

Kinetic Approach on Stabilization of LDPE in the Presence of Carnosic Acid and Related Compounds. I. Thermal Investigation

S. Jipa,^{1,2} T. Zaharescu,¹ R. Setnescu,^{1,2} L. M. Gorghiu,² C. Dumitrescu,² C. Santos,³ A. M. Silva,³ B. Gigante³

¹Advanced Research Institute for Electrical Engineering, 313 Splaiul Unirii, P. O. Box 87, Romania 74204

²"Valachia" University, Faculty of Sciences, 2 Carol I Av, Targoviste, Romania 0200

³INETI, DTIQ, Estrada do Paço do Lumiar, 1649-038 Lisbon, Portugal

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ABSTRACT: Carnosic acid and similar compounds exhibit antioxidant behavior in a polyethylene matrix. Thermal resistance of LDPE was investigated at three temperatures (190, 200, and 210°C) by isothermal chemiluminescence. The main kinetic parameters: oxidation induction period (t_i), half oxidation time ($t_{1/2}$), maximum oxidation time (t_{max}), and propagation rate of oxidation (v_{ox}^{max}) were calculated. The inhibition of thermal degradation is proved by the values of these parameters relative to unstabilized polymer: the induction times of stabilized low density polyethylene are of one order of magnitude greater than raw polyethylene, and half oxidation periods are three to five times longer than initial LDPE. Thermal aging of protected low density polyethylene occurs at a much slower rate in comparison with

unmodified LDPE. The depletion of stabilizers was also evaluated and the kinetic characteristics (the half-life and the rate constant of consumption for each antioxidant) at three concentrations of all tested additives (0.125, 0.25, 0.50, and 0.75% w/w) were determined. The effectiveness of stabilization was depicted by two values of activation energies calculated from oxidation induction times and maximum oxidation periods. Some considerations on stabilizing mechanism are presented. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1571–1577, 2005

Key words: thermal degradation; carnosic acid; low density polyethylene; chemiluminescence

INTRODUCTION

Thermal stability of polymer products is of great importance either for manufacturers of polymers or for users. Stabilization of polymers is an intensively studied subject because the durability of any material depends on its ability to delay degradation. Various causes lead to more or less fast oxidation: the molecular structure, which includes weaker bonds, the intense transfer of energy onto polymer, or the manner of operation. In most cases, macromolecular materials need protection to improve the oxidation resistance. On the market there are available several classes of antioxidants, the most well known being sterically hindered phenols and amines. There have been many investigations concerning the efficiency of commercial antioxidants.^{1–4} Nonconventional compounds exhibiting the features of stabilizers like triazines,⁵ rosin derivatives,^{6,7} calixarenes,^{8,9} fullerenes,^{10,11} and selenium¹² have been also studied; proper conditions and

mechanisms of stabilization have been proposed. Recently the effect of natural compounds and vitamins acting as antioxidants^{13–15} by the increase in polymer life-time has been preferentially investigated because they are well tolerated by the human body.

The present trend to inclusion of natural products or similar compounds in the formulation of pharmaceutical packaging requires detailed studies on a polymer's capacity to retard premature, or to slow down efficiently, oxidative aging. Carnosic acid is one natural stabilizers that can be easily obtained from rosemary. The abundance of its source (medicinal herb) and the favorable biological effects simultaneous with antioxidant activity stimulate the use of carnosic acid and its derivatives as thermal stabilizers in a polymer.

The addition of any new stabilizing compound to polymers must respect the requirements of ecology and industrial toxicology. Materials containing antioxidants have to be safely in contact with the packaged products and not hazardous for people's health. Carnosic acid and related compounds obey the rules of public health regulations by their curative properties.^{16,17}

This paper is an attempt to prove the stabilizing potential of carnosic acid and structurally related com-

Correspondence to: T. Zaharescu (zaharescut@gw-chimie.math.unibuc.ro).

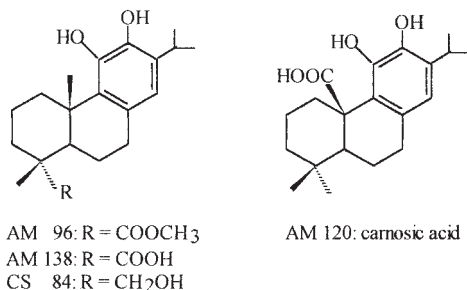


Figure 1 Molecular structures of studied compounds.

pounds¹⁸ in the thermal stabilization of low density polyethylene by a kinetic approach using chemiluminescence information. The next step of this series will be an investigation on the radiochemical behavior of polyethylene stabilized with these oxidation inhibitors to offer proof of activity in polymer usage under difficult conditions.

EXPERIMENTAL PROCEDURES

Materials

LDPE (K322[®], Brazi Chemical Company, Romania) was used as the polymer support. Some material characteristics are density 0.920, crystallinity 45.5%, number of CH₃ per 100 carbon atoms 3.1. Raw polymer was purified by dissolution in hot *o*-xylene followed by fast precipitation of polyethylene from hot solution by pouring in cool methanol. After complete cooling of the system, supernatant was removed by filtration. This solid was allowed to dry during gentle heating (30°C) in an air-circulating oven, obtaining a coalescent powder. This powder was rinsed many times with acetone and dried at room temperature.

Additives

The molecular structures of stabilizing compounds are presented in Figure 1. These compounds were obtained by solvent extraction (carnosic acid, marked as AM 120) or by synthesis (compounds CS 84, AM 96, and AM 138).¹⁸

Sample preparation

The addition of stabilizer to polyethylene powder was carried out in a mortar by dropwise pouring a low concentration of additive solution in chloroform under vigorous grinding. Finally, LDPE powder samples, containing 0.125, 0.25, 0.50 or 0.75% w/w of each additive, were prepared. The compounded materials, consisting of polyethylene and stabilizer, were dried in a desiccator at room temperature for 24 h. Aliquots

of 25 mg were placed on an aluminum tray before measurements.

Measurements

Chemiluminescence investigations were performed on an OL-94 unit built in our laboratory.¹⁹ Because of the high thermal stability of the organic support, isothermal determinations were carried out at elevated temperatures (190, 200, and 210°C). The oxidation environment for thermal degradation in CL equipment was a continuous air stream.

RESULTS AND DISCUSSION

Stabilization efficiency

The protective action of studied antioxidants against thermal oxidation is effective during the first two steps of oxidation: induction and propagation, until the rate of RO₂· depletion exceeds its formation rate. If in the induction period the stabilization efficiency reaches maximum and the chemiluminescence signals are closed to background, during the propagation stage of thermal degradation the depletion of additives leads to a sigmoidal dependence of CL intensity with time. In Figure 2 several chemiluminograms are presented. Figure 2(a) proves that the oxidation process is effectively retarded due to the presence of carnosic acid (AM 120) and to the other three diphenol compounds (CS 84, AM 96, and AM 138). For comparison, Figure 2(b) presents chemiluminograms obtained on LDPE containing known commercial antioxidants usually added to polymers during manufacture for minimal protection. It may be noted that the investigation temperature (200°C) is high enough to be close to real thermal conditions under which low density polyethylene is industrially processed.²⁰

The most important parameter, oxidation induction time, has satisfactory values as may be noticed from Figure 3(a). The samples containing carnosic acid are 12.8 times more stable than purified polyethylene at 190°C, while the oxidation induction times measured at 200 and 210°C exceed the similar parameter of raw LDPE sixfold. It means that the scavenging action of AM 120 molecules is very efficient due to pseudohindered hydroxyl groups. At higher temperatures this effect is weakened because of the lower screening ability at higher kinetic energies of reactive entities. The other three compounds, the synthetic diphenols, show induction periods one order of magnitude higher than the initial low density polyethylene at 190°C, and 6 to 10 times longer than the periods obtained at 200 and 210°C.

