In Situ Detection of Hindered Amine Stabilizer Consumption in Polymer Through Oxidation by Indirect Electron Spin Resonance

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ABSTRACT: The stabilization mechanisms of hindered amine stabilizers (HAS) involve various oxidation products of the piperidine structure. Thus, we propose a novel method, based on electron spin resonance (ESR) spectroscopy, to check *in situ* the consumption of the total piperidyl species (intact HAS and all of its byproducts) in polypropylene (PP) films through photooxidation. First, the concentration of nitroxyl radicals produced upon irradiation in stabilized PP has been measured by direct ESR analysis. Then, the changes of concentration of the overall stabilizing species have been detected by indirect ESR, after conversion of the overall HAS derivatives into nitroxyl-free radicals by exposure of photooxidized PP to peracetic acid vapor at room temperature. Results were compared with those obtained by the conventional Fourier transform infrared method in the particular case of [2,2,6,6-tetramethyl piperidinyl]sebacate, and the reliability of both techniques was discussed. Thus, we assume that indirect ESR experiments consist of a easy, accurate, and very sensitive method to monitor the time evolution of a low-molecular weight HAS–NH concentration in PP upon photooxidation. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1107–1114, 1998

Key words: hindered amine stabilizer; polypropylene; *in situ* detection; ESR spectroscopy

INTRODUCTION

Hindered amine stabilizers (HAS) are among the more extensively used additives for protecting various polymers from degradation by the combined effects of light, temperature, and atmospheric oxygen. Numerous publications have been devoted to the stabilization mechanism of HAS.[1–3] It is now generally admitted that photoantioxidants based on 2,2,6,6-tetramethyl piperidine structure (HAS–NH) are partially oxidized to the

corresponding nitroxyl radicals (HAS–NO•) that act as scavengers of macro alkyl radicals, resulting in alkyl hydroxylamine structures (HAS–NOP; see Scheme 1). Furthermore, HAS–NO• radicals are continuously regenerated from HAS–NOP during UV exposure, so that they can exert their stabilizing action many times before being depleted. Although several mechanisms have been proposed, in all cases, HAS–NO• has been assumed to be the main active species of the stabilization process.

Because nitroxyl radicals are very long-lived species, they can be easily detected by electron spin resonance (ESR) spectroscopy. Several authors have used direct ESR measurements to monitor the concentration of nitroxyl-free radicals
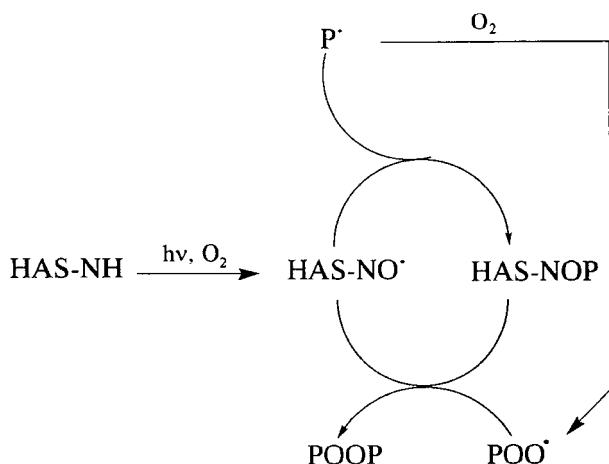
Scheme 1 Cyclic regenerative mechanism.

in polymer films doped with HAS as a function of exposure time to oxidation.[3-5]

But, the ideal approach to predict the lifetime of a polymer would be to monitor the concentration of HAS together with all of its byproducts on oxidation at any time before any loss of the physical and mechanical properties of the material. Such attempts have been made to discuss the overall mechanism of photoprotection by HAS. However, these measurements always require extractive processes.[5-8]

Thus, the main goal of this work is to develop a method to check *in situ* the consumption of the total stabilizer in polypropylene (PP) through oxidative degradation.

Our study is especially focused on the bis[2,2,6,6-tetramethyl-4-piperidinyl]sebacate (HAS-1), which is considered a model compound. The characterization of the chemical changes in the host polymer during photooxidation is based on Fourier transform infrared (FTIR) spectroscopy. Measurements of the nitroxyl radicals concentration upon photooxidation are performed by direct ESR spectroscopy. Moreover, the consumption of the overall stabilizer is followed by indirect ESR analysis after oxidation of HAS—NH and all of its byproducts into nitroxyl radicals. Reliability and disadvantages of this novel method are finally discussed.

EXPERIMENTAL

Materials

PP (Targor, LilleJonne, France) was issued from the Spheripol® process.

As additives, commercially available HAS have been used. Low-molecular weight HAS—HAS-1 is bis[2,2,6,6-tetramethyl-4-piperidinyl]sebacate purchased from Ciba-Geigy as Tinuvin® 770. HAS-2 and HAS-3 are experimental additives from Clariant (Huninque, France). (See Scheme 2 for chemical structures.)

Peracetic acid (32 wt % solution in dilute acetic acid) was supplied by Aldrich Chemical Co. (Milwaukee, WI).

Sample Preparation

The polymer and stabilizers were mixed without further purification in a Henschel mixer, then extruded at 220°C, and granulated. All samples contain paraffin oil at a concentration of 0.5 wt % to prevent bad mixing of additives.

Polymer pellets were converted into films (110 $\pm$ 10 μm) by compression molding between two Teflon sheets at 185°C under 200 bars for 1 min.

Photooxidation Procedure

Films were fixed on aluminum holders, and photooxidation was performed either in a SEPAP 12-24 chamber (MPC, Neuilly sur Marne, France) at 60°C or in a ultrahigh accelerated SEPAP 50-24 device (MPC, Neuilly sur Marne, France) at 70°C.

These units have a UV source supplying radiations longer than 300 nm (representative of natural exposure). Samples are rotated at a constant speed and distance from the source. For PP, the accelerating factor is about 8 and 16 for SEPAP 12-24 and SEPAP 50-24, respectively, considering 8 h daily sunlight.

Films were analyzed after various exposure times.

FTIR Spectroscopy

The chemical changes in irradiated films were monitored by FTIR spectroscopy (Nicolet Impact 400, Omnic software).

ESR Spectroscopy

ESR spectra were obtained at an ambient temperature with a Bruker spectrometer (ER 200), operating in the X-band (10 GHz). All spectra were recorded at a fixed modulation amplitude setting of 1.25 G and a power setting of 5 mW. The samples (two layers of film, 18 $\times$ 3.5 mm) were held in an ESR tube (ϕ, 4 mm), which was positioned at the same position inside the cavity for all runs

HAS-1

HAS-2   HAS-3
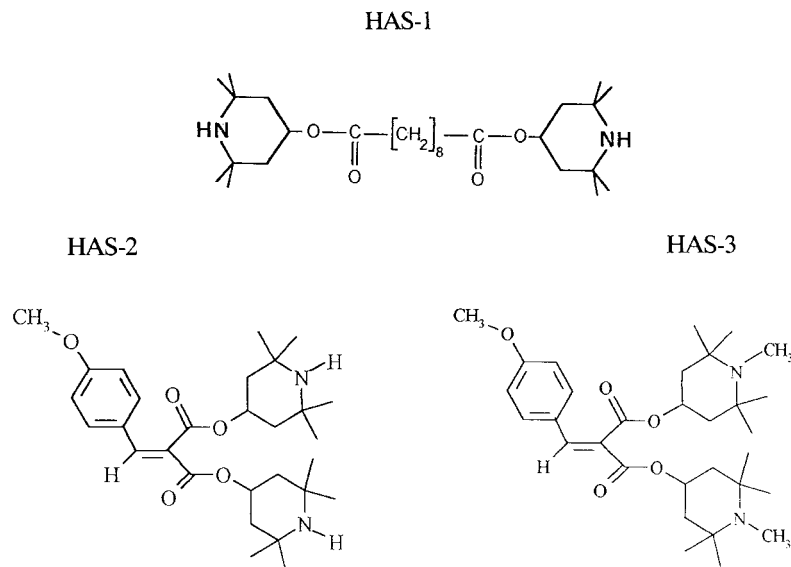
Scheme 2   Chemical structure of HAS.

