

Synergistic Effect between Hindered Amine Light Stabilizers and Partially Hindered Oligomeric Amines in Polyethylene

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ABSTRACT: The synergistic effect between novel synthesized oligomeric amines and a commercial hindered amine light stabilizer (Chimassorb 944) was studied in medium-density polyethylene (MDPE). Mixtures of the synthesized oligomeric amines and commercial additives were prepared at different concentrations and then were evaluated by ultraviolet and thermal aging. The evaluation was carried out on films prepared by compression molding, and the oxidation rates were monitored with Fourier transform infrared, which was used to measure the formation of different func-

tional groups: carbonyl, vinylic, and hydroperoxide. The data showed that, independently of the concentration of the commercial additives, when they were combined with oligomeric amines, they produced a synergistic effect with a magnitude depending on the MDPE aging conditions and the additive concentrations. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 280–287, 2004

Key words: polyethylene (PE); charge transfer; polyamines; HALS; stabilization

INTRODUCTION

To explain the activity of some amines, the mechanism proposed by Gijsman¹ assumed a central mechanism involving the deactivation, by charge transfer, of excited polymer–oxygen complexes. In his study, Gijsman examined amines that did not show an important effect on the stabilization of polyethylene (PE) but, when combined with a hindered amine light stabilizer (HALS), improved the activity in comparison with formulations only using HALS. To explain this synergism between HALS and an amine, it has been theorized that HALS is capable of neutralizing peroxy radicals while another amine quenches the polymer–oxygen charge-transfer complexes (CTCs),^{2,3} and this produces excited CTCs (amine–oxygen complexes; Fig. 1).

The same pattern was observed when oligomeric amines were evaluated under ultraviolet (UV) and thermal aging. When HALS was not present, the concentration of the peroxy radicals became very high because of polymer degradation, and the quenching of the polymer–oxygen CTCs became insignificant in the polymer stabilization process. Complementary activity between

oligomeric amines and Chimassorb 944 that could stabilize PE was observed and is further reported here.

EXPERIMENTAL

Materials

2,2-Dichloropropane, 2,2-dimethyl-1,3-propane diamine, 1,2-diamine-2-methylpropane, and sodium bicarbonate were supplied by Aldrich Chemical Co. (Milwaukee, WI). Tetrahydrofuran, methanol, chloroform, and diethyl ether were obtained from J. T. Baker (Phillipsburg, NJ). Medium-density polyethylene (MDPE) in a powder and nonstabilized form was obtained from BP Chemicals (Grangemouth, United Kingdom). The commercial additives Chimassorb 944 and Irganox 1330 were acquired from Ciba–Geigy Corp. (Basel, Switzerland).

Synthesis of the oligomeric amines [additive 1 (A1) and additive (A2)]

Oligomeric amines were synthesized from 2,2-dichloropropane with 1,2-diamine-2-methylpropane and 2,2-dimethyl-1,3-propane diamine.

In a typical procedure, a mixture of 2,2-dichloropropane (5 g, 4.6 mL, 0.04425 mol), 1,2-diamine-2-methylpropane (3.9 g, 4.38 mL, 0.04425 mol), sodium bicarbonate (7.43 g, 0.0885 mol), and 3 mL of distilled water in 160 mL of tetrahydrofuran was maintained under vigorous

