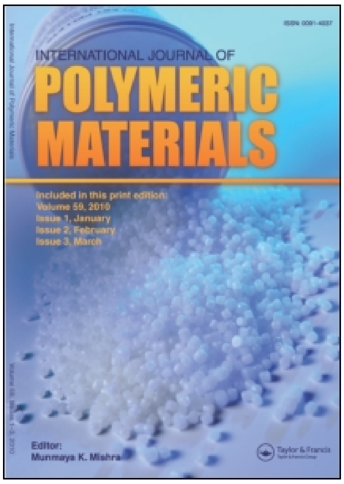

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L. Matisová-Rychlá[a]; J. Rychlý[a]; Z. Fodor[b]; K. Barabas[b]; M. Iring[b]; F. Tüdös[b]
[a] Polymer Institute, Centre of Chemical Research, Slovak Academy of Sciences, Bratislava, Czechoslovakia [b] Central Research Institute for Chemisty, Hungarian Academy of Sciences, Budapest, Hungary

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Thermo-Oxidation of Polyethylene Stabilized with Irganox 1010 and Tinuvin 622

L. MATISOVÁ-RYCHLÁ and J. RYCHLÝ

Polymer Institute, Centre of Chemical Research, Slovak Academy of Sciences, 842 36 Bratislava, Czechoslovakia

Z. FODOR, K. BARABAS, M. IRING and F. TÜDÖS

Central Research Institute for Chemisty, Hungarian Academy of Sciences, H-1025 Budapest, Hungary

Thermal oxidation of polyethylene stabilized with the mixture of Irganox 1010 and sterically hindered amine Tinuvin 622 confirmed that the occurrence of synergism or antagonism in the effect of sterically hindered amines towards antioxidants is concentration dependent. Provided that the concentration of phenolic antioxidant Irganox 1010 in polytheylene exceeds that of Tinuvin 622, synergism is observed at 185 and 190°C. Chemiluminescence, oxygen absorption method, nonisothermal differential scanning calorimetry (DSC) and differential thermal analysis (DTA) were used for testing of stabilizing efficiency of mixtures of stabilizers and the mutual correspondence of the results have been pointed out.

KEYWORDS: Irganox 1010, tinuvin 622, polyethylene, chemiluminescence, oxygen absorption

INTRODUCTION

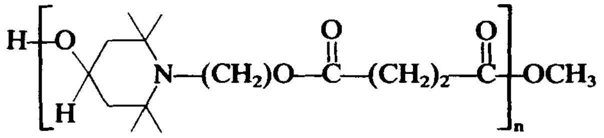
Considerably less attention paid to the effect of hindered amine light stabilizers (HALS) on the thermal oxidation of polyolefins hitherto is due to a lower antioxidative efficiency of HALSes when compared with commonly used phenolic antioxidants such as Irganox 1010, Irganox 1035, etc., the results of antioxidative tests with HALSes being sometimes contradictory.[1] The systems composed of HALS and phenolic antioxidant, where the antioxidative effect of the latter may be modified to a different extent of HALS are, however, interesting from the practical viewpoint of polymer processing. Both, the antagonism and synergism between HALS and phenol were referred to at different occasions without finding some more general rule governing it and without the correspondance to the behaviour of the same system in photo-oxidation tests. It appears that nitroxyl radicals related to a parent amine act as weak antioxidants; in the mixture with phenol, they may induce the disproportionation of phenoxyl radicals and increased concentration of quinone structures may be formed in the system. Within the classical concept of synergism the parent HALS may be also functioning as a reservoir of hydrogen atoms for phenoxyl radicals and thus prolong their lifetime in the polymer but some other effects are possible as well.

In the present paper we have studied the antioxidative efficiency of stabilizing mixtures composed of different concentrations of phenolic antioxidant Irganox 1010 with Tinuvin 622 which is tertiary amine and its effect as a source of hydrgen atoms for phenoxyl radicals is less probable. The experiments were carried out with polyethylene at 185 and 190°C and the results were compared with thermal analysis tests.

