau and Pan characterised them as the most active hindered piperidine derivatives of the synthetised series [18]. The additives were homogeneously incorporated into the polyethylene mass by wet grinding in the presence of small amounts of poured chloroform used as the diffusion carrier of antioxidant during preparation stage. The solvent was added drop by drop on each 5 minutes, considering that the liquid allows additive to penetrate easy into the polymer bulk. The antioxidant concentration was 0.25 % (w/w). The powder materials (control and modified low density polyethylene) were placed into an oven provided with the electronically controlled temperature device (mean error: ± 0.5^0C). The drying conditions: temperature 30^0C, which avoids the initiation of oxidation. The inside air circulation ensures continuous removal of evaporating solvent.

Aliquots consisting of differently formulated LDPE powder materials (including purified polymer) were weight as 2 mg samples on aluminum trays, which will be placed on the oven of CL device.

Table 1. Molecular structure of additives

Symbol	Molecular structure	Symbol	Molecular structure
PYP		HALS B	
HALS A		HALS C	
HALS T			

Isothermal chemiluminescence measurements were performed in air at 180, 190 and 200^{0}C in laboratory equipment Oxyluminograph OL-94. The device scheme was reported earlier [9]. The kinetic parameters determined in this paper are defined in the typical CL curve (figure 1).

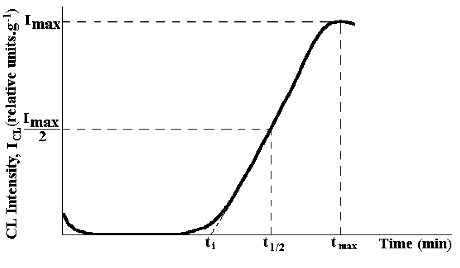


Figure 1. General shape of CL curve

Results and discussion

The excellent performance of Hindered Amine Light Stabilisers (HALSs) in various polymers is an appropriate solution for the improvement of plastics lifetime. The antioxidative activity of HALS in polyolefins is based on their capacity in the providing reactive radicals under the thermal conditions. The kinetic approach of stabilisation in which HALSs are involved has been reported by Gugumus [19].

The contribution of the studied compounds on the deceleration of thermal oxidation in low density polyethylene can be remarked in figure 2 and table 2. The main kinetic parameters that are listed in this table emphasise that the presence of substituted piperidine structure is only a primary condition for an antioxidant activity.

The shortest oxidation time is conferred by 2,2’,6,6’-tetramethyl-piperidine. This parameter for oxidising LDPE blended with PYP is only two times higher than the induction time exhibited by control. On the other hand, the other four tested compounds with similar molecular structures (HALS A, B, C and T) contribute more efficiently to the delay in the start of oxidation. The oxidation rates are also different, because the intramolecular effects would present different intensities.

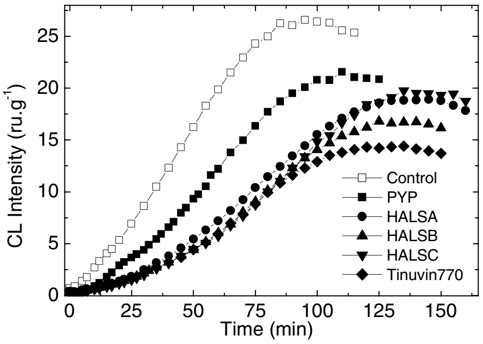


Figure 2. Isothermal chemiluminescence curves drown for LDPE samples under different stabilisation state. Testing conditions: 200^{0}C in air environment.

At the lowest selected temperature (180^{0}C), the thermal stability of low density polyethylene stabilise with HALS A, B, C and T is more than six times longer than the similar characteristic exhibited by control. Normally, the increase in the temperature of degradation causes a shortening in the induction time of thermal oxidation, but the response of stabilised polypropylene remains about four times higher than for control. As it may be predicted, the decrease in service temperature will enlarge the difference between induction time of the oxidation for control and the samples containing HALS. Except oxidation induction time, the other two temporal parameters that depict the progress in the process of degradation are less satisfactory for the protection action of PYP in LDPE, in spite of convenient $\sum_{0}^{20\,\mathrm{min}} I_{CL}$ values (last column from table 2). It can be assumed that oxidation takes place on polyethylene and additive, as well, but with different rates.

