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Polypropylene stabilization: during γ-irradiation and during post-γ storage*

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The effects of additives on the stability of γ-irradiated polypropylene film have been examined, both during irradiation and after prolonged post-irradiation reaction up to the embrittlement point. Additives were drawn from the tetramethylpiperidine family and compared with a conventional blocked phenol. Oxidation products from the polymer were determined by FTIR spectroscopy coupled with chemical derivatization. Polymer physical degradation was measured by an instrumented bend test. Although the stabilizers had very little effect on the radical products or oxidation products measured immediately after γ-irradiation, very different oxidation product levels and distributions were found at the onset of brittle failure. Brittle failure occurred at a very low level of total oxidation products for the well-stabilized samples as compared to the unstabilized samples. Nevertheless ketonic product levels were very similar in all cases and the levels of carboxylic acid and groups appreciably higher for the stabilized samples.

INTRODUCTION

Polypropylene medical equipment is being sterilized increasingly by γ- or electron beam irradiation. These processes are replacing the hazardous and environmentally destructive use of ethylene oxide/CFC mixtures which are vented into the atmosphere after use. For unstabilized polypropylene, polymer degradation occurs both during the high energy irradiation step and during subsequent post-irradiation storage. This latter effect appears to result predominantly from an oxidative process driven by the slow, thermal decomposition of hydroperoxide groups formed from peroxyl radicals produced by the irradiation.[1]

Phenolic antioxidants are extremely effective at preserving polymer physical properties during and after γ-irradiation, but at the expense of unacceptable colour formation.[1,2] New additives are being developed to overcome this limitation.[1–4]

The authors have previousy reported on the effects of some additives on the very early stages of the oxidation process (0–20 h), subsequent to γ-irradiation.[3] This paper explores the effects of various additives on the products generated both during the irradiation step and during the post-irradiation reactions, right up to embrittlement.

EXPERIMENTAL

Polypropylene (Himont 6501) was compounded with selected additives. Each compounded polymer sample was then injection moulded into $1{\cdot}25 \times 12{\cdot}5 \times 125\ \mathrm{mm}^3$ test strips and also melt pressed into film under a nitrogen blanket. Film thickness ranged from 60 to $90\ \mu\mathrm{m}$ and was determined for each sample by micrometer. The structure of the additives used are shown in Fig. 1, together with the abbreviations used in this paper.

The test strips were injection moulded through a gate central at one end of the strip. The sprue residue was used to index test locations along the

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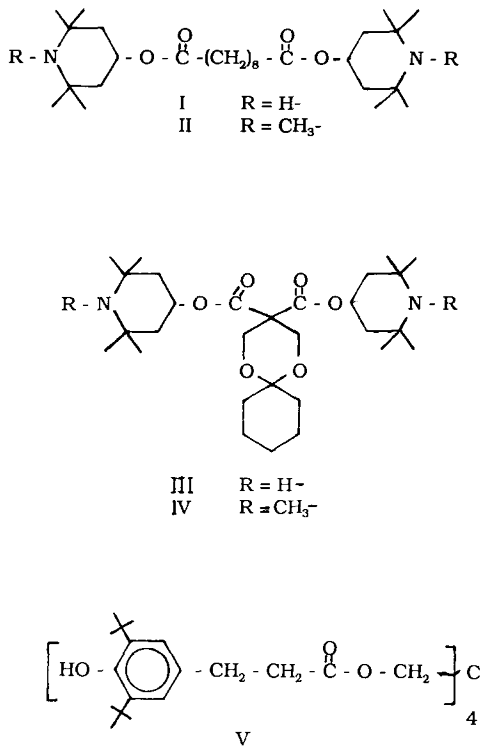


Fig. 1. Structures of the additives used in this study.

strips so as to compare data at regions of similar morphology.

Additives I and II are produced by Ciba-Geigy as Tinuvin 770, bis(2,2,6,6-tetramethyl-4-piperidinyl) decanedioate and Tinuvin 765, bis(1,2,2,6,6-pentamethyl-4-piperidinyl) decanedioate. Additives III, bis (2,2,6,6-tetramethyl-4-piperidinyl) 1,5-dioxaspiro [5,5] undecane-3,3-dicarboxylate and IV, bis(1,2,2,6,6-pentamethyl-4-piperidinyl) 1,5-dioxaspiro [5·5] undecane-3,3-dicarboxylate are produced by ICI Americas as Topanex 500 H and 516 H respectively. Additives I–IV are often referred to as HALS. Additive V, tetrakis-[methylene 3-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)-propionate] methane, is produced by Ciba Geigy as Irganox 1010. Additives were compounded individually at the 0·125 %wt level. All film samples, including the control, contained 0·10 %wt of the antiacid calcium stearate.