by using an insertion depth limiting ring to ensure measurement consistency. Gain setting (adjusted as necessary in each case) was normalized to a standard setting by ratioing the signal from a external reference sample with the signal. Each sample recording was immediately followed by the recording of the external reference. The reference sample was prepared by grinding a Mn^{2+} doped cray to a powder, then sealed in a borosilicate capillary tube.

Spectra were recorded on oxidized films before and after exposure to peracetic acid vapor (32 wt % solution in dilute acetic acid) at an ambient temperature until no further increase in signal intensity was observed (24 h in routine measurements).

In first approximation, radical concentrations were estimated from peak-to-peak intensity measurements and were reported in arbitrary units.[9,10]

RESULTS

FTIR Spectroscopy

Significant chemical changes occuring on PP films upon accelerated photooxidation were largely reviewed.[11] The most visible changes in infrared absorption spectra are observed in the carbonyl groups absorption region. In particular, the formation of typical carbonyl species at around 1715 cm^{-1} is easily detected.

Oxidation of the unstabilized PP starts imme-

diately after the beginning of exposure. On the contrary, oxidation of the HAS-stabilized films starts after an induction period. The induction time of carbonyl development upon photooxidation of PP films is directly proportional to HAS concentration, as it is plotted in Figure 1 for the low molecular weight HAS-1. Similar data have already been published.[2,12,13]

During this induction period, monitoring of the HAS-1 consumption is well-known to be possible by FTIR spectroscopy. Indeed, it has already been reported that the decrease of the ester groups of HAS-1 (absorbing at 1735 cm^{-1}) is correlated to the decrease of the stabilizer concentration through photooxidation.[5]

Figure 2 shows both the evolution of the amount of intact additive in a 0.35 wt % HAS-1 stabilized PP and the formation of carbonylated photoproducts at 1735 and 1718 cm^{-1}, respectively. It can be seen that the host polymer oxidation (carbonyl growth up) starts when the concentration of intact HAS drops to a very low value.

ESR Spectroscopy

Formation of Nitroxyl Radicals on Irradiation

Nitroxyl radicals from hindered piperidine derivatives are observed during irradiation. Radicals can be detected in a very low concentration already in the initial stabilizer. Upon irradiation, a spectrum (with three wide and asymmetrical lines, 60 G total width) similar to that of PP containing deeply penetrating nitroxide mole-
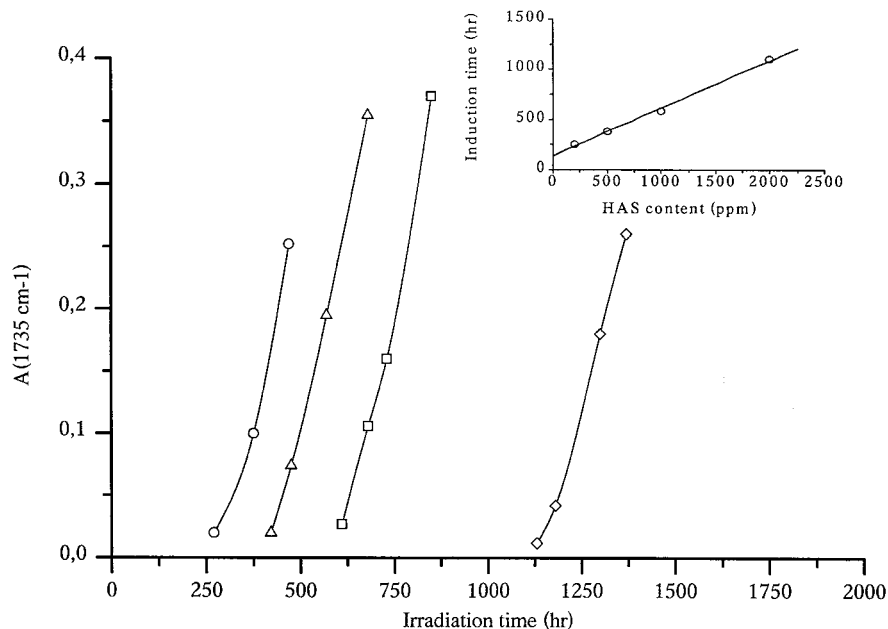
Figure 1 Kinetics of photoaging in SEPAP 12-24 at 60°C. Influence of the concentration in HAS-1 on the stability of PP films (110 μm): (○) 200 ppm, (△) 500 ppm, (□) 1000 ppm, (◇) 2000 ppm. (Inset) Correlation between HAS content and induction time.

cules[14,15] is recorded in all cases. The shape of ESR spectra in Figure 3 is explained by the fact that some of the radicals are in a restrictive environment; thus, each spectrum is a superposition of lines characteristic of mobile and immobile species. However, the shape of the ESR spectrum taken at room temperature is not changed during irradiation [i.e., the ratio of the two types of radicals (mobile and immobilized)] does not change, whereas their concentration increases and decreases.

Figure 4 plots the concentration of nitroxyl rad-
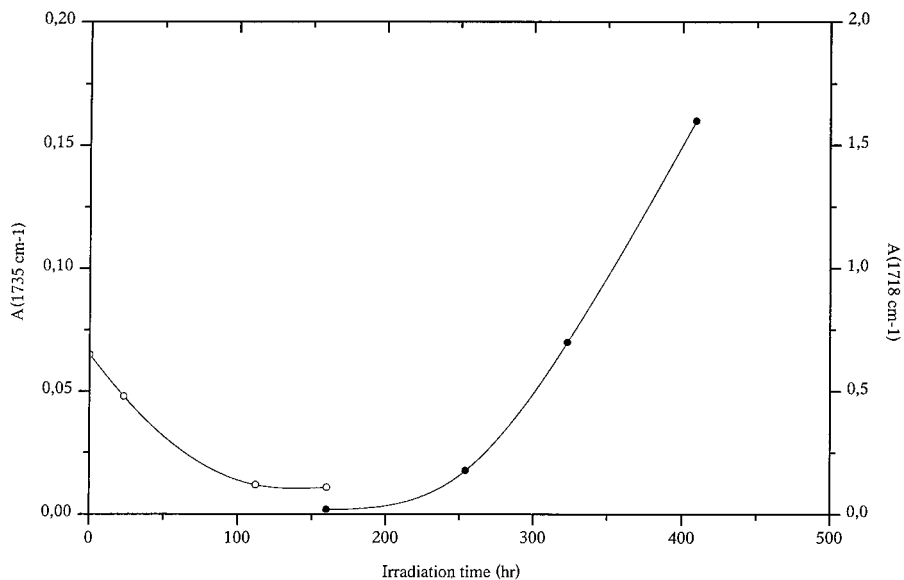
Figure 2 FTIR changes through photooxidation (SEPAP 50-24 at 70°C) of [PP + 0.35 wt % HAS-1] films (110 μm). (○) Ester groups of the additive at 1735 cm^{-1}. (●) Carbonyl groups at 1718 cm^{-1}.
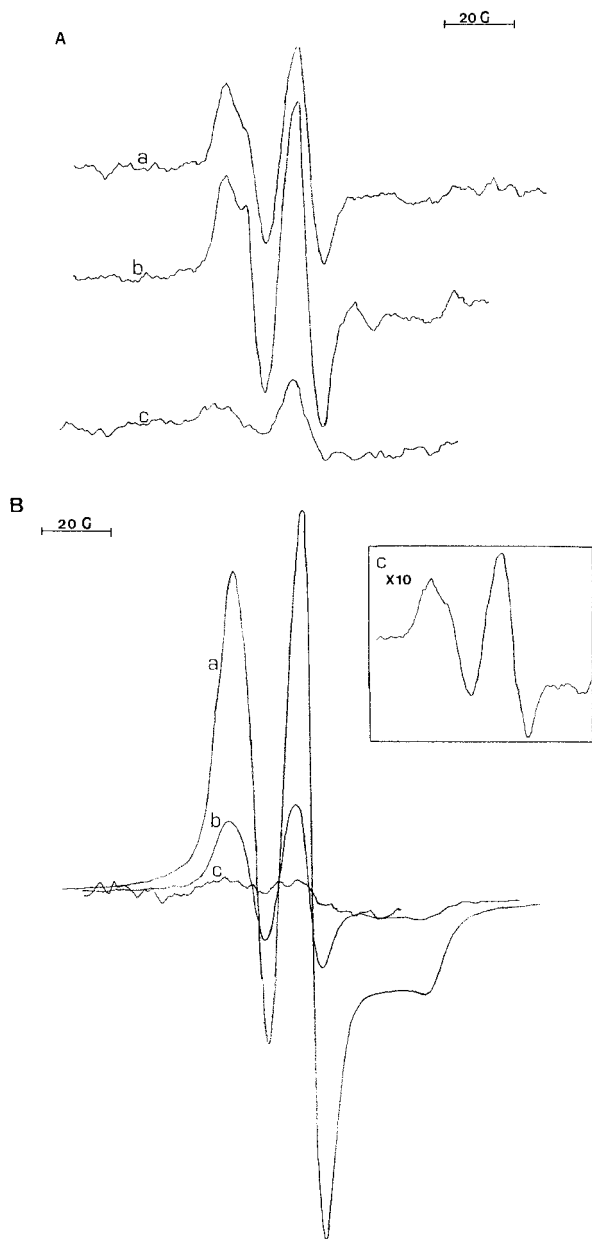
Figure 3 ESR spectra of nitroxyl radicals produced from HAS-1 through photooxidation (SEPAP 12-24 at 60°C) in 0.2 wt % stabilized PP films (two layers, 110 μm). The vertical scales are arbitrary. (A) Direct ESR: before peracetic acid treatment—gain, 8×10^5; modulation, 1.25. (a) 23 h, (b) 155 h, (c) 433 h. (B) Indirect ESR: after peracetic acid treatment—gain, 8×10^4; modulation, 1.25. (a) 0 h, (b) 89 h, (c) 433 h. (Inset) Gain 8×10^5.

icals, determined by ESR, in PP stabilized with different contents of HAS-1 as a function of exposure time.

In all cases, the nitroxyl radicals concentration is found to increase to a maximum, then decreases and gradually levels out. Figure 4 points out that

the maximum nitroxide concentration and the time to this maximum increase with increasing initial concentration of HAS. The variation of nitroxyl radical concentration reflects the balance of formation and consumption of HAS-NO[•]; such results have extensively been published for different polymers.[3,4,15,16] Therefore, the end of the induction period seems to be a consequence of a very low concentration of intact HAS–NH as corresponding nitroxyl radicals HAS–NO[•].

Oxidation of HAS–NH into HAS–NO[•]

Mechanism studies postulate that the secondary amine group of sterically hindered piperidines can be easily oxidized to corresponding nitroxyl radical by numerous species expected to be present in a polymer during photooxidation.[2] In particular, organic peracids have been found to be good reagents for the oxidation of hindered secondary amines as HAS–NH to corresponding nitroxyl radicals (HAS–NO[•]).[17–19] Several piperidyl species (NH, NOH, NOC, etc.) have been shown to be quantitatively converted to NO[•] groups by treatment with a solution of *m*-chloroperbenzoïc acid, so that the total concentration of these species may also be estimated in PP samples by ESR.[5,8,20]

To monitor the concentration of HAS–NH and all of its byproducts as a function of exposure time *in situ,* (i.e., without any extraction process), we choose to submit PP films to peracetic acid vapor both before and after oxidation.

The first time, ESR spectra were recorded for unoxidized PP films containing different concentrations of HAS-1 (0.05–0.35 wt %) after exposure to peracetic acid for 24 h. Peracetic acid treatment generates a strong signal and may be very useful for the detection of small changes. The shapes of these spectra are quite similar to those previously observed by direct ESR analysis of photooxidized PP films stabilized with HAS-1 (Fig. 3). The relationship between the peak-to-peak intensity of the ESR spectra (recorded after peracetic acid treatment) and the initial HAS-1 concentrations is plotted in Figure 5. The curve has a good linearity up to 0.2 wt %. Thus, we assume that the oxidation of HAS–NH by peracetic acid is quantitative, but that above 0.2 wt %, the nitroxyl radical concentration in the film is too high and induces known saturation effects.

Nevertheless, tertiary amines were reported to be generally unreactive toward *p*-nitroperbenzoic acid nor *m*-chloroperbenzoic acid.[18] Thus, peracetic acid treatment of HAS-3 does not succeed,
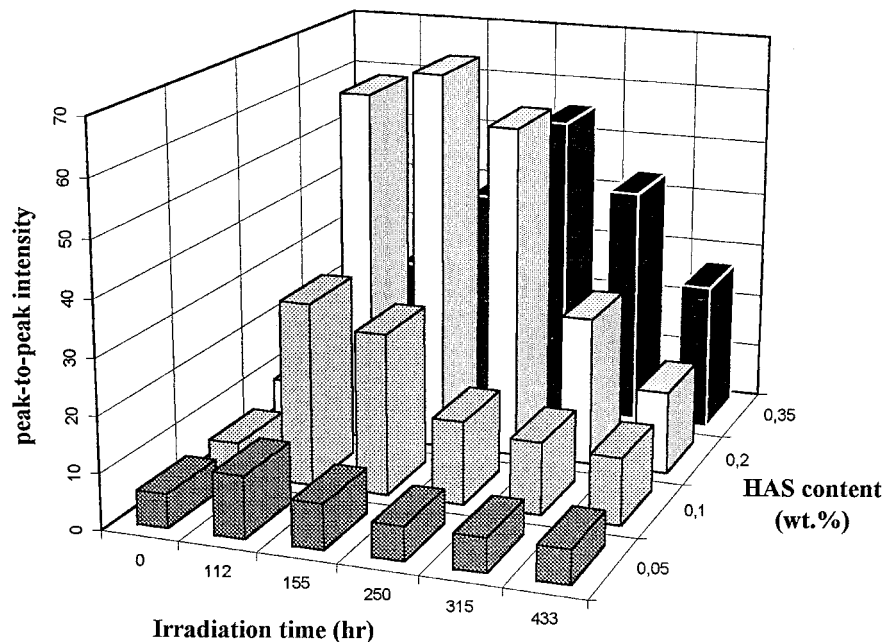
Figure 4 Nitroxyl radicals level versus exposure time in SEPAP 12-24 at 60°C and HAS-1 content in PP films (110 μm).

whereas a PP film doped with the parent secondary amine (HAS-2) gives a strong ESR signal after exposure to peracetic acid vapor.

Thus, our study should be confined to HAS–NH.

However, it is thought that peracid treatment involves quantitative conversion of all piperidyl species [not only —NH, but also —NOH, —NOC—, —NO(C=O)—] to the nitroxyl radical (—NO•).[20] The total concentration of these species (i.e., the overall byproducts of HAS upon oxidation at any time) may be estimated by ESR after acid peracetic vapor exposure of photooxidized PP films.
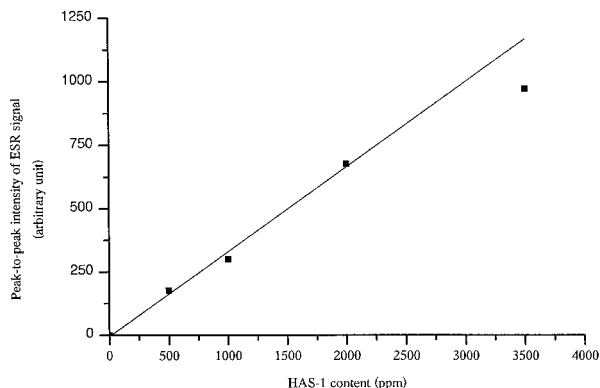
Figure 5 Peak-to-peak intensity of ESR spectra versus concentration of HAS-1 in PP films after peracetic acid exposure. Ordinates were expressed in arbitrary units.

Consumption of Overall HAS Through Irradiation

For different photooxidation times, ESR spectra of oxidized PP films originally containing 0.2 wt % of HAS-1 are recorded both before and after peracetic acid treatment. All kinetic data are collected in Figure 6.

It can be seen that, at any time, free nitroxyl radical yields from HAS–NH in photooxidizing PP are quite low (magnified scale). Nitroxyl groups (measured by direct ESR) account for not larger than 30% of the total piperidyl species (intact HAS plus byproducts on irradiation, measured by indirect ESR). Similar (or lower) concentrations have already been reported.[3,5]

The free radical level, recorded after peracetic acid treatment of photooxidized samples, drastically decreases as increases irradiation time. It is important to point out that the kinetic curve of the decay of those nitroxyl radicals is consistent with this of the consumption of intact HAS-1 obtained on the basis of FTIR measurements.

Thus, the induction period of carbonyl formation in the polymer lasts for a long time, during which the concentration of all species involved in the stabilization decreases exponentially.

CONCLUSIONS

FTIR Spectroscopy

In particular cases, FTIR analysis gives the amount of *intact HAS* (i.e., unreacted HAS) than
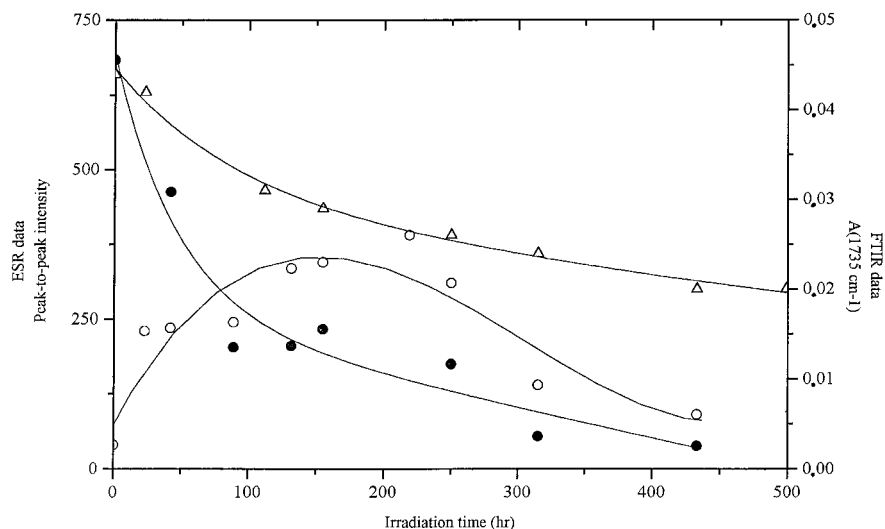
Figure 6 Physicochemical changes upon photooxidation in SEPAP 12-24 at 60°C of [PP + 0.2 wt % HAS-1] films (110 μm). FTIR data: ($\triangle$) ester groups of the additive at 1735 cm^{-1}. ESR data: nitroxyl radicals concentration ($\bigcirc$) before peracetic acid treatment in a magnified scale $\times$10 (gain, 8×10^5; modulation, 1.25) and ($\bullet$) after peracetic acid treatment (gain, 8×10^4; modulation, 1.25).

HAS that is not involved in the cyclic regenerating mechanism.