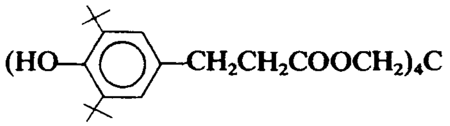
EXPERIMENTAL

Chemicals

The structures of Tinuvin 622 and Irganox 1010 were:



Tinuvin 622 (Ciba Geigy)



Irganox 1010 (Ciba Geigy)

Polyethylene was Marlex TR 125 (LDPE) produced by Phillips Co. with following specification: density 0.934 g/cm^3, $\bar{M}_n = 16500$, $\bar{M}_w/\bar{M}_n = 14$, 1-hexene comonomer content was 6.5/1000 C atoms, vinyl group content 0.52/1000 C atoms. The stabilizers were mixed with polyethylene in the Rheomix 600 mixing chamber of Haake Rheocord at 180°C at 50 rpm for 15 minutes under nitrogen and cold pressed in the Fontijne press.

The concentrations additives in polymers were expressed in miliequivalents/kg of polymer.

1 miliequivalent = molecular weight/$n \times 10^{-3}$ g, where $n = 4$ for Irganox 1010 and $n = 1$ for Tinuvin 622.

Methods

The chemiluminescence measurements were performed on PU SNK 7M spectrometer (made in the USSR) having an analogous output. The photomultipler FEU 38 (the cathode Sb, Na, K, Cs with a maximum spectral sensitivity at 460 nm) worked at the voltage 1400 V. The intensity of chemiluminescence was expressed in relative units, 1 relative unit corresponding to the current 10^{-13} A at the resistence of the circuit 10^{11} ohm. The experiments were carried out with 100 mg samples at 190°C; the permanent flow of oxygen (4 dm^3/h) was introduced above the polymer melt. For more detailed description of the method see papers 2, 3 and 4.

Oxygen absorption tests were performed on films of polymer of 20–30 μm thickness in pure oxygen of 100 kPa at 185°C.

DSC measurements were carried out on DSC 2M apparatus (USSR production) under the conditions of a programmed heating (8 K/min); for the estimation of stabilizers efficiency, the temperature T_{OX} of the onset of oxidation exotherm was used. The initial weight of sample was 4 mg, the samples were gastightly closed in aluminium pans in the air atmosphere.

DTA measurements were carried out on Derivatograph Q 1500 D (made in Hungary) under the conditions of linear programmed heating (10 K/min); air was introduced into a platinum reaction pan of the profile  (upper diameter 10 mm, lower diameter 8 mm, the height 12 mm) in the flow rate 6 dm^3/h. The initial weight of sample was 50 mg.

RESULTS

Chemiluminescence—time records for polyethylene with additives demonstrate that HALS stabilizer Tinuvin 622 alone has only slight effect on thermal oxidation of polyethylene performed at 190°C in oxygen atmosphere (Figure 1). At the same time the effect of Irganox 1010 is quite distinct. The subsequent decrease of the light emission after the maximum may be due to the formation of coloured oxidation products and their filtration and absorption effect or alternatively, to the decrease of concentration of fresh oxidizable polymer in the surface layer.

From the values of induction periods of thermal oxidation of polyethylene at 190°C may be seen (Table I), that the effect of Tinuvin 622 in its mixture with Irganox 1010 is rather complex. The additional 5 miliequivalents of Tinuvin 622 e.g. to the sample (10; 5) lead to the increase of induction period by more than 15 minutes, while sample (0; 5) with only Tinuvin yields 6 minutes. At concentrations of phenolic antioxidant exceeding that of Tinuvin 622, synergistic effect of Tinuvin 622 on thermal oxidation seems to be pronounced. At the lower concentration ratii, the antioxidative efficiency of Irganox 1010 is gradually depressed. This may be e.g. demonstrated on samples (5; 0) and (5; 10), where the decrease of induction period of oxidation by 10 miliequivalents of Tinuvin 622 is quite distinct. (The first value in the brackets denote always the concentration of Irganox 1010 in miliequivalents/kg of polymer.)

The similar tendency may be also seen on induction periods of thermal oxidation determined by oxygen absorption method at 185°C in co-operating laboratory of Hungarian Academy of Sciences. (Table I). Here again, 20 minutes for the system (0; 5) and 218 minutes for the system (5; 0) are transformed into 316 minutes for the system (5; 5). The expected value is the simple sum, i.e. 238