Films and test strips were γ-irradiated for pre-determined times in an AECL Gammacell 220 at 0·7 Mrad/h (7 KGy/h) in air. A normal sterilization dose of 2·5 Mrad (25 KGy) was used for all samples. The ambient temperature inside the cell was 35°C.

After γ-irradiation some samples were thermally oxidized at 60°C in a forced air oven to give an accelerated test of post-irradiation stability. During oven aging, film samples and test strips for a given formulation were isolated from one another inside 150-ml glass beakers covered by a loosely fitting Petri-dish lid. This was essential to prevent inter-sample ‘infection’ resulting from the vapour-phase transfer of some additives between samples at 60°C.

After γ-irradiation and various times at 60°C, film samples were analyzed by iodometry (reflux in acetic acid/propanol-2 with sodium iodide) to give total reactive peroxidic species (hydroperoxide, peracid and perester).[5] Other films were analyzed by transmission Fourier Transform Infrared (FTIR) spectroscopy (Perkin–Elmer 1500, DTGS detector, $4\,\text{cm}^{-1}$ resolution or Nicolet 7199, liquid nitrogen cooled MCT detector, $1{\cdot}8\,\text{cm}^{-1}$ resolution with 200 scans averaged in each case). To enhance the resolution of the FTIR technique, derivatization reactions were used as described previously.[5–7] These reactions comprised treatment with sulfur tetrafluoride (SF_4) gas, when all-OH species are destroyed and the broad, complex carboxylic acid absorption (1755–$1705\,\text{cm}^{-1}$) is replaced by the sharp acid fluoride absorptions at $1841\,\text{cm}^{-1}$ [$—CH(CH_3)C({=}O)F$] and $1848\,\text{cm}^{-1}$ [$—CH_2—C({=}O)F$]. In addition, the carbonyl product envelope becomes much easier to interpret after SF_4 destruction of hydrogen bonding species. In addition, other oxidized film samples were treated with gaseous nitric oxide (NO). NO converts primary, secondary and tertiary hydroperoxides into their corresponding nitrates which can be separately quantified by FTIR.[6] Furthermore NO reacts with primary, secondary and tertiary alcohol groups to form the corresponding nitrites with distinctive FTIR absorptions.

Free-radical species in irradiated film were identified and quantified by electron spin resonance (esr) spectroscopy (Varian X-band E4 spectrometer with computerized double integration).[8] Initial peroxyl radical yields were measured by double integration after irradiation of film scrolls at −78°C in air in the Gammacell. Cupric acetylacetonate was used to calibrate the esr spectrometer. After irradiation, films were stored for 15 h at −78°C in air to allow conversion of all alkyl radicals to peroxyl radicals before transfer of the film samples under liquid nitrogen into unirradiated esr tubes. The spectrometer was precooled to −140°C before recording each spectrum. The precise nature of the initial peroxyl radical mix resulting from the

γ-irradiation of stabilized films was again established by trapping the radicals as the corresponding nitrates through reaction with NO at -78°C.[8] The nitrates formed were identified and quantified by FTIR spectroscopy.

To explore the effects of the stabilizers on the rates of peroxyl radical decay, each initial spectrum was recorded after γ-irradiation at -78°C and then the films were quickly warmed by immersing each esr tube in water at 22°C. Spectra were recorded periodically during decay at room temperature. At chosen times, the decay was arrested by cooling in liquid nitrogen before radical quantification at -140°C.

Degradation of the physical properties of the test strips was measured by the use of an instrumented bend test. This was devised to simulate the dominant failure mode of irradiated polypropylene medical synringes (bend fracutre of the grip tabs on either side of the barrel during use). In this test, using the hinge system shown in Fig. 2, test strips were forced to bend around the 1·5-mm diameter hinge pin. The hinge system was driven by an Instron 1123 (load cell C, 25 kg full scale) with the hinge bend angle at failure being read from the pre-calibrated Instron chart output. Bend angles from flat (0°) up to 140° could be achieved. The use of a hinge-like support in our modified three-point-bend assembly constrains the sample so that it curves tightly around the central hinge pin, without additional bending of the sample on either side of the hinge pin. The test strip was accurately located in the machined channel of the hinge arms, and could be advanced under the hinge pin after installation as shown in Fig. 2. The tightly controlled nature of each bend allowed bend tests to be performed at 1·0-cm intervals along the length of each strip. Because of the systematic variation of bend failure along the strips resulting from morphological changes, bend failure was always averaged at three, 1-cm spaced points about the mid point of the injection moulded strips.