The half oxidation time, describing the moment when the formation rate of peroxy radicals equals the rate of their depletion, presents superior values in

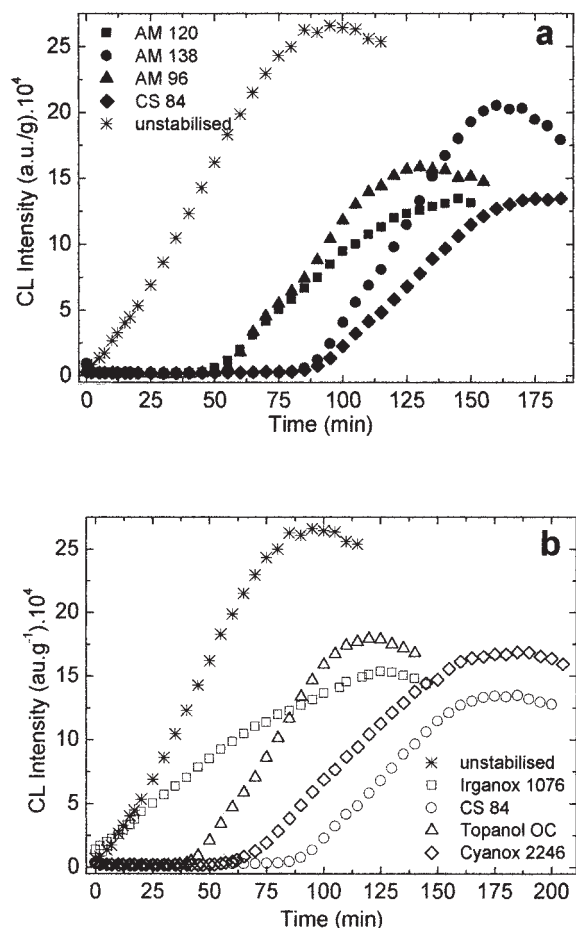


Figure 2 Chemiluminescence dependencies recorded for various stabilized LDPE. Concentration: 0.25% (w/w). Temperature: 200°C.

comparison with the similar parameter for unadded low density polyethylene [Fig. 3(b)]. Analogous behavior can be observed for maximum oxidation time [Fig. 3(c)], when all the degradable sites (weaker bonds) reacted with oxygen during thermal aging in the CL oven. Figure 3(d) demonstrates the tendency of carnosic acid and studied biphenols to slow down the oxidation, proving their capacity for scavenging free radicals. Other kinetic features, namely maximum CL intensity and the integrated CL signal for the first 20 min of oxidation, demonstrate these same characteristics, that all diphenol compounds tested in this paper improve the thermal resistance of LDPE in the following order:

$$\text{AM 138} \geq \text{CS 84} > \text{AM 96} =$$

$$\text{AM 120} \gg \text{un stabilised LDPE}$$

As can be seen from Figure 2(b), these compounds induce a similar effect on the thermal stabilization of LDPE.²¹ It would be expected that other related polyolefins (polypropylene, ethylene-propylene elas-

tomers) would have similar protective action with the studied diphenols. It means that these compounds would be more suitable for thermal protection of engineering polymer materials than some hindered phenols, because they do not form toxic quinones.

The structural analogy of carnosic acid and related diphenols with hindered phenols that play the role of oxidation retardants during thermal degradation and the cascade mechanism of the oxidation of carnosic acid²² suggest the formation of quinone configurations during thermal degradation of polymer substrate (Fig. 4). The hydroxyl units placed in the positions 11 and 12 are quasiequivalent. The hydroxyl group from site 11 is closer to the carboxyl function on C10, being influenced by it due to an electrophilic effect. It means that the proton from this hydroxyl group is somewhat more mobile than the proton from the hydroxyl group of site 12. However, this α position, relative to C13, is protected by the isopropyl substituent, which hinders the rejection of an added hydrocarbon radical, R, scavenged during degradation. On the other hand, the vicinity of the two hydroxyl groups causes easier removal of the proton from one of these functions. An additional slight effect that leads to the significant antioxidant activity of carnosic acid and related biphenols is brought about by the two methyl groups on C4, substituents that tend to decrease the electron density on this site.

According to the mechanism proposed by Wenkert et al.,²² this class of compounds may form other intermediates such as carnosol and rosmarol. They can also act as oxidation inhibitors due to the new molecular configurations.

Effect of additive concentration

Thermal stability of any polymer may be conferred by a stabilizer at a proper concentration. The increasing concentration of additive promotes significant resistance to the oxygen attack. Figures 5 and 6 present the influence of additive concentration of the most efficient diphenols on the progress of degradation.

Despite a higher temperature (210°C), low density polyethylene containing 0.125% CS 84 is 1.5 times more resistant than un stabilised LDPE at 190°C based on the values of oxidation induction times. With the greatest amount of the same additive (0.75%), oxidation induction time at 210°C is more than three times longer than the similar parameter measured at 190°C and 15 times more than the induction obtained at 210°C for purified polyethylene. A similar comparison can be made for low density polyethylene stabilized with various concentrations of AM 138. Concerning the effect of increasing concentration on the values of oxidation induction times of LDPE, as the AM 138 concentration rises from 0.125 to 0.75%, oxidation

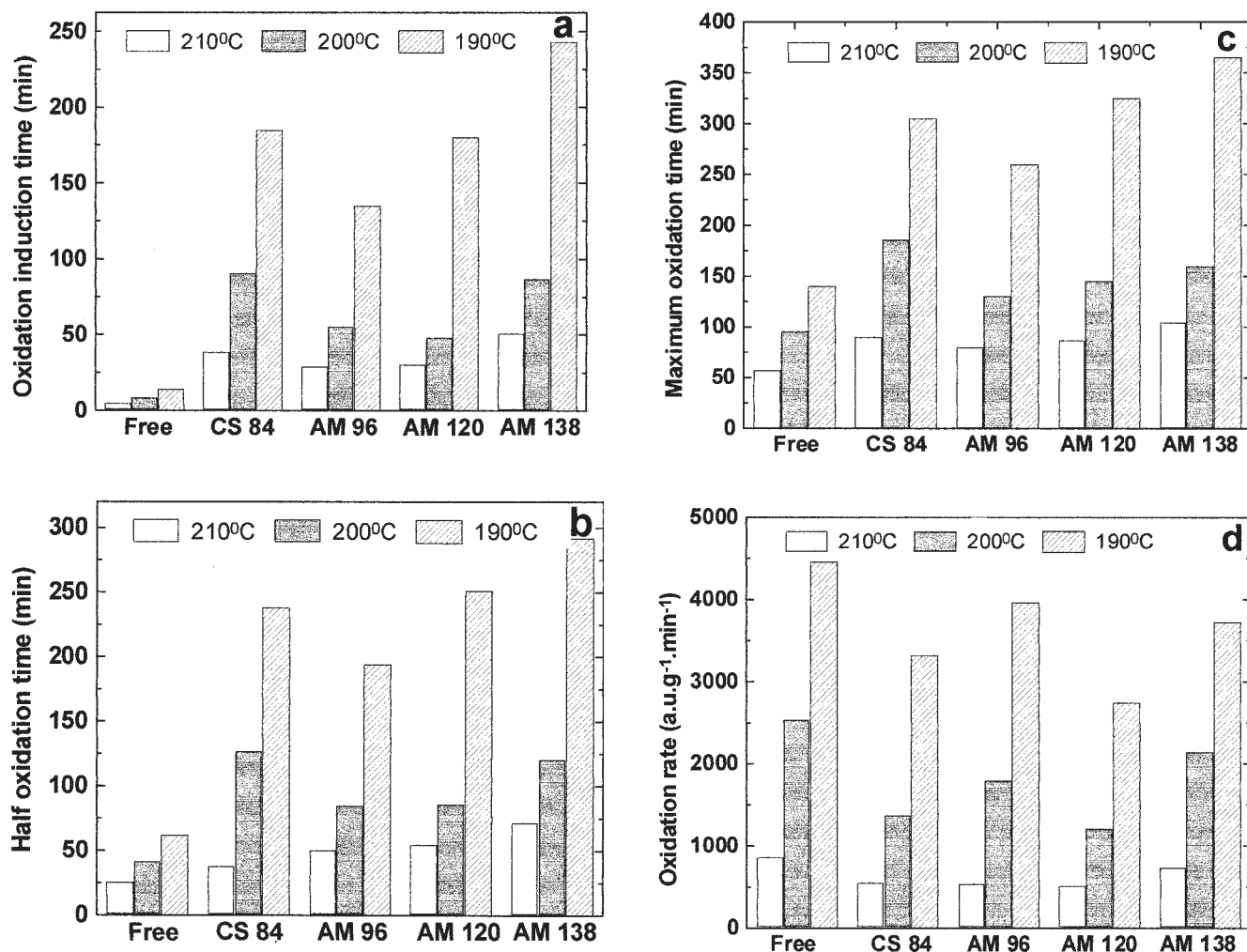


Figure 3 Kinetic parameters for LDPE stabilized with studied compounds. Concentration: 0.25% (w/w). (a) oxidation induction time; (b) half oxidation time; (c) maximum oxidation time; (d) maximum oxidation rate.

induction periods are longer: 11.2 to 34.3 times longer than the analogous period measured on LDPE samples without additive.

The peculiar behavior of stabilized polyethylene proves that the antioxidant activity of this class of compounds places them with the most suitable additives for durability improvement of polyolefins. In addition, the studied diphenols can be easily obtained as natural products by extraction from common medicinal herbs (for example, *Rosmarinus officinalis* and *Salvia officinalis*). It means that their compatibility with the human body is historically satisfactory, and their efficiency recommends them to be inserted in formulations at low concentrations.

The technical protection of LDPE against oxidation involves not only the excellent qualities of an additive, but also the optimal concentration conditions by reducing the rate of chain initiation in competition with hydroperoxide homolysis and by reducing the rate of chain propagation by scavenging radicals RO_2 and R.

Depletion of stabilizers

The determination of the rate constant that characterizes the depletion of studied diphenols during the thermal aging of low density polyethylene was done according to zero order kinetics.²³ Figure 7 presents the dependencies of the induction periods of oxidation on additive concentrations of the most efficient diphenols tested in this paper. The existence of negative critical concentrations for these antioxidants, CS 84 and AM 138, is the result of multifactorial contributions. The first factor is the reaction with peroxy radicals, through which the antioxidant is consumed. Another factor is the migration of antioxidant at the testing temperatures.

The linear dependency of induction periods on additive concentrations describes the correlation between the efficiency of antioxidants and the thermal stability of antioxidants. The antioxidant molecules may have various structural forms that show the sta-

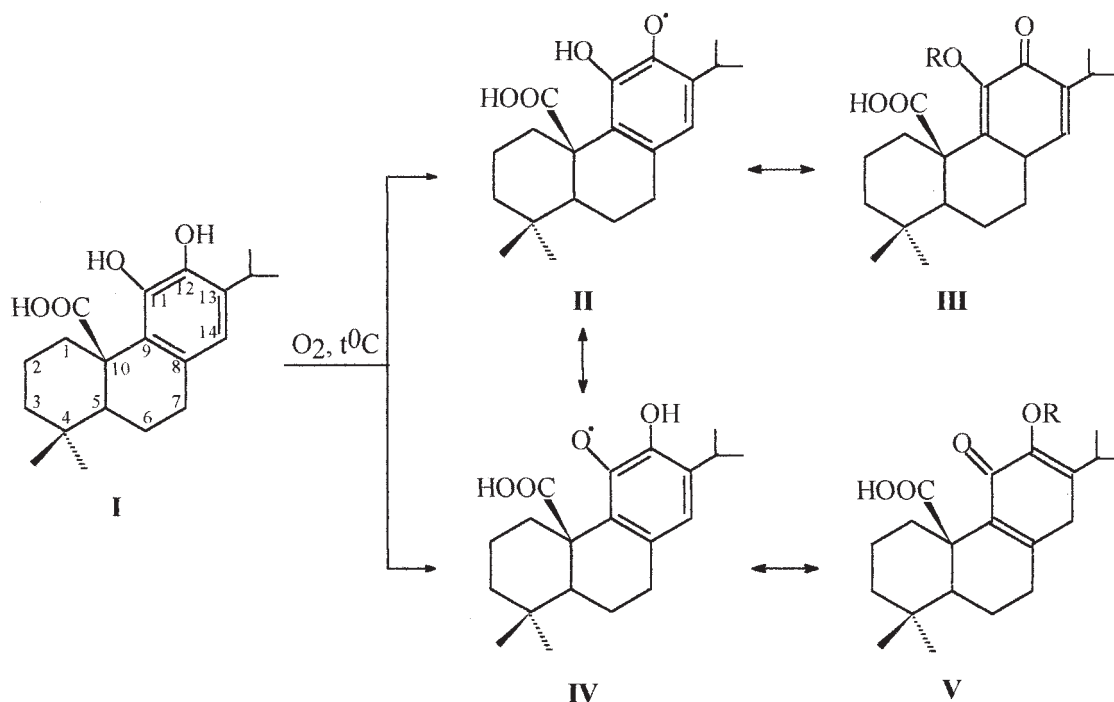


Figure 4 Mechanism of thermal stabilization of LDPE promoted by carnosic acid and related diphenols.

bilization activity assuring effective slowing of oxidation.

Table I presents the rate constants calculated for the consumption of two compounds, CS 84 and AM 138, at four concentrations. The analysis of these data reveals the relative superiority of AM 138, because the values of rate constants are lower. It means that the depletion of additive is caused by the lesser number of collisions. On the other hand, the higher the rate constant, the less efficient the scavenging action of a stabilizer. This correlation can be related to the bond

strength, which indicates the stability of the complex consisting of an antioxidant molecule and a captured radical.

The linear dependency of antioxidant half-life on the concentration of additive may be found in Figure 8. The high efficiency of the diphenols CS 84 and AM 138 in stabilization efficiency is depicted by the constant increase in half-life and by the roughly constant ratios between the values of this parameter for maximum and minimum concentrations, of about 6, at all temperatures.

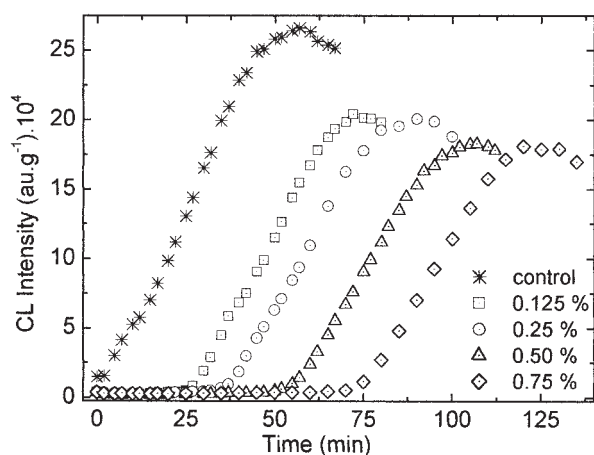


Figure 5 CL intensity dependencies of degradation time recorded at $210^\circ C$ for LDPE stabilized with various concentrations of CS 84.

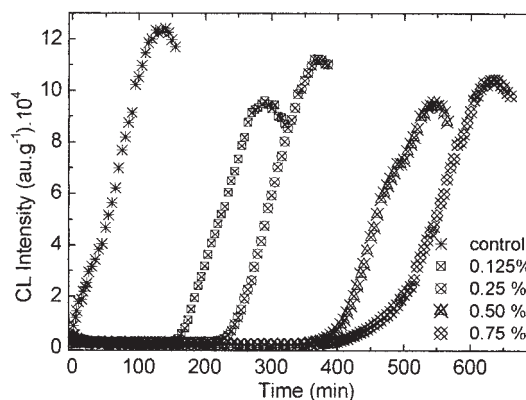


Figure 6 CL intensity dependencies of degradation time recorded at $190^\circ C$ for LDPE stabilized with various concentrations of AM 138.