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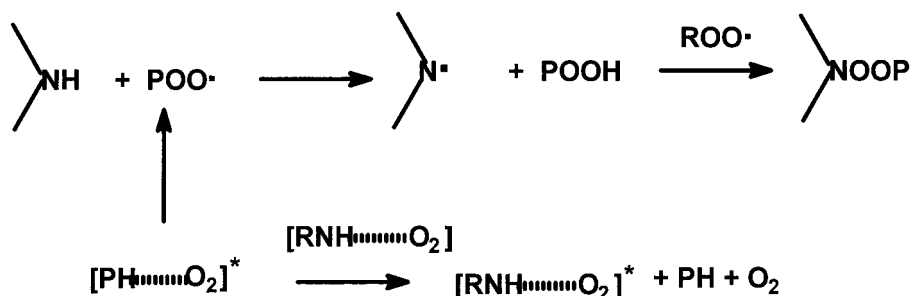
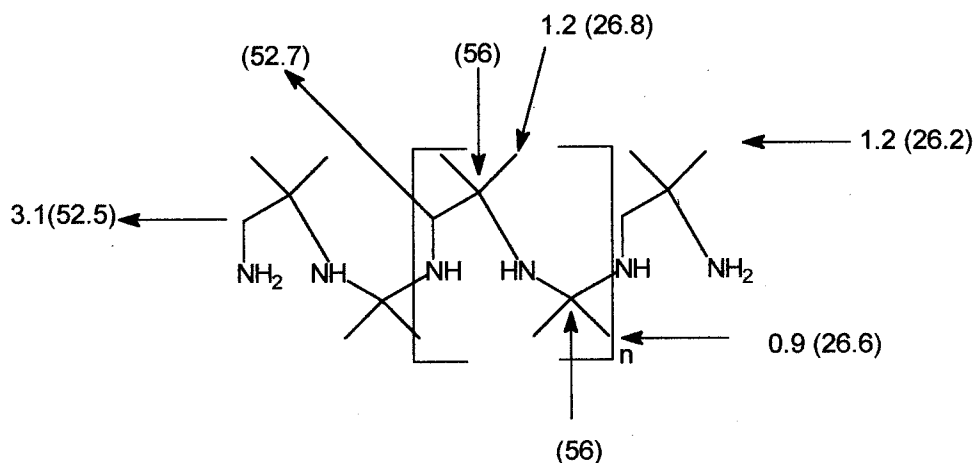


Figure 1 Formation of excited CTCs of amine and oxygen.^{2,3}

stirring at room temperature for 288 h. A solid was filtered off and washed with chloroform/methanol and was purified by precipitation from hot methanol with diethyl ether. The product was dried in a vacuum oven at 40°C to obtain 8.7 g of the product. The chemical structure for A1 was determined as follows.

¹H-NMR [tetramethylsilane (TMS), CD₃OD, ppm]: 1.2 [S, C(CH₃)₂], 3.1 (S, CH₂). ¹³C-NMR (TMS, CD₃OD,

ppm): 26.2, 26.6, 26.8 [C(CH₃)₂], 52.5, 52.8 (NCH₂), 56.59 [C(CH₃)₂]. Fourier transform infrared (FTIR): (cm⁻¹): 3421, 3380, 1500 (NH), 2960, 2920, 1400 (CH), 1480, 1372 [C(CH₃)₂]. Differential scanning calorimetry (DSC): mp = 183.4°C. Gel permeation chromatography (GPC): weight-average molecular weight (M_w) = 1078 g/mol, number-average molecular weight (M_n) = 1011.



Poly(-N-isopropyl-1,1-dimethyl ethylenediamine) (additive A1).

TABLE I
Formulations of the Additives Tested in MDPE

	Evaluation														
	A	E1 Ir	CH	A	E2 Ir	CH	A	E3 Ir	CH	A	E4 Ir	CH	A	E5 Ir	CH
PE															
PEIr		0.025			0.05			0.075			0.1			0.15	
PECH			0.025			0.05			0.075			0.1			0.15
PEM		0.075	0.0025		0.05	0.05		0.025	0.075		0.1	0.1		0.15	0.15
PEAn	0.05			0.05			0.05			0.05				0.05	
PEAnIr	0.05	0.025		0.05	0.05		0.05	0.075		0.05	0.1		0.05	0.15	
PEAnCH	0.05		0.025	0.05		0.05	0.05		0.075	0.05		0.1	0.05		0.15
PEAnM	0.05	0.033	0.033	0.05	0.05	0.05	0.05	0.033	0.033	0.05	0.1	0.1	0.05	0.15	0.15

Ir = Irganox 1330; CH = Chimassorb 944; An = A1 or A2; M = commercial additive mixture.