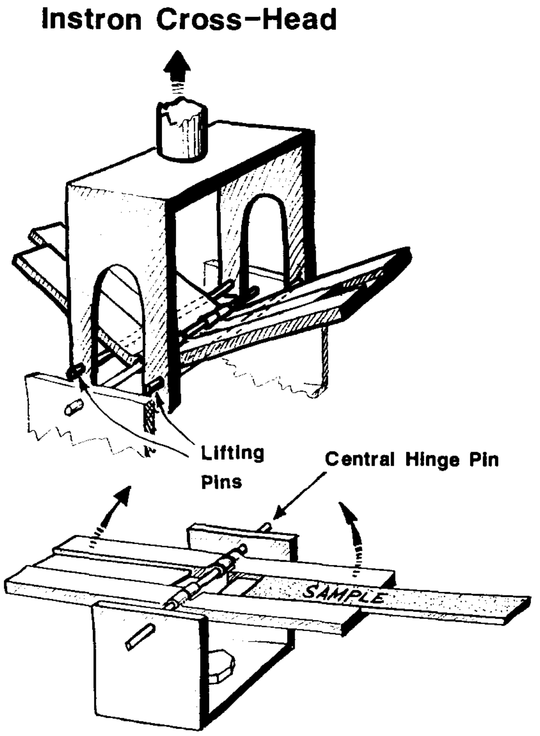


Fig. 2. Artists impression of the hinge-bend device. The lower component was bolted to the Instron base plate and the upper component connected to the load cell on the cross head. The sample shown is $1{\cdot}25 \times 12{\cdot}5 \times 125\ mm^3$ in size.

Load at failure was also measured for each bend test. However, load was quite insensitive to the degree of oxidative degradation except at very extensive degrees of degradation (>5 times the 100° bend-failure time). Because sample lifetime can exceed 400 days for well stabilized samples, bend test conditions were chosen to increase the severity of the test so that the onset of degradation could be detected. To do this, the hinge was closed as rapidly as practicable around the smallest practicable pin (1·5-mm diameter with a cross-head speed of 200 mm/min) after samples had been cooled in ice-water. The ice-water bath was removed immediately before bend testing. With this test procedure, sample temperatures were at 2 ± 0·5°C during the test, as measured by a thermocouple on several samples.

Because additives may nucleate the crystallization of polypropylene, all films were characterized by differential scanning calorimetery (DSC, TA Instruments 910 DSC system coupled to their 2100 Thermal Analyzer Controller).

RESULTS

Stabilizer changes and oxidation product generation were measured both immediaely after irradiation and during the subsequent aging at 60°C.

Immediate results of irradiation

Peroxyl radicals in PP neither propagate nor terminate at ≤ -60°C.[7] In order to compare the concentration of peroxyl radical, yields were measured for control and stabilized film samples after irradiation in air at −78°C (immersed in Dry Ice). Films were held at this temperature for 15 h to allow complete conversion of any residual traces of alkyl radicals to peroxyl. Within the limits of double integration, all stabilized samples had peroxyl yields identical to the control sample ($1{\cdot}2 \times 10^{-3}$ mole/kg for each 1 Mrad dose). These initial peroxyl radicals were trapped by reaction with nitric oxide at −78°C to form the corresponding nitrates as described previously.[8]