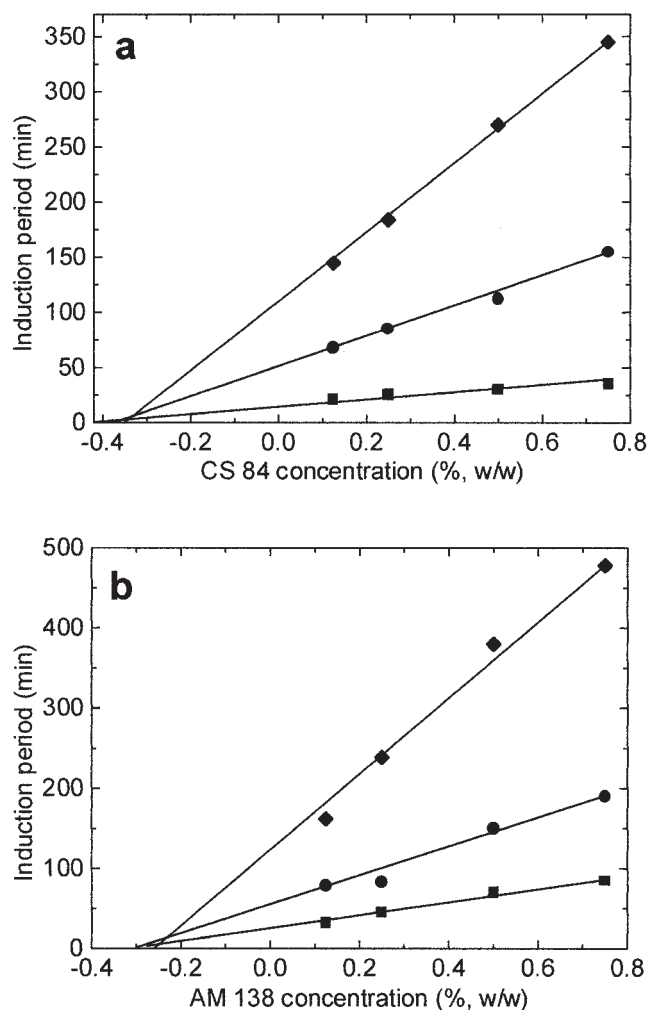


Figure 7 Dependencies of oxidation induction time on the initial concentration of additive at three temperatures. (a) CS 84; (b) AM 138. (◆) 190°C; (●) 200°C; (■) 210°C.

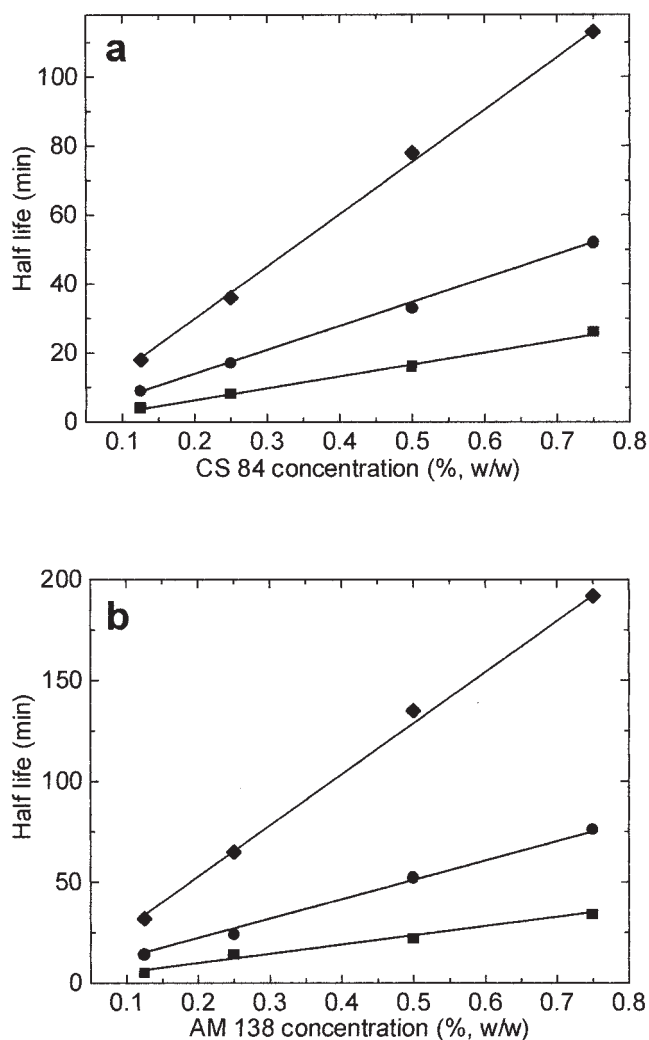


Figure 8 Dependencies of antioxidant half-life on the initial concentration of additive at three temperatures: (◆) 190°C; (●) 200°C; (■) 210°C. (a) CS 84; (b) AM 138.