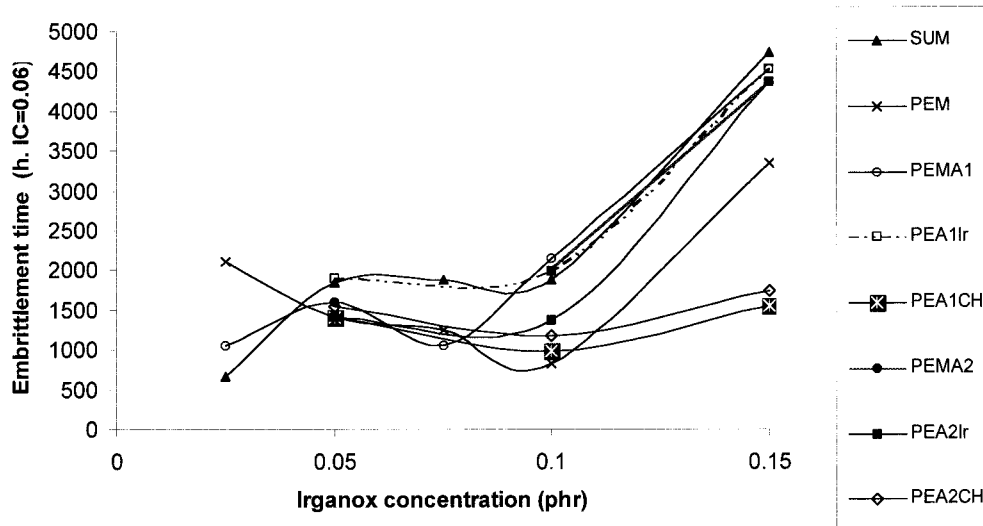


Figure 2 Thermal aging times corresponding to CI = 0.06 (0.05 phr A1 and A2).

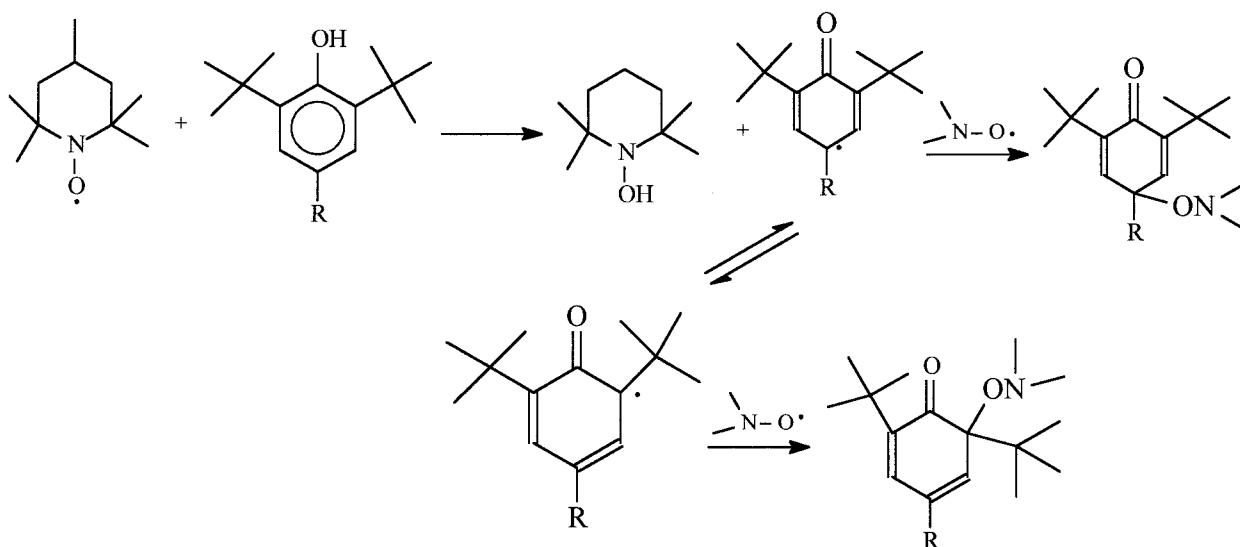


Figure 3 Reaction between phenols and nitroxyl radicals.

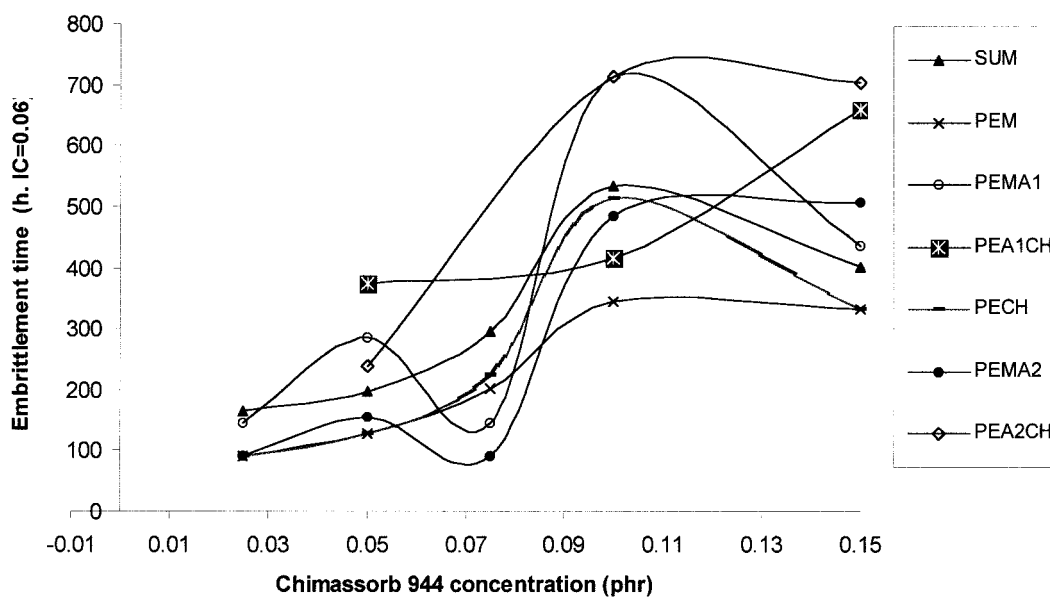


Figure 4 UV aging times corresponding to CI = 0.06.

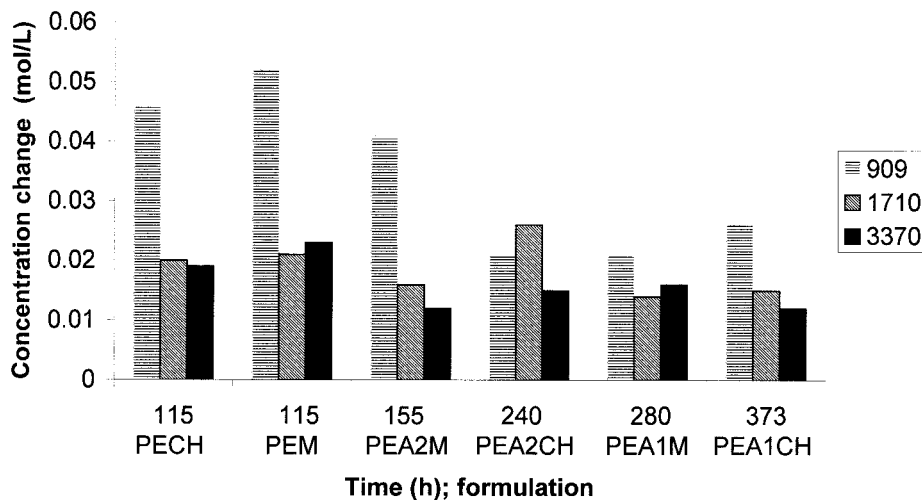


Figure 5 Functional group formation in PE films under UV aging with 0.05 phr Chimassorb.

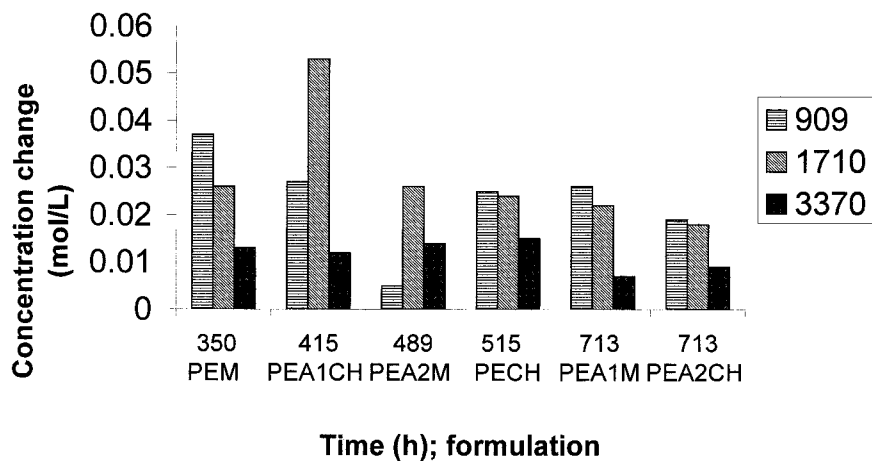


Figure 6 Functional group formation in PE films under UV aging with 0.1 phr Chimassorb.