The maximum oxidation time (the fifth column from table 2) that describes the longest period on which the material integrity can be foreseen. This term has got adequate values for the processing of polyethylene at high temperatures. However, the thermal effect on stabilised polyethylene is more diminished at medium temperatures; the material viscosity is maintained at low level and the probability of bimolecular reactions between diffused O_2 and radical moieties is significantly decreased.

The antioxidant ability of the tested compounds was checked by Lau and Pan [18] on polypropylene subjected to photodegradation. It can be remarked that the experimental conditions are smoother and the additive concentration is somewhat higher than in our study.

Analysing the values of the CL intensity sum over the first twenty minutes elapsed from the start of oxidation listed in the last column of table 2, it can be noticed the enlargement in the discrepancy between the free radical amounts provided substrate during degradation in different formulated polyethylene. The lower the CL intensity sum, the higher the protection activity of antioxidant.

The values of maximum chemiluminescence intensity are presented in the sixth column of table 2). They define the maximum quantity CL photons emitted by triplet state of ketone structures formed starting from free radicals, become double as the temperature increases with 10^{0}C. It means that the lessening in degradation temperature induces a smaller number of split macromolecules with a factor of 2^n, where n denotes the number of each ten degrees intervals [20]. However, the effect of substitution in piperidine structure (HALS A, B, C and T) on the induction periods, is emphasised as molecular mass increases, when the insignificant changes occurred in material structure and properties.

Table 2. The values of main kinetic parameters obtained for thermal oxidation of LDPE for different formulations

Additive	Induction time t_i (min)	Half oxidation time $t_{1/2}$ (min)	Maximum oxidation time t_{max} (min)	Oxidation rate v_{ox} (ru.g^{1}.min^{-1})	Maximum intensity I_{max} (ur.g^{-1})	$\sum_{0}^{20\ min} I_{CL}$ (ur.g^{-1})
Testing temperature: 180^{0}C						
Control	26	112	205	289	48259	23980
PYP	50	123	235	270	57015	12969
HALS A	163	288	445	190	51500	8768
HALS B	158	258	410	260	50333	10267
HALS C	156	286	470	178	58467	8567
HALS T	158	269	420	155	38867	10700
Testing temperature: 190^{0}C						
Control	14	62	140	856	82824	80559
PYP	40	87	155	1063	99469	24479
HALS A	73	144	255	582	86667	18934
HALS B	51	76	180	648	70600	35433
HALS C	85	117	210	661	95067	25267
HALS T	55	77	145	894	81393	71127
Testing temperature: 200^{0}C						
Control	8	41	95	2533	177327	163598
PYP	17	55	110	1930	143800	70902
HALS A	24	70	145	1408	126033	45932
HALS B	30	70	125	1365	112000	39400
HALS C	35	78	135	1535	131800	37101
HALS T	30	65	135	1250	96033	39133

* $v_{ox} = \mathrm{tg}\ \alpha$

It is generally assumed that the mechanism of thermal oxidation of polyolefins is well depicted by the formation of peroxyl radicals as the intermediates that assist the chain of oxidative degradation. In this respect, it has been shown that the hydroperoxides that are generated thermally. They are formed through the abstraction of a hydrogen atom by peroxyl entity and act as an initiator of degradation process. The understanding on the stabilisation mechanism in which HALSs are involved is sustained by the general scheme presented in Figure 3, according to other previous reports [21, 22]. Carlsson et al have [23] presented similar considerations on the stabilisation action of substituted pyperidine, which act as prevention antioxidants by scavenging of mobile hydrogen. In addition, Dunn at al [24] have suggested the manner by which amines prevent oxidative degradation.

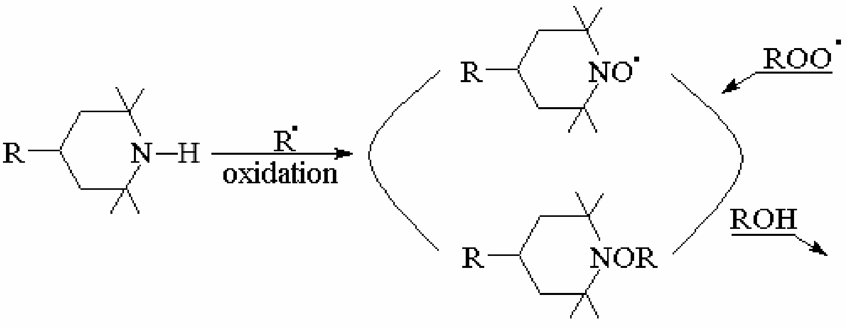


Figure 3. General scheme for the action of HALS.