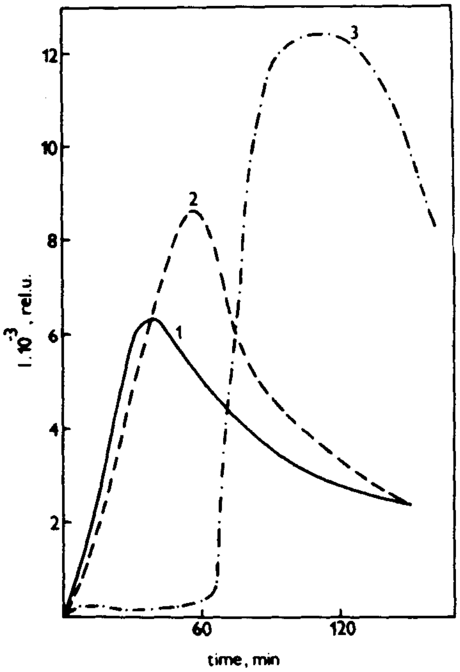


FIGURE 1 Chemiluminescence intensity vs. time records for polyethylene stabilized with 2—Tinuvin 622—5 miliequivalents/kg of polymer 3—Irganox 1010—5 miliequivalents/kg of polymer Curve 1 is a reference line of the pure polymer, temperature 190°C, oxygen atmosphere.

TABLE I

Induction periods τ_{190} and τ_{185} for oxidation of polyethylene stabilized with Irganox 1010 and Tinuvin 622 as determined by chemiluminescence measurements at 190°C, by oxygen absorption method at 185°C, temperatures T_{OX} of the onset of oxidation exotherm (DSC) and $\bar{T}_{OX}$ determined from DTA.

Concentration of Irganox 1010 (miliequivalents/kg)	Tinuvin 622	$^{m)}\tau_{190}$ min	τ_{185} min	$^{n)}T_{OX}$ K	$\bar{T}_{OX}$ K
0	0	4.7	3.5	454.0 ± 7.0	—
0	5	6	20	465.8 ± 4.0	480.9
5	0	72	218	515.5 ± 0.5	523.2
5	5	120	316	516.5 ± 0.5	—
2.5	2.5	27.5	138	503.0 ± 0.5	521.2
7.5	2.5	153	488	518.0 ± 0.5	528.8
2.5	7.5	29	194	500.5 ± 0.5	510.6
7.5	7.5	95	543	518.7 ± 1.6	525.7
10	0	148	385	526.8 ± 0.2	533.5
0	10	6	26	458.5 ± 1.5	—
10	5	200	674	525.0 ± 0.5	530.4
5	10	58	392	516.2 ± 0.2	525.1
10	10	217	720	524.6 ± 2.2	

[m)] Average value of 2 parallel runs.

[n)] Average value of 3 parallel runs.

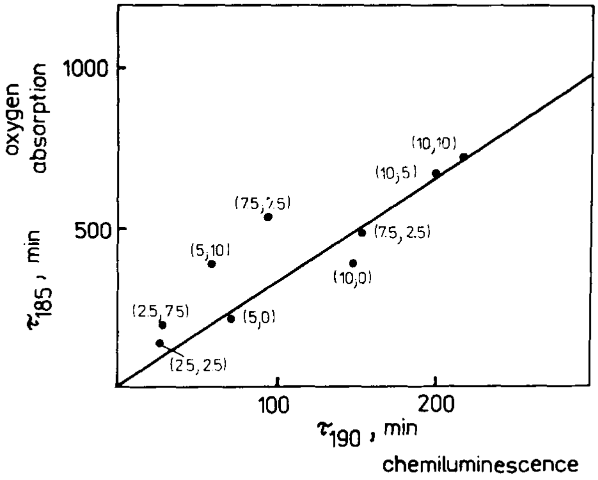


FIGURE 2 Correlation between induction periods of oxygen absorption test at 185°C and chemiluminescence test at 190°C.

minutes. This synergism is even more pronounced in the system (10; 10) where 720 minutes of induction period may be compared with 385 minutes of (10; 0) and 26 minutes of (0; 10) systems. Induction periods from oxygen absorption method correlate relatively well with those determined by chemiluminescence method at 190°C (Figure 2).

The slope of the correlation line is however 3.25 which corresponds to nonrealistic activation energy about 420 kJ/mol. This may be explained by the fact that induction periods determined by oxygen absorption express the time of reaching maximum chemiluminescence intensity. The tests with a dynamic flow of oxidizing gas, moreover, yield lower ratings than those with static atmosphere (absorption of oxygen).

The above values of induction periods of thermal oxidation of polyethylene were optimized by the use of Eq. (1)

$$\tau = a_1 c_A + a_2 c_B + a_3 c_A \sqrt{c_A c_B} + a_4 c_B \sqrt{c_A c_B} + \tau_0 \qquad (1)$$

which is the most simple way how to express addition, synergistic and antagonistic effects of both additives in parameters a_1, a_2, a_3, and a_4 (indices 1, 3 and A are related to Irganox 1010, 2, 4 and B to Tinuvin 622 (τ_0 is the induction period of oxidation of pure polymer).