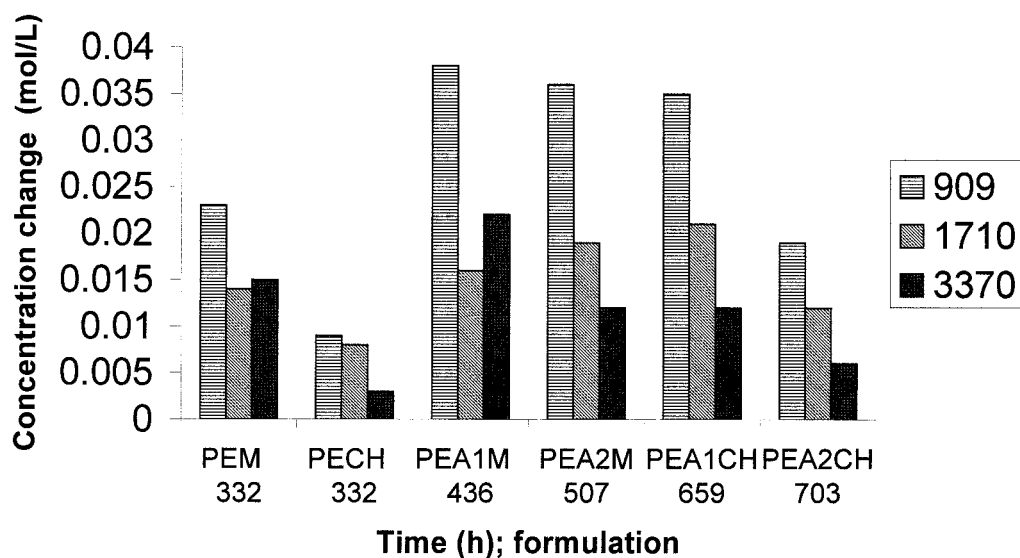
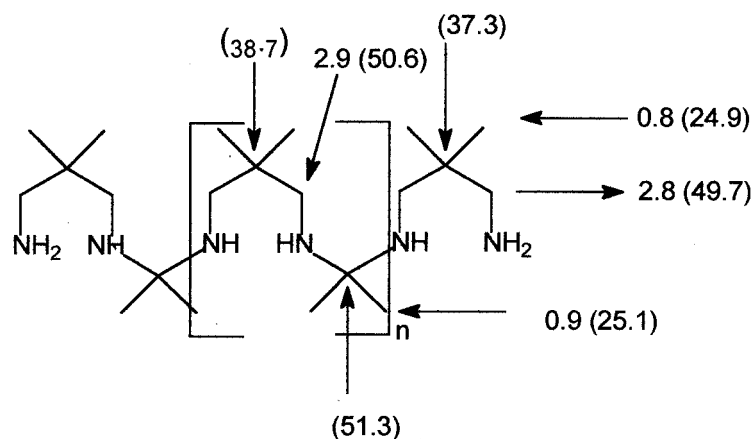


Figure 7 Functional group formation in PE films under UV aging with 0.15 phr Chimassorb.

The product derived from 2,2-dimethyl-1,3-propane diamine (A2) was prepared in the same way as a white solid with a weight of 8.8 g. The chemical structure of A2 was verified as follows.

$^1\text{H-NMR}$ (TMS, CD_3OD , ppm): 0.8 [S, $\text{C}(\text{CH}_3)_2$], 0.9 [S, $(\text{CH}_3)_2$], 2.8–2.9 (S, CH_2). $^{13}\text{C-NMR}$ (TMS,

CD_3OD , ppm): 24.9, 25.1 [$\text{C}(\text{CH}_3)_2$], 37.3, 38.72 (NCH_2), 47, 49 [$\text{C}(\text{CH}_3)_2$], 51.3 [$\text{NC}(\text{CH}_3)_2$]. FTIR (cm^{-1}): 3400, 1500 (NH), 2960, 2920, 1400 (CH), 1450, 1380 [$\text{C}(\text{CH}_3)_2$]. DSC: mp = 353°C. GPC: M_w = 1039 g/mol, M_n = 963.