The hindered tertiary amines, which are used seldom for the protection of polymers against oxidation, act as antioxidants through α-hydrogen attached to nitrogen atom [25]. The extraction of α-H by alcoxy (or peroxy) radicals represents the basic step in the antioxidative protection of macromolecular materials.

The presence of substituents brings about a certain electronic influence on the hydrogen atom belonging to amine unit. Its mobility is modified by the donor effect of substituents and diminishes the N – H bond strength and consequently, the antioxidant efficiency of oxidation protector is increased. Figure 4 illustrates the change in the initial stability of low density polyethylene modified by the addition of studied compounds. The large difference between the oxidation induction times emphasizes the importance of substitution in the activation of amine hydrogen.

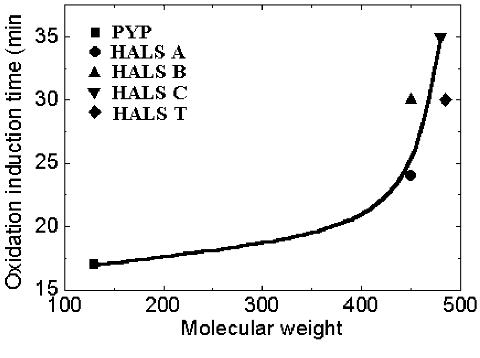


Figure 4. Dependency of oxidation induction time on the molecular weight of stabilisation additive for thermal oxidation of modified LDPE. Testing temperature: 200^{0}C.

Table 3 lists the energetic parameters that characterise the benefit brought by studied compounds on the thermal stabilisation of LDPE. If the Arrhenius evaluation of

activation energy required by the thermal oxidation of protected polyethylene is done, it is easy to remark the advantage of the substitution on piperidine molecule, which elevates the capability of additive to delay oxidation. As it was discussed earlier, 2,2',6,6'-tetramethyl-piperidine (PYP) is able to protect LDPE at moderate temperatures, where the depletion of additive is slower that the damage of macromolecules, promoting a real protection to polymer matrix. For the other four HALS compounds the values of activation energy necessary for thermal oxidation of LDPE rise of about 1.5 times in comparison with raw material.
There is a large difference between the activation energy values calculated starting from oxidation induction period and maximum oxidation time.

Table 3. Energetic conditions for thermal oxidation of stabilised LDPE

Antioxidant	Parameter	Basic data for energetic calculation	
		Oxidation induction time	Maximum oxidation time
Control	Activation energy (kJ.mol^{-1})	104.17	67.94
	ln (frequency factor)	-24.44	–12.74
	correlation factor	0.999	0.999
PYP	Activation energy (kJ.mol^{-1})	94.91	67.11
	ln (frequency factor)	-21.21	-12.39
	correlation factor	0.943	0.999
HALS A	Activation energy (kJ.mol^{-1})	169.05	99.06
	ln (frequency factor)	-39.79	-20.23
	correlation factor	0.994	0.999
HALS B	Activation energy (kJ.mol^{-1})	147.15	105.23
	ln (frequency factor)	-34.15	-22.03
	correlation factor	0.981	0.979
HALS C	Activation energy (kJ.mol^{-1})	131.86	110.43
	ln (frequency factor)	-29.95	-23.26
	correlation factor	0.993	0.988
HALS T	Activation energy (kJ.mol^{-1})	147.10	100.89
	ln (frequency factor)	-34.10	-20.94
	correlation factor	0.990	0.898

The free radicals that are consumed on different reaction ways are present in higher amount after the end of degradation term. On the other side, the energetic calculation of activation energy must take into account simultaneously the energy spent for the splitting of chemical bonds in the macromolecular backbones of polymer and the energetics of the diffusion of oxygen that feeds the inner layers of degrading material. On the start stage of oxidation, very low amount of free radicals and small quantity of molecular oxygen initially existing in polymer samples determine high values of the activation energy and smaller probability of reaction depicted by the frequency factors shown in Table 3. By the progress in thermal degradation, energetic conditions are modified confirming the advanced ageing of basic polymer.