The determined values of $a_1 = 14.1$, $a_2 = -0.09$, $a_3 = 1.32$ and $a_4 = -0.81$ indicate what was already illustrated on Figure 1, namely that Tinuvin 622 alone has hardly any antioxidative effect ($a_2 = -0.09$) when compared with Irganox 1010 ($a_1 = 14.1$). Irganox 1010 is synergistic with an equimolar mixture of both stabilizers ($a_3 = 1.32$) while Tinuvin 622 is antagonistic ($a_4 = -0.81$).

The values for oxygen absorption method at 185°C are as follows: $a_1 = 40.9$, $a_2 = 3.67$, $a_3 = 3.22$ and $a_4 = -0.11$. Here the ratio of the effect of pure Irganox 1010 involved in a_1 and of its synergistic term a_3 remains practically the same as observed at 190°C. The relative extent of antagonistic effect becomes however

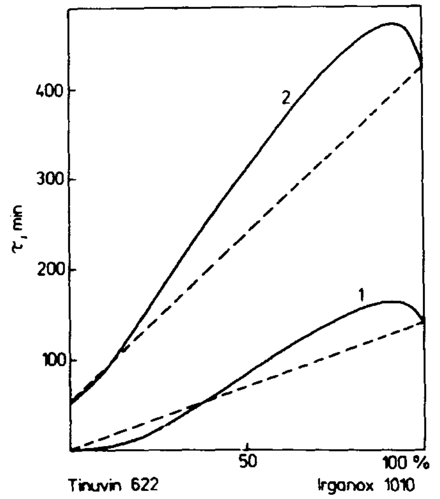


FIGURE 3 Theoretical dependence of induction periods of oxidation of polyethylene at 190°C (line 1) for chemiluminescence method and at 185°C (line 2) for oxygen absorption method on the ratio (in %) of Irganox 1010/Tinuvin 622 (the overall amount of additives—10 miliequivalents/kg of polymer). The Dashed lines imply the additivity behaviour.

less distinct at lower temperature. This may be also seen on theoretical curves constructed from known values of parameters a_i of Eq. (1) for overall amount of 10 miliequivalents of additives in 1 kg of polymer. (Figure 3)

The correspondence of results obtained by two different methods—by chemiluminescence and by oxygen absorption may be further supported by nonisothermal DSC and DTA tests as evidenced on the Figure 4 where induction periods determined by chemiluminescence are plotted against the initial temperature T_{OX} of the heat rate rise.

The curve where different concentrations of antioxidants in polyethylene fall

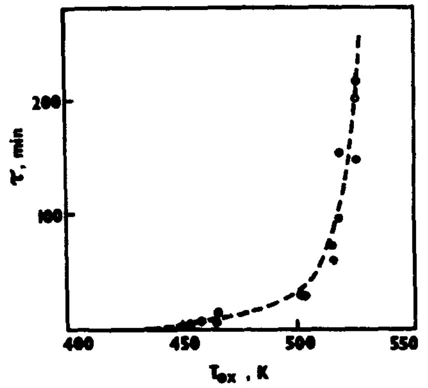


FIGURE 4 The plot of induction periods of thermal oxidation of stabilized polyethylene determined by chemiluminescence at 190°C and the temperatures T_{OX} of the onset of oxidation determined by DSC for stabilization system of Irganox 1010 and Tinuvin 622.

apparently into one line (data from the Table I) may be converted into Arrhenius' coordinates following the equation

$$\tau = Ae^{-E/RT_{ox}} \quad [\text{min}] \tag{2}$$

Parameters A and E determined in such a way are: $\ln A = 28$ and $E = 101$ kJ/mol; coorelation coefficient r is -0.9659. This is an indiction that the oxidation of the pure polymer is a decisive process in the consumption of antioxidant. (The value of E for oxidation of low density polytheylene determined by nonisothermal and isothermal DTA is 113 kJ/mol.[5]).

As it was already referred to earlier, for a certain initial concentration, the good antioxidants in a polymer give a considerably higher values of activation energy of polymer oxidation[5] when compared with a pure polymer. These values may be thus interpreted as a perturbation of the oxidation course by an antioxidant, which leads to the shift of a minimum value of the least squares sum corresponding to the optimum fit of experimental results along the long and narrow valley of $\ln A$ and E coordinates[6] (compensation effect). The relation 2 provides a rapid and direct means for the evaluation of induction periods for polymers with additives from faster DSC tests. The induction periods are playing here the role of the relative rate constants at the temperatures of the observable onset of oxidation. This is also a reason why oxidation exotherms of well inhibited samples are much sharper and better distinguished when compared with unstabilized polymer (Figure 5).