Poly(-N-isopropyl-2,2-dimethyl propylendiamine) (additive A2).

Formulations of the additives tested in MDPE

MDPE films, from the formulations listed in Table I, were prepared by compression molding and were degraded by UV aging at 60°C and by thermal degradation at 100°C to determine the time needed to reach a carbonyl index (CI) of 0.06.^{4–6} The stabilizing activity of the synthesized products was compared with commercial additives: HALS (Chimassorb 944) and an antioxidant (Irganox 1330).

RESULTS AND DISCUSSION

Thermal aging

When oligomeric amines A1 and A2 were added to PE with Chimassorb 944, Irganox 1330, or both under thermal aging, A1 and A2 assisted the Irganox in stabilizing the PE films. This was evident, even for the sample PEM, in which there was apparent antagonism between Irganox 1330 and Chimassorb 944 because PEIr performed better than PEM. To compare the activities of A1 and A2 in the different formulations and to distinguish between accumulative and synergistic effects,⁷ we computed a theoretical stabilization curve from the stabilization time required for each additive (Irganox 1330 and Chimassorb 944) to obtain a CI of 0.06. The resulting curve is identified as a sum in Figure 2. This sum is superior to the stabilization times corresponding to the PEM formulation. This clearly indicates that an antagonistic effect existed between the components.

The antagonism could be explained by the reaction of a cyclohexadienyl radical with a nitroxyl radical

from the HALS to form an ether of hydroxylamine (Fig. 3).⁸

The PEMA1 formulation displayed results similar to the curve simulated for the commercial additives, and

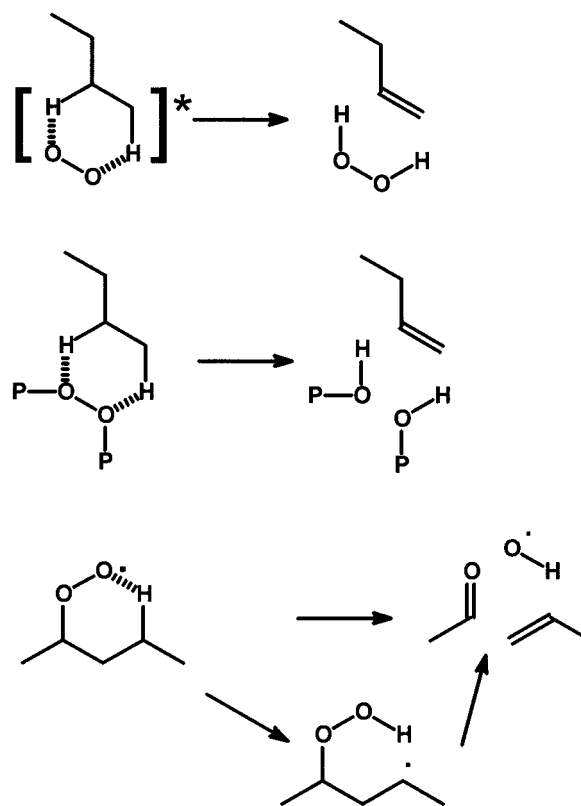


Figure 8 Paths to double-bond formation.

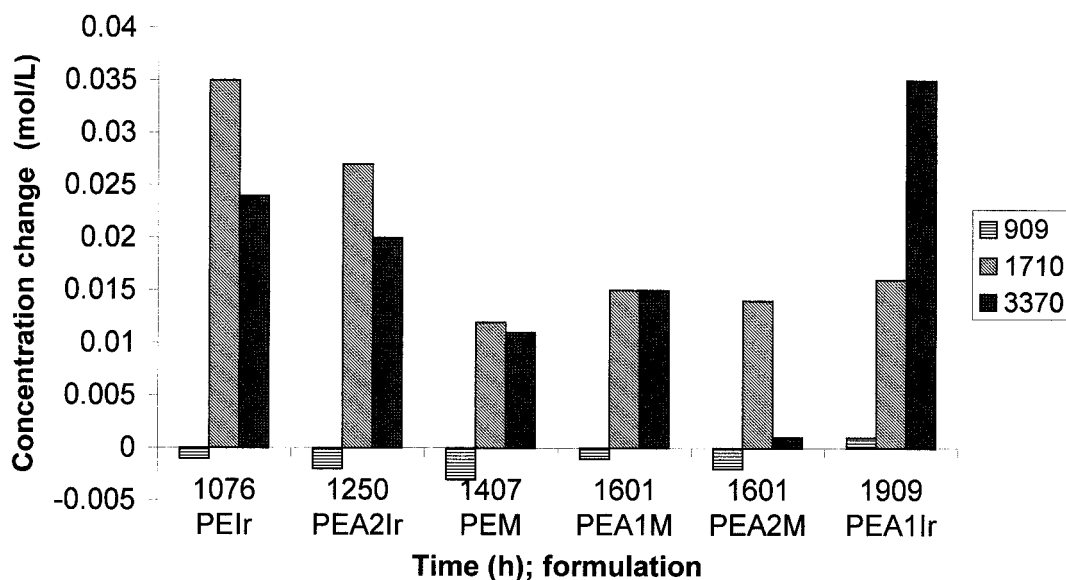


Figure 9 Functional group formation in PE films under thermal aging with 0.05 phr Irganox.

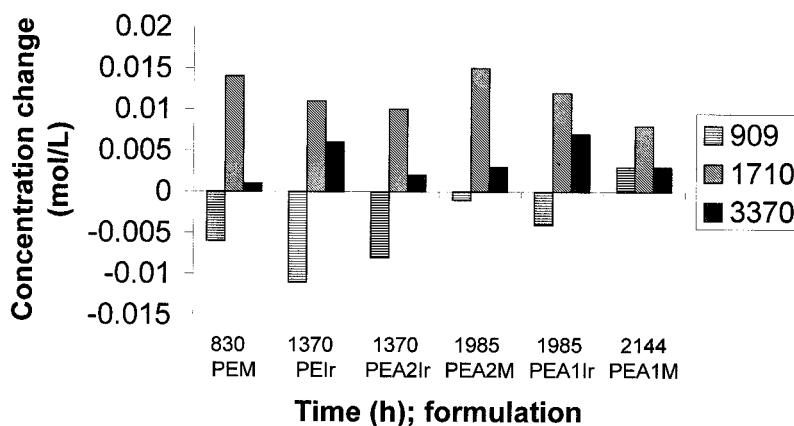


Figure 10 Functional group formation in PE films under thermal aging with 0.1 phr Irganox.

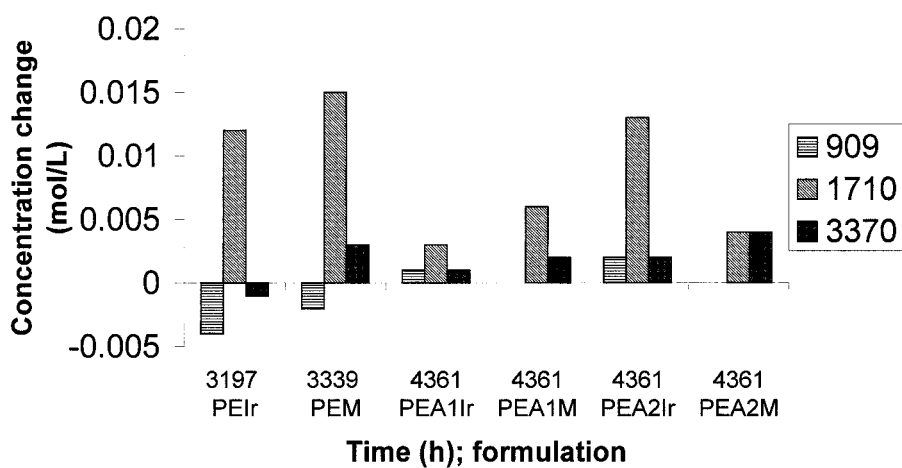


Figure 11 Functional group formation in PE films under thermal aging with 0.15 phr Irganox.

this indicated that additive A1 or A2 overcame the antagonistic effect mentioned earlier (Fig. 2). The samples with A1 or A2 and Chimassorb showed improved stability in comparison with the sample containing only Chimassorb 944.

The antagonistic effect disappeared or was reduced by the action of additives A1 and A2, and this indicated that there was a reduction in the nitroxyl radicals from Chimassorb 944 able to react with PE, suggesting that products from the interaction between PE and A1 or A2 were thermally stable and reduced the probability of the formation of nitroxyl radicals from Chimassorb 944.

UV aging

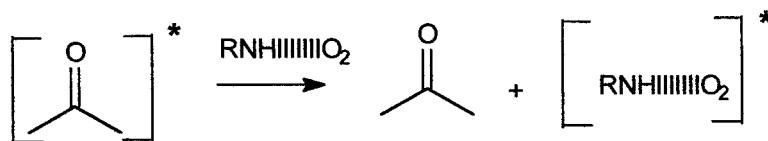
At concentrations higher than 0.1 phr Chimassorb 944, there was a decrease in its activity because a high concentration of nitroxyl radicals propagated free-radical formation from the polymer. Additives A1 and A2 counteracted this effect, A2 giving better results than A1. In this set of experiments, the best results arose from formulations in which additives A1 and A2 interacted with Chimassorb 944 (Fig. 4).

The interaction of oligomeric amines with the polymer-oxygen complex was apparently more effective in quenching their excited complex (CTC) than the interactions of Chimassorb with polymer-oxygen CTCs. The final effect was a concentration reduction of nitroxyl radicals from Chimassorb 944.

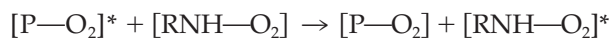
Functional group formation

UV aging

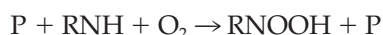
Following the concentration changes for functional groups formed between the end of the induction time



The quenching of polymer-oxygen CTCs delayed the formation of peroxy radicals:



Oligomeric amines, rather than the polymer, reacted preferentially with O_2 , delaying peroxy radical formation:



The reaction of amines with peroxy radicals produced stable species under thermal degradation. Oxygen

and the embrittlement time, we observed that formulations with lower stabilization showed double-bond concentrations higher than those of the carbonyl groups. This indicated that more paths existed for the formation of double bonds than for the formation of carbonyl groups or that these groups were transformed into some other chemical groups (Figs. 5-7). The α scissions were among these transformations, as well as dehydrogenation via polymer-oxygen complexes and polymer-peroxide interactions (Fig. 8).

When the Chimassorb 944 concentration was between 0.05 and 0.1 phr, the carbonyl and vinyl group concentrations tended to be practically the same in formulations with better stability (PEA1M, PEA1CH, and PEA2CH), and this meant that processes such as Norrish type II were the most important.

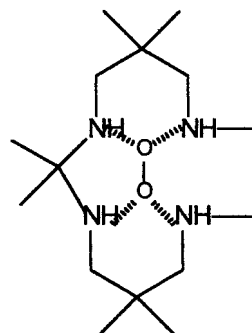
Thermal degradation

The functional group formation patterns under thermal degradation were different from those observed under UV aging. The double-bond concentrations decreased, being more evident in samples with lower stability. The formation of double bonds was slower than their transformation (Figs. 9-11).

The stabilization times were much longer than those observed in UV aging, and this suggested that oligomeric amines suppressed the formation of oxidizing species. Some possible explanations follow.

The quenching of ketone groups formed by the heating of PE was one possibility. The excited amine-oxygen CTC dissipated energy without producing new radicals:

was partially immobilized between the nitrogen atoms of the additive:



CONCLUSIONS

Data from UV irradiation showed that, independently of the concentrations of the commercial additives, when an amine additive, A1 or A2, was combined with Chimassorb 944, there was a synergistic effect, and a good correlation between carbonyl and double-bond formation was observed that could be explained by the Norrish type II process.

In the case of thermal aging, a synergistic effect was observed when A1 or A2 was combined with Irganox 1330. The concentration of vinylic groups decreased when the concentration of carbonylic and peroxide groups increased, and this indicated that double-

bond-formation processes were less important than carbonyl formation.

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