TABLE I
Rate Constants for Antioxidant Depletion during Thermal Degradation of LPDE

Temperature (°C)	Antioxidant concentration (% w/w)	Rate constant, k (% w/w.min ⁻¹) × 10 ³	
		CS 84	AM 138
190	0.125	3.299	2.043
	0.25	3.297	1.893
	0.50	3.197	1.775
	0.75	3.304	1.979
200	0.125	7.071	4.136
	0.25	6.888	5.287
	0.50	7.436	4.494
	0.75	6.957	4.638
210	0.125	13.519	10.130
	0.25	12.895	10.000
	0.50	13.455	9.048
	0.75	13.200	10.100

Energetics of stabilization

The energetics of degradation involve the conditions under which this process occurs and describe the minimum probability required for the progress of oxidation. Figure 9 shows that the values of activation energies are in agreement with the antioxidant content. Of course, lower values are obtained for unstabilized samples, even if the calculation was based on oxidation induction time (E_{ind}) or on maximum oxidation time (E_{max}). The values of activation energies look different for LDPE in the presence of CS 84 or AM 138 due to the presence of different radicals with various electronic effects. While, for the LDPE/CS 84 specimens, E_{ind} decreases as the stabilizer concentration increases or remains about constant under the same circumstances, in the case of the oxidative degradation of LDPE/AM 138, either E_{ind} or E_{max} increases when the amount of additive is increasing.

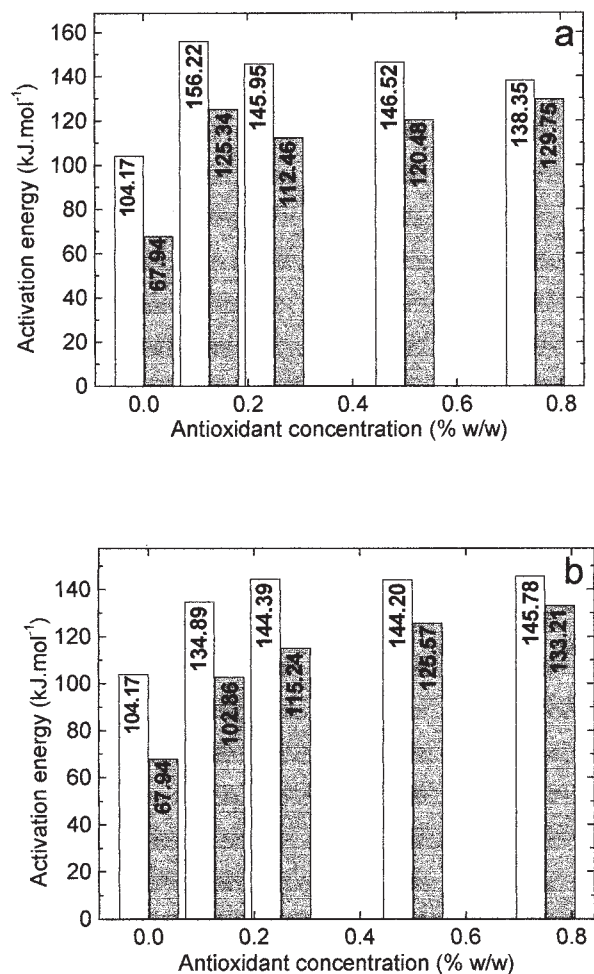


Figure 9 Activation energies for thermal oxidation of LDPE stabilized with (a) CS 84; (b) AM 138 at various concentrations. White columns: values calculated from oxidation induction times. Gray columns: values calculated from maximum oxidation times.

This behavior can be explained by the contribution of various stabilizing intermediates that act at different points in the degradation. It may be assumed that the depletion of CS 84 takes place faster than with AM 138. In addition, AM 138 would provide more active intermediates that assure a supplementary activity in the inhibition of thermal oxidation.

The depletion of stabilizer causes a decrease in activation energy values. It means that the steady state concentration of peroxy radicals and hydroperoxides cannot be efficiently counteracted by the decreasing amount of stabilizer.

The high activation energies determined for LDPE stabilized with diphenols, as well as kinetic parameters obtained for added low density polyethylene, are

strong arguments for recognizing the useful antioxidant features. It has been demonstrated that diphenols are capable of delaying thermal oxidation of LDPE even under severe operational conditions. It would be expected that an investigation of high energy degradation would provide similar results, taking into account the great differences between the activation energy of primary LDPE and corresponding values for stabilized polymer.

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