In fact, FTIR spectroscopy is essentially reported as a method to follow the disappearance of HAS-1 through oxidation. Indeed the consumption of a HAS-1 molecule is described to be more or less simultaneous with the loss of one of its ester groups.[2] However, the IR method has poor sensitivity and such quantitative FTIR measurements are limited to thick samples (2 mm sheets) or to a high content of HAS-1 (up to 0.2 wt %) for films. Furthermore, at the end of the induction period, estimation of ester groups from the 1735 cm^{-1} absorption band is complicated by the overlapping carbonyl absorptions assigned to the oxidation products of the host polymer.

Moreover, FTIR analysis cannot be generalized to any HAS molecule, because this method is based on the monitoring of a strongly absorbing group linked to the original HAS–NH molecule. Then, HAS-1 appears as a really peculiar case.

Thus, FTIR measurements cannot be considered as a reliable method to follow the consumption of any HAS in any stabilized PP sample through oxidation.

Direct ESR

Stable nitroxyl radicals, postulated to be the key of the stabilization process, are easily detected in photooxidized systems by ESR spectroscopy.

Their concentration changes in the course of irradiation reflect the cyclic mechanism of HAS action as stabilizers, including consumption and regeneration of nitroxyl radicals.

In agreement with already published results, nitroxyl radicals are observed in really low concentration through photooxidation of stabilized PP films. Thus, poor ESR signals are obtained for PP samples originally containing a too-low concentration of HAS (down to 0.1 wt % for HAS-1).

Besides several regeneration mechanisms that have been proposed, it is now clear that, during photooxidation, the 2,2,6,6-tetramethylpiperidine-based additives convert through a series of oxidation products of HAS, several of which are themselves stabilizers.[2,7] Consequently, it is quite obvious that it is necessary to monitor *all species* involved in stabilization of the polymer throughout its oxidative lifetime.

Elsewhere, direct ESR spectroscopy cannot provide the residual concentration of intact HAS, which is not already involved in the stabilizing process, but consists in a "reservoir" of stabilizer at any time.

For these reasons, direct ESR could not be considered as an ideal method to follow the consumption of HAS in PP through oxidation.

Indirect ESR

The change of concentration of the overall piperidyl species, intact HAS (unreacted HAS) and all

of its oxidation products involved in the stabilizing cyclic process (reacted HAS), can be monitored by indirect ESR as a function of exposure time of PP films.

This so-called indirect ESR method involves conversion of all HAS derivatives into nitroxyl radicals by gaseous treatment of photooxidized samples with peracetic acid.

Similar approaches have been previously made.[4,5,8] Film samples were analyzed quantitatively at frequent intervals up to the embrittlement, after the separation of products into those that were extractable and those that were not extractable. The first were analyzed by gas chromatography, ESR, and liquid chromatography (high-performance liquid chromatography). The latter was estimated by direct or indirect ESR after the addition of a solution of *m*-chloroperbenzoic acid to preextracted film.

It should be pointed out that our indirect ESR technique appears to be an easier, faster, accurate, and very sensitive method.

Indeed, the entire procedure for conducting complete analysis of a given sample at various irradiation times exists to put peracetic acid vapor in close contact with the photooxidized stabilized PP films for 24 h. The reaction occurs *in situ* in solid state and at room temperature. Thus, no extraction, of which efficiency could be questionable, is needed. Finally, peracid treatment gives a strong ESR signal and affords a great sensitivity for detection of small amount of stabilizer and small changes.

We have shown that indirect ESR experiments provide important information on the time evolution of the HAS–NH stabilizer concentration on photooxidation of PP films. Unfortunately, it is clear that our method is not available to monitor the consumption of methylated HAS.

Nevertheless, further investigations are needed to fully generalize our experimental observations. For instance, the present work is devoted essentially to the low-molecular weight HAS-1, and our experimental data concern PP. Therefore, the study must be extended to other systems (e.g., other polyolefins or coatings, pigmented polymers, polymers stabilized with a mixture of additives, etc.).

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