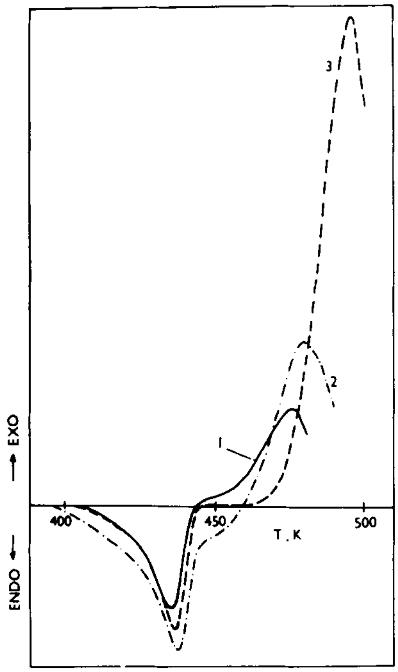


FIGURE 5 Nonisothermal DSC records for polypropylene (1), +5 miliequivalents/kg Tinuvin 622 (2), +5 miliequivalents/kg Irganox 1010 (atmosphere of air, the rate of heating 8 K/min).

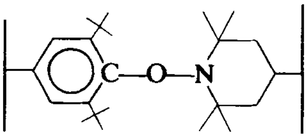
The good estimation of antioxidative efficiency of a stabilizing system may be received also from the exotherm of DTA line determined by Derivatograph. When compared with DSC nonisothermal tests, the obtained value of the temperatures $\bar{T}_{OX}$ of the start of oxidation exotherm is shifted to higher values. This is due to a higher initial loadings of the polymer; the values of $\bar{T}_{OX}$ correlate well with those received in DSC test (Table I).

DISCUSSION

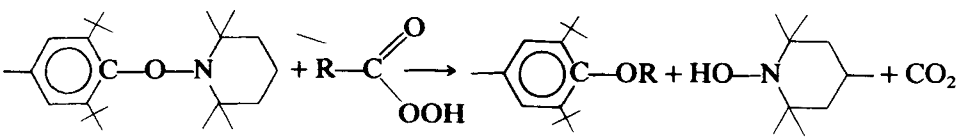
Synergism of tertiary amine Tinuvin 622 with Irganox 1010 at the excess of the latter in polyethylene cannot be understood as a simple process. Although Tinuvin 622 may be in the course of oxidation reaction gradually converted to secondary amine, there is no marked difference between its effect and the effect of secondary amine Dastib 845 on Irganox 1010 in thermooxidation of polyethylene at 190°C. For the mixture (7.5; 2.5) of Irganox 1010 and Dastib 845, the induction period 174 minutes was determined compared to 153 minutes for the analogous system of Irganox 1010 and Tinuvin 622.[7] Oxygen absorption test gives at 185°C for the same system of Irganox 1010 and Dastib 845 the values of induction periods even lower (322 minutes) than for corresponding system with Tinuvin 622 (488 minutes). Hydrogen donating mechanism does not seem to be very likely in the explanation of synergism.

Klemchuk[8] recently suggested an idea that HALSes are involved in both major mechanisms which operate in polyolefins oxidation, namely in hydroperoxides and aldehyde formation route. He emphasized their potential effect on oxidation particularly in the latter stage.

From this viewpoint we may express the synergistic effect of Tinuvin 622 on Irganox 1010 as follows. Firstly, it is an inhibition of hydroperoxides formation by Irganox 1010 itself, while in the second step, when Irganox was already consumed, the products of its interaction with Tinuvin come into a play and slow down the oxidation of aldehydes occurring via peracids to carboxyls. It may be presumed that the efficient structure of the product of phenol and HALS involves C—O—N bonds which are commonly accepted as being responsible for the regeneration of nitoroxyls in photo-oxidation of polyolefins.



This structure is able to react with peracids so that



and inhibiting particles are regenerated.

In the excess of Tinuvin 622, the primary inhibition effect of Irganox 1010 is eliminated due to its reaction with HALS and the stabilization occurs only as a consequence of peroxy acids elimination. As a matter of fact, the antagonism may result.

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