Conclusions

The present study points our some practical features concerning the prevention of thermal oxidation in low density polyethylene stabilised with studied HALS:

- the antioxidant efficiency of piperidine based compounds is improved by substitution, which increases the lability of amine hydrogen;
- the studied HALSs promote the delay of thermal degradation even at high operation temperatures around 200^0C; the benefit of their use at low temperatures is demonstrated by the convenient kinetic parameters determined at 180^0C;
- the activation energy required on the earlier stage of oxidation is significantly higher than the energy asked by damaging unmodified low density polyethylene;
- low concentration of additive (0.25 % w/w) ensures an increase in oxidation induction time of about 5.7 times at 180^0C, 3.9 times at 190^0C and 3.7 times at 200^0C, while the rates of oxidation decrease significantly due to the presence of substituted piperidine compounds;
- chemiluminescence method is able to provide reliable information on thermal stability of polymers under various formulations.

References

1. Popa L, Giurginca M, Zaharescu T (2004) Mater. Chem. Phys. 86:11
2. Schwetlik K, Habicher WD (2002) Polym. Degrad. Stabil. 78:75
3. Gijsman P. Gitton-Chevalier M (2003) Polym Degrad. Stabil. 81:483
4. Zaharescu T, Kaci M, Herbal G, Setnescu R, Setnescu T, Khima R, Remili C, Jipa S (2004) Macromol. Mater. Eng. 289:524
5. Smoliak LYu, Prokopchuk NR (2003) Polym Degrad. Stabil. 82:169
6. Kaci M, Sadoun T, Mussaceb K, Akroune N (2001) J. Appl. Polym. Sci. 82:3284
7. Hassaini N, Guenachi K, Hamou A, Saiter JM, Marais S, Beucher E (2002) Polym Degrad. Stab. 75247
8. Molom X, Cañavate J, Suñol JJ, Pagès P, Saurina J, Carrasco F (2003) J. Appl. Polym. Sci. 87:1685
9. Jipa S, Zaharescu T, Setnescu R, Setnescu T, Brites MJS, Silva AMG, Marcelo-Curto AJ, Gigante B(1999) Polym. Int. 48:414
10. Pospíšil J, Nešpůrek S (1995) Polym. Degrad. Stabil. 4999
11. Real LP, Pereira Rocha A, Gardette JL (2003) Polym. Degrad. Stabil. 82:235
12. Russell GA (1957) J. Amer. Chem. Soc. 79:3871
13. Kellogg R (1969) J. Amer. Chem. Soc. 91:5433
14. Kohler DR, Krohnke C (1998) Polym. Degrad. Stabil. 62:385
15. Pospíšil J, Horák Z, Pilař J, Billingham NC, Zweifel H, Neśpůrek S (2003) Polym. Degrad. Stabil. 82:145
16. Tiemblo P, Gómez-Elvira JM, Navarro O, Matisová-Rychlá L, Rychlý J (2001) Polym. Degrad. Stabil. 72:23
17. Matisová-Rychlá L, Rychlý J, Slovák K (2003) Polym. Degrad. Stabil 82:173
18. Lan WWY, Pau JQ (1998) Polym. Degrad. Stabil. 60:459
19. Gugumus G (1990) Angew. Makromol. Chem. 176/177:241
20. Wenkert E, Fuchs A, McChesney JD (1965) J. Org. Chem. 30:2931
21. Shilov, YB, Debnisov YT (1974) Vysokomol. Soedin. A16:2316
22. Sealar Y, in A. Patsis (ed), "Advances in the Stabilization and Controlled Degradation in Polymers", Technomie Publ. Co., Basel, 1989, vol. I, p. 227
23. Bauer RF, Carlsson DJ, Chmela S, Cooke J.M (1988) Polym. Degrad. Stabil. 24:1651
24. Dunn TS, Williams EE, Williams JL (1982) J. Polym. Sci., Polym. Ed. 20:1599
25. Kurumada T, Ahsawa H, Oda O, Fujita T, Toda T, Yoshioka T (1985) J. Polym. Sci., Polym. Chem. Ed. 23:1477