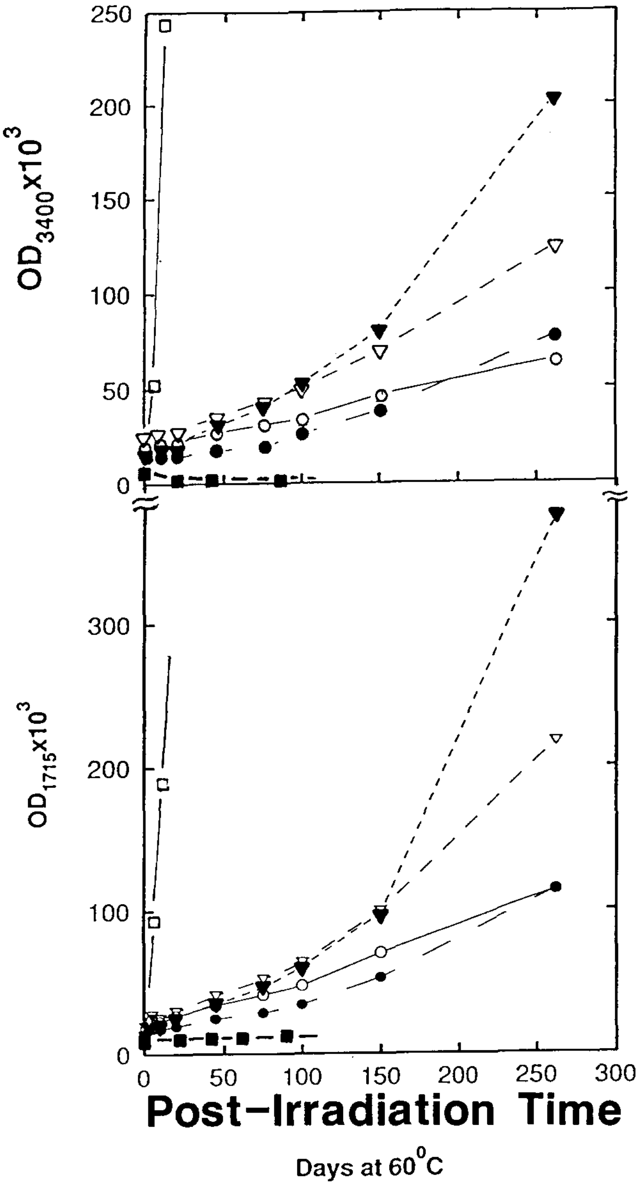


Fig. 3. IR optical density changes for γ-irradiated films, oven aged at 60°C. □, Control; ▽, additive III (sec. HALS); ○, additive I (sec. HALS); ▼, additive IV (tert. HALS); ●, additive II (tert. HALS); ■, additive V (phenolic). Film thicknesses 80 ± 5 μm. All additives at 0·12 %wt.

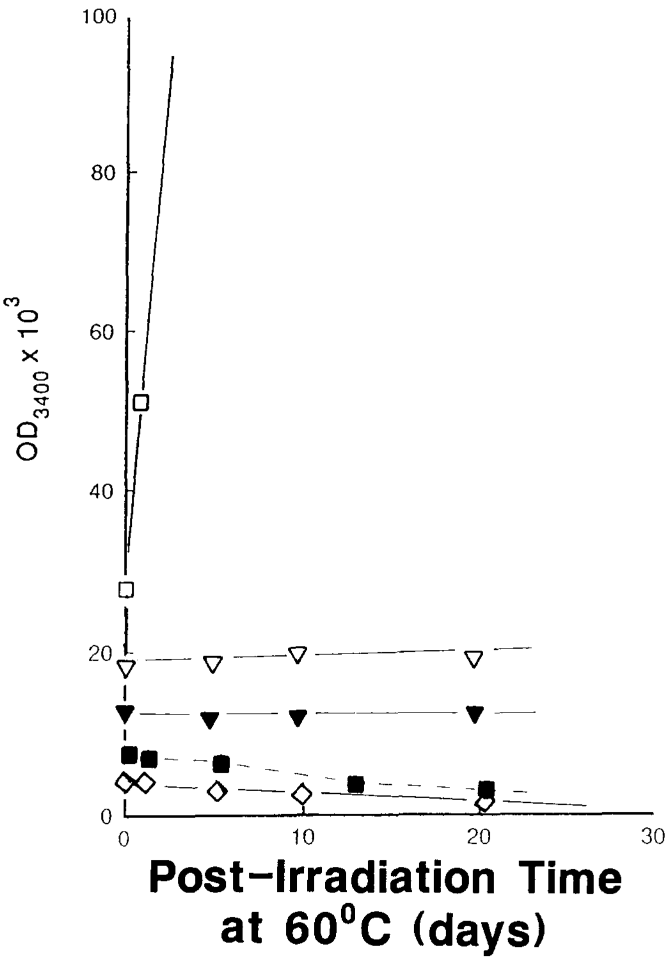


Fig. 4. IR optical density changes for γ-irradiated films. Early stages of oven aging at 60°C. Symbols as in Fig. 3.

The nitrate mix was identified and quantified by FTIR. The ratio of tertiary to secondary to primary nitrates was 1·2:0·2:0:0·3 for all samples including the stabilizer-free control. Although these experiments could only be performed at well below ambient temperature, they imply that the additives studied (at 0·12 %wt) are unlikely to participate in the very fast reactions leading to the formation of the initial peroxyl radicals.

For samples irradiated at ambient temperature in the Gammacell (~35°C), the $3400\,\mathrm{cm}^{-1}$ absorbance immediately after irradiation indicated the presence of —OH species in all samples (Figs 3 and 4). Application of the NO exposure method to samples immediately after irradiation at ambient temperature showed that negligible alcohol was present and that the main —OH species were sec. and tert. hydroperoxide (Table 1).

The phenolic additive was extensively attacked during irradiation as was shown by the decrease

Table 1. γ**-Irradiation of iPP—products immediately after irradiation**[a]

Additive (0·12 %wt)	[tert-OOH][b]	[sec-OOH][b]	Additive unchanged (%)[c]
—	32	11	—
Hindered phenol (V)	15	7	42[c]
sec. HALS (III)	23	9	100[d]
Phenol (V) + sec. HALS (III)	9	5	—

[a] 2·5 Mrad dose in air at ambient.
[b] Concentrations mmole/kg. Analysis by NO reaction within 1 h of irradiation.
[c] From FTIR changes at 3645 cm^{-1} (phenolic —OH).
[d] From FTIR changes at 1740 cm^{-1} (ester bridge) and esr (nitroxide formation).

of the phenolic —OH absorption at 3649 cm^{-1} (Table 1). In contrast, no nitroxide was detected by esr in any of the piperidine-containing, irradiation samples immediately after a standard sterilization dose (2·5 Mrad).

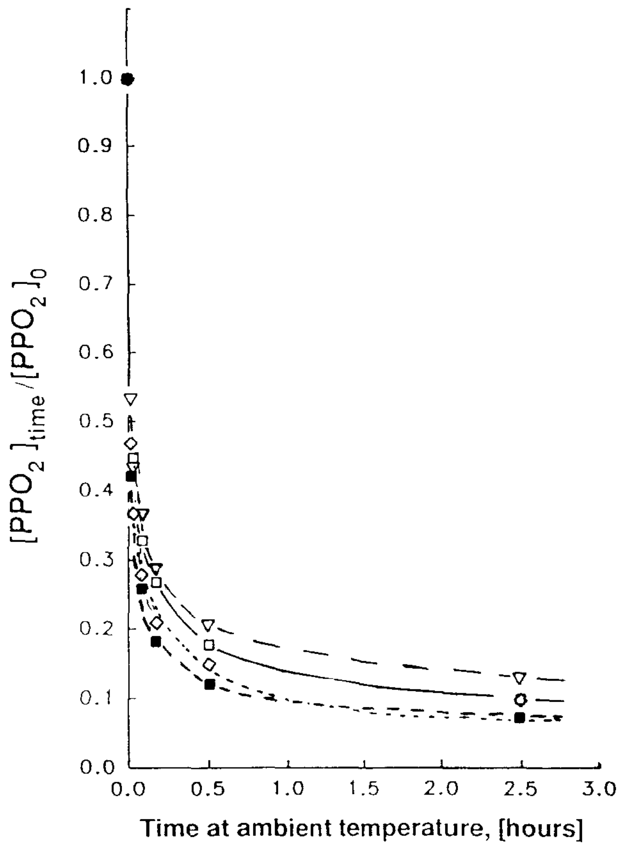


Fig. 5. Relative rates of peroxyl radical decay at 22°C in γ-irradiated film. Films were initially γ-irradiated at −78°C in air. □, Control or additive I or additive II; ▽, additive III (sec. HALS); ■, additive V (phenolic); ◇, additive V + additive III.

Post-irradiation degradation

When a population of peroxyl radicals was generated by irradiation at −78°C in air, upon warming to 22°C, a rapid initial decay occurred for all samples (Fig. 5). Alkyl radical formation was not detected even when spectra were recorded at very low microwave power to avoid saturation of any alkyl signal.[8] Small differences in the rate of peroxyl decay were observed between the various stabilized samples (Fig. 5). Samples containing the phenol V showed a somewhat faster peroxyl decay than all other samples. The authors have previously shown that radical decay is strongly dependent on polymer morphology differences which may result from small nucleation effects caused by additives. DSC scans of the as-prepared films showed only minor variations in thermal properties and hence morphology. For example the maximum of the crystalline melt endotherm and the heat of fusion (corrected for some permelting at −42°C) were 161·1°C and 86·4 J/g (control), 161·2°C and 90·9 J/g (additive IV), 162·9°C and 89·2 J/g (additive V) and 161·0°C and 91·3 J/g (additive I plus additive V).

For amine-containing samples, although nitroxide was undetectable immediately after irradiation, nitroxide radical signals grew during peroxyl signal decay as has been reported previously.[3]

Irradiated films and test strips were stored at 60°C after irradiation in order to compare the effectiveness of the stabilizers within a tractable test duration. Test strips were periodically subjected to the hinge bend test. Immediately after γ-irradiation in air at ~35°C, the samples (including the unstabilized control) did not fail at the most acute angle that could be attained on the equipment used here (140° bend). However, the angle of bend failure dropped dramatically for the control after only a few hours storage at 60°C in air (Fig. 6). High levels of oxidation caused the bend failure angle to actually increase again, possibly as a result of plasticization by the high level of products from oxidative chain scission. Stabilized samples showed a slow decline in bend failure angle (Fig. 6).

IR spectral changes at 3400 cm^{-1} (—OH region) and ~1715 cm^{-1} (carbonyl region) have been extensively used to give a broad indication

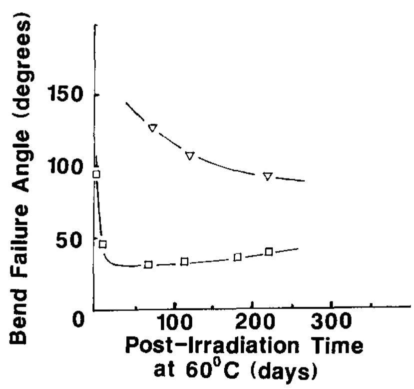


Fig. 6. Bend failure angle of irradiated strips. □, Control; ▽, additive III (sec. HALS).

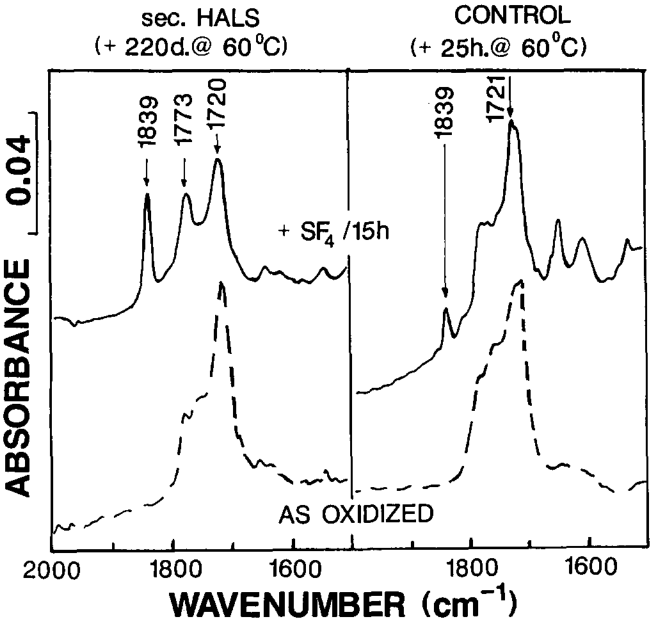


Fig. 7. IR carbonyl envelope for films oven aged to 100° bend failure point. ----, Films as oxidized; ——, oxidized films after 15h SF$_4$ treatment. Sec. HALS was additive I or III. Tert. HALS and phenolic antioxidant showed IR spectra very similar to that of the sec. HALS (but at longer times to failure).

of the extent of PP oxidation.[1-3] Actual spectra are not shown here, but are very similar to those reported previously.[9] Overall IR absorbance changes for films stored at 60°C after γ-irradiation are shown in Fig. 3 for the —OH (~3400 cm^{-1}) and carbonyl (~1715 cm^{-1}) regions. This data extends to beyond the bend failure of the control (~25 h) and the secondary amine stabilized samples (~220 days). Bend failure was chosen arbitrarily as the time of first failure at a bend angle of 100° in the hinge bend test on the 1·25-mm test strips. These strips had been exposed to identical γ-irradiation followed by 60°C storage as for the film samples.

The early stages of post-irradiation oxidation show a clear difference between amine, phenol and unstabilized film in the —OH region (Figs 3 and 4). Unstabilized samples show a very rapid growth of —OH products, whereas amine-containing samples show only a slow growth. In marked contrast, the phenol I containing film show a steady decline in —OH species.

In order to compare the oxidation product mix for samples degraded to the same (arbitrary) bend failure point, IR spectra of films were recorded on all samples after a standard γ-irradiation and then progressive oven aging at 60°C up to a time corresponding to the failure of test strips at the 100° bend angle. Both the control, amine stabilized and phenol stabilized films showed virtually identical carbonyl IR envelopes at failure (Fig. 7). After SF$_4$ treatment, however, the IR of the unstabilized control indicated a product mix distinctly different from that in the well stabilized samples (Fig. 7). Detailed product analyses from IR derivatization are shown in Table 2.

Table 2. Polypropylene oxidation products from 2·5 Mrad γ-irradiation

Sample	Time at 60°C (days)	Oxidation product (mmole/kg)					
		Total —OH	sec. OOH	tert. OOH	>C=O	—C(=O)OH	>C=O / —C(=O)OH
Control	0	48	11	32	12	3	~4
	1·0[a]	220	45	120	50	4	~12
sec. HALS,	0	39	9	23	10	2	~5
III (0·12 %wt)	220·0[a]	60	ND[b]	ND[b]	38	10	~4
Phenol V	0	30	7	15	7	2	3·5
(0·12 %wt)	395·0[a]	59	12	40	51	14	~3·5

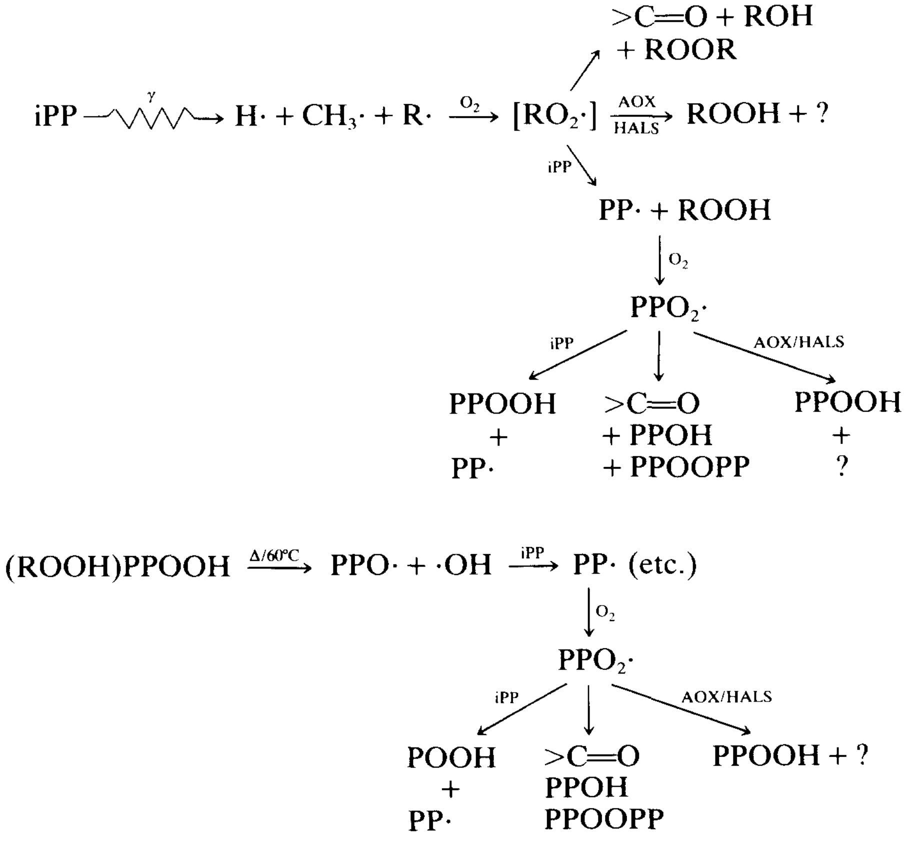
[a] Time in oven at 60°C to failure of 1·25-mm thick strips when bent through 100°.
[b] Not determined.

DISCUSSION

Within esr experimental error, neither the phenolic antioxidant nor the hindered amines affected the formation of peroxyl radicals from polypropylene during the irradiation at −78°. Total peroxyl levels were insensitive to the presence or absence of the additives at 0·12 %wt, as were the relative proportion of sec. and tert. peroxyl species measured by trapping with NO. Peroxyl radical decay at 22°C showed some variation with the additive content, phenol-containing samples showing a slightly faster decay rate than other samples (Fig. 5). The hydroperoxide levels measured immediately after the irradiation step at ambient temperature decreased in the sequence: control > sec. HALS > phenol > (phenol + sec. HALS) (Table 1). Both sec. and tert. hydroperoxide formation was reduced in this order although tert. hydroperoxides were most affected. This is consistent with tert. hydroperoxides resulting from an oxidative reaction with a longer kinetic chain length than the sec. hydroperoxides. Formation of the latter competes with the fast termination of sec. peroxyl radicals.

The phenol was extensively attacked in the oxidation process which accompanied irradiation at ambient temperature. This was shown by the decrease of the 3645 cm^{-1} absorption of the phenolic —OH. After a 2·5 Mrad irradiation, only ~40% of the original phenolic OH groups remained.

Comparison of the oxidation products immediately after irradiation and then at the bend-failure point clearly shows the effect of amine and phenol additives (Fig. 7 and Table 2). As compared to the control, the phenol markedly suppressed sec. and tert. hydroperoxide formation during irradiation, as did the sec. amines although to a lesser extent. At the brittle-failure point, both phenol and sec.-amine stabilized films showed quite similar product levels (although at quite different oxidation times at 60°C) which differed strongly from the control at brittle failure (Table 2). Stabilized samples showed only a relatively small accumulation of hydroperoxides whereas this product clearly dominated in the control. In addition, sec. carboxylic acid groups had increased significantly in the stabilized film, but showed only a marginal increase in the control. This group must come from backbone

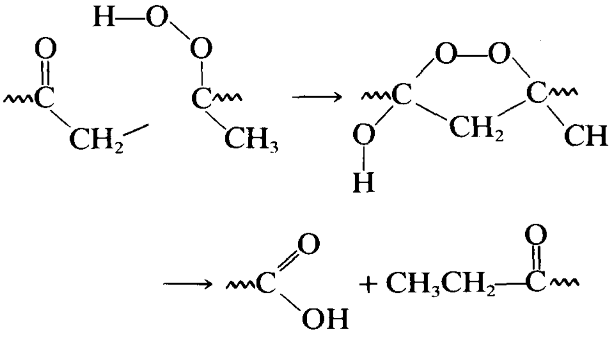


Scheme 1. γ-Degradation/stabilization.

scission and implies an important cause of embrittlement in the stabilized samples. Chain-end ketone groups can be expected to form part of the overall ketone yield but could not be resolved from the in-chain analogue (absorptions at 1724–1718 cm^{-1}).

The post-irradiation time dependence of the bend failure angle (Fig. 6) implies very different rates of accumulation of chain scission products for stabilized and non-stabilized samples. It is quite possible that failure at any one bend angle corresponds to the same number of backbone scissions.

In broad outline, the radiation-induced oxidation of PP in the presence of additives is given by Scheme 1. Additives can react both with the atypical peroxyl radicals ($RO_2\cdot$) produced as a direct consequence of radiation damage of the polymer, as well as with the conventional peroxyl radicals resulting from propagation. During oven aging at 60°C, additives can scavenge peroxyl radicals and possibly alkyl radicals (in the case of nitroxides) which are formed as the result of hydroperoxide thermal decomposition. This is the most likely cause of the low hydroperoxide yield in the stabilized samples at the brittle failure point. The increased importance of carboxylic acid groups in the stabilized samples as compared to the control suggests that the acid results from a slow, non-radical process. This could be a relatively insignificant process during the short lifetime of the control, but becomes much more apparent over the protracted lifetimes of the stabilized samples. This proposal is consistent with carboxylic acid concentration being highest in the most stable sample (Table 2). A possible non-radical route to the acid might be the thermal decomposition at 60°C of 1,3-ketohydroperoxides through a hemi-peroxyketal intermediate (reaction 1).



(1)

Jensen *et al.* have proposed that an analogous reaction is a major source of carboxylic acid in the thermal oxidation of hexadecane at 160°C.[10] The 1,3-ketohydroperoxide group is a reasonable conversion product from the intramolecular oxidation leading to 1,3,5... runs of hydroperoxide sites.

CONCLUSIONS

Both phenol and piperidine-based stabilizers protect polypropylene against the effects of γ-sterilization doses. Although none of these additives affected the initial fromation of peroxyl radicals during the irradiation step, they subsequently suppressed hydroperoxide formation during the slow 60°C oxidating, possibly by peroxyl radical scavenging. At equivalent brittle failure points, stabilized samples showed little total hydroperoxide as compared to the control. Surprisingly high levels of the chain scission product, carboxylic acid end groups, were found in the long-lived, stabilized samples.

ACKNOWLEDGEMENT

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