Oxidation of Stabilized Polypropylenes

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ABSTRACT: Reaction rates of stabilized polypropylene films with oxygen have been investigated during the induction periods in photooxidations at 35 °C and in thermal oxidations at 90–150 °C, with the object of devising a reliable prediction of service life (time to brittleness). Of the several methods tried, the best is measuring by gas chromatography the oxygen depletion from air in a small cell. In photooxidation, with some films containing a single stabilizer, smooth plots of oxygen consumption against time might permit prediction of lifetimes, but with other single stabilizers and some combinations, prediction would be very difficult. The most important finding is that in a stabilizer combination containing a peroxide decomposer, the time to brittleness does not depend on the total light exposure or the oxygen consumed as much as on the light intensity during continuous illumination and on dark periods during intermittent illumination. More time available to the peroxide decomposer permits it to decompose more hydroperoxide. The most durable films often have absorbed the most oxygen at brittleness. Accelerated tests with high continuous light intensities must therefore underestimate the effects of peroxide decomposers. In photooxidations, the rate also depends on oxygen pressure; initiation may occur by reaction of oxygen with stabilizer. In thermal oxidations, oxygen consumption during the induction period is immeasurably slow, but then it increases very abruptly, making predictions difficult. However, depletion of stabilizer at or below 150 °C can be easily followed by thermogravimetric analysis at 176 °C and useful lifetime predictions may be possible. Several films were exposed to γ radiation before oxidation in a search for an accelerated aging test. The induction periods were always shortened by the radiation, but its usefulness in a test is limited.

Prediction and extension of service lives have always been major problems in the polymer industry. Many efforts to extend service life have been successful, but efforts to predict service life have not. The testing situation has been neatly summarized by Bakker: "There seem to be two widely separated views. One is that these artificial or accelerated tests are indicative of service performance, and the other is that they mean absolutely nothing. As usual, the true answer is probably between the two extremes."[1] Nevertheless, certain standard tests are widely used, apparently because both buyers and sellers specify that polymers shall meet these tests and because they provide a rough comparison of polymer stabilities, but the relation to actual service life is dubious.

Upon exposure to light or heat, polyolefins usually exhibit an induction period (IP), during which little oxygen uptake or change in physical properties is observed, followed by a period of rapid change and abrupt failure. The original object of this work was to predict lifetimes (time to brittleness) of stabilized polypropylene (PP) films under specified conditions by measuring the early, but slight, rate of oxidation and extrapolating these data to failure. However, we found that oxygen absorption at failure depends on light intensity and dark periods. We conclude that the desired predictive test should probably be based on measurements of chain cleavage and cross-linking.

Oswald and Turi[2] have reported a careful study of oxygen absorption by PP, mostly unstabilized and mostly at 75 °C, in 100% oxygen, along with measurements of physical properties. Oxygen uptake became very rapid at about 20 h, but the viscosity, density, ultimate elongation, and ultimate tensile strength began to decrease gradually at about 5 h. At 25 h the ultimate elongation approached zero, but the sample still retained 40% of its ultimate tensile strength. With added stabilizers at 100–140 °C, relations varied.

Another approach to measuring reactions during IPs is Vink's,[3] which measured the rates of disappearance of three types of stabilizers in the photooxidation of PP and found three types of reactions, zero order, decreasing rate of disappearance, and a relation to the oxidation rate of PP. Many papers have dealt with transformations of stabilizers during IPs without relating these to oxidations of the polymers.

Experimental Details

Photooxidations. Our light source was an Illumination Industries 500-W high-pressure mercury lamp, fitted with 5-cm quartz collimating lens at a distance of 12.5 cm. Radiation <290 nm was eliminated with a Corning 0-53 UV cutoff filter and radiation >900 nm by an external water-cooled IR trap. However, the pressure in the cell increased by 0.25–0.8 torr when the light was turned on.

Our first photooxidations were followed by pressure changes in a small cell. A modification of Nemzek's cell[4] for measuring pressure changes was used for the measurement of oxygen consumption. The 316 stainless steel cell was about 5 cm in diameter and had a quartz window, a total volume of 5 mL, a Nupro SS-4BKT bellows valve, and a septum port for sampling. A 5-cm-diameter film was placed in the cell, which was then evacuated to 1 μm (0.13 Pa) for 30 min and filled to ambient pressure with a synthetic 79/21 nitrogen/oxygen mixture. The 25-μL samples were removed through the septum with a gastight locking syringe, compressed to operating pressure within the chromatograph, and injected into a 2.44 m × 0.32 cm SS column at 0 °C packed with 80–100 mesh 13X molecular sieves. He carrier was used at a 30 mL/min flow rate. The nitrogen served as a standard for calibrating the thermal conductivity detector and measuring the oxygen. Corrections for gas withdrawals were made. Detector response was linear for 1–98% O_2 concentration, and a sensitivity of 0.1 ppm could be routinely maintained. The activity of the 13X molecular sieves was a function of the amount of H_2O injected into the column and that present in the carrier gas. The column must be periodically reactivated with dry N_2 at 450 °C for 2 h when peak separation becomes ≥1 min.

We next tried to follow the photooxidation of PP films by evolution of the water vapor formed. The gold–aluminum oxide hygrometer probe was very sensitive and generally unaffected by volatile oxidation products. We used an Ondyne Model 31 probe equipped with a Series 1400 digital meter that was specially adapted for use in our 155-mL, all-Pyrex reaction cell. Because of water/glass interactions, the reaction cell first was thoroughly silylated, using Petrarch's 10% solution of (dimethylamino)trimethylsilane[5] in toluene. To establish equilibrium before light aging, the reaction cell, with sample, was evacuated to 5 μm (0.65 Pa) and then purged with dry N_2 at 5 mL/min for 6 h at 35 °C. The purge gas was then changed to dry, low-hydrocarbon ("zero grade") oxygen at the same rate for 1 h. The isolated cell was then equilibrated for 16 h in the 35 °C water bath. The meter value was then recorded, and oxidation was begun with the lamp and filters described above.

Thermal Oxidations. For some thermal oxidations, the oxygen method described was modified as follows. A 1.0-g sample

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Table I
Properties of Unaged PP Films

film desig	manufacturer	stabilizers/concn, wt %	thickness, mils	strain at break, psi	elongation at break, %
C	Exxon	BHT/calcium stearate/DSTDP/3114	3.5		300
D	Northern Petrochemical	Irganox 1010/0.14%, BHT/0.16%, calcium stearate/0.1%	3.7	1300	300
F	Ciba-Geigy	Tinuvin 770/0.25%, Irganox 1076/0.2%	4.3	1490	550
G	Exxon	none	5.1	3290	1200
H	Exxon	BHT/0.05%	4.3	3160	1200
I	Exxon	DSTDP/0.15%, Irganox 1010/0.05%	4.7	2810	1100
J	Shell	Ethanox 330/0.1%	1.1	1090	590
S	Exxon	BHT/460 ppm, Tinuvin 770/2000 ppm, W-618/500 ppm	3.9	650	450

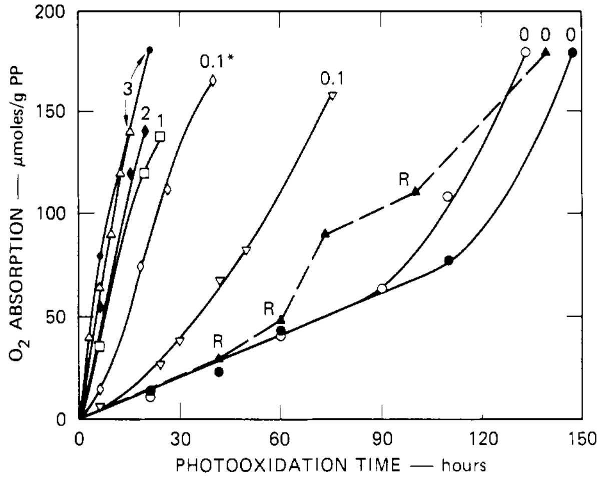

Figure 1. Oxygen absorption by film I in photooxidations at 35 °C. R indicates replenishment of oxygen. The number on each curve indicates the exposure to ^{60}Co γ radiation in megarads before illumination. The asterisk indicates that film was heated for 20 min at 150 °C between irradiation and illumination to destroy peroxides.

was put in a 2.8 × 14.5 cm Pyrex tube with a 24/40 ground glass joint and a 6 mm o.d. × 2.5 cm side arm. To permit sampling with a gastight locking syringe, a 6-mm SS union with Teflon ferrules was placed on the side arm and a gas chromatography (GC) septum fitted to the other end. The upper joint, equipped with a vacuum stopcock and a 12/20 joint, was placed on the tube, evacuated to 1 μm for 30 min, and filled to ambient pressure with 79/21 nitrogen/oxygen. A 25-μL was taken for each oxygen determination by the method described above. This cell was modified later to reduce its total volume to 23 mL and to permit immersion of 95% of the cell volume in the oil bath.

Our thermal oxidations started with a procedure like that introduced by Nemzek.[4] Most samples were aged thermally at 150 °C in an 39-L convection oven with a forced air flow of 20 mL/min. Film samples were removed at intervals and examined by isothermal thermogravimetric analysis (TGA) and by IR spectroscopy. Fusion and contraction of PP film samples in the TGA, which generally occur at 170 °C, were prevented and access of air was facilitated by coiling samples with 165-mesh, 316 stainless steel gauze.

Samples were then examined by isothermal TGA at 176 °C, which measures the amounts of stabilizers surviving previous exposures at lower temperatures. TGA analyses were carried out on 20–60-mg samples with a Cahn RG-2000 electrobalance with a 5 mL/min air flow over the sample. Weight and temperature were recorded simultaneously, using a type K (chromel–alumel) thermocouple positioned near the sample. After remaining constant during the IP at 176 °C, the sample weight usually increased abruptly by 0.5–1.0 mg and then decreased at a steady rate. The IP at 176 °C decreased from several hours for a well-stabilized PP to zero for an embrittled PP.

This old thermogravimetric analyzer eventually failed and work was continued with a DuPont high-pressure differential scanning calorimeter (DSC) thermal analyzer. Results with the two instruments should be equivalent in measuring ends of IPs at 176 °C.

To measure oxidations of PP films during oxidations at 150 °C, oxygen consumption and water formation were measured by GC. Film samples were thermally aged by coiling them with stainless steel gauze in a 20-cm Pyrex tube with a side arm, capping the tube with an inert septum, evacuating via the side arm, and sealing. The evacuated tube was then filled to ambient pressure with a dry 80/20 argon/oxygen mixture, using a long syringe needle. Gas samples were taken through a gas-sampling syringe. Subsequent analyses were performed on a 1.83 m × 0.32 cm SS column with a Porpak Q solid phase, with a thermoconductivity detector at 250-mV sensitivity; the temperature program was 50 °C for 3 min, 20 °C/min to 110 °C, and hold for 1 min. The important oxidation products were H_2O and CO_2; O_2 was estimated from the Ar/O_2 peak areas.

γ Irradiations. Irradiations were made in containers under water at 15 °C with the SRI ^{60}Co source, which provided 20 000 (rd/cm^2)/h at the distance used. Dose calculations assume a planar sample perpendicular to a line to the source.

Films Used. Table I lists the films used in this work, their stabilizer systems, and their tensile properties.

Results and Discussion

A. Photooxidations. Pressure Change. Previous work in this laboratory[4] showed that measurement of pressure changes during IPs is possible with a small cell, using a sensitive pressure transducer. With the light source described and a modification of the Nemzek cell,[4] we obtained smooth curves for pressure decrease in torr against illumination time in hours in two experiments. With unstabilized film G, the empirical expression $\Delta p = 0.0188t^2 + 0.00222t^3$ fitted the experimental points within experimental error up to the point where the film became brittle at 32 h. With film H, stabilized only with BHT, the expression $\Delta p = 0.20t + 0.0003t^3$ fitted the experimental data to embrittlement at 62 h. These results offered promise of predicting lifetimes. However, this technique measures net pressure change, oxygen consumption offset by evolution of water and carbon dioxide (about 1% by Figure 9). Because the apparatus was unreliable over long periods, the method was abandoned when the direct measurement of oxygen concentration by GC became available.

Water Formation. An effort was made to follow photooxidation of a PP film by measuring the water formed with an Ondyne Model 31 gold–aluminum oxide hygrometer probe. Even after silylation of the 155-mL Pyrex cell and careful equilibration with dry oxygen, the results were too erratic to permit predictions of rates or lifetimes. The difficulty appeared to be with absorption and desorption of water on the cell wall and not in the sensitivity of the instrument. In our best experiment with 0.4577 g of unstabilized film G in a 7-cm-diameter disk, the millimoles of water formed approximated 0.89 + 0.39t (in hours) until the film became brittle in 55 h.

Oxygen Consumption by Gas Chromatography. Our most successful method for following oxidations during IPs

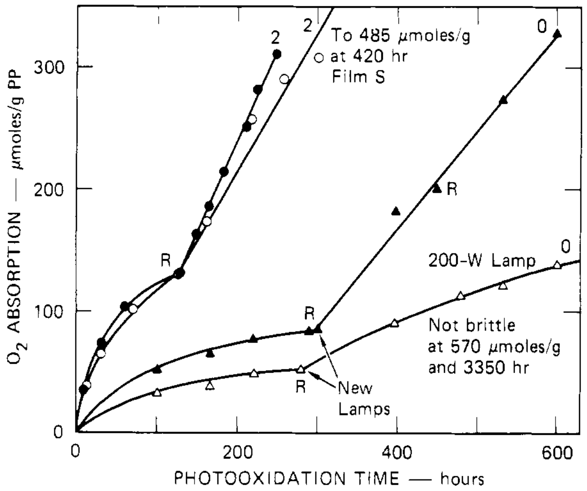

Figure 2. Oxygen absorption of film F (and film S as marked) in photooxidations at 35 °C. R and numbers have the same significance as in Figure 1.

measured oxygen consumption by GC. Figure 1 summarizes data on film I, containing a peroxide decomposer and phenolic inhibitor. Two experiments show a low, steady rate of oxygen absorption for 65–75% of film I's useful life and then an increasing oxidation rate during the remaining life. This increased oxidation rate during the last period makes predicting time to brittleness from early rate measurements difficult. The result may be due to two stabilizers in contrast to the use of one or none in experiments at the beginning of this section. In this and other figures, films were brittle at the last experimental point, except as indicated.

Preirradiation with γ rays was introduced in an effort to shorten reaction times. The other experiments in Figure 1 show that increasing doses of γ radiation before illumination accelerate the oxidation rate from the beginning of illumination but do not help to predict failure.

The γ radiation should either deplete the stabilizer system or produce stable hydroperoxides;[6] either promotes subsequent photooxidation. In one experiment, at the lowest dose, the film was heated for 20 min at 150 °C under vacuum before photooxidation. Because this film then oxidized about twice as fast as the unheated film, the net effect of the heating appears to have been at least partial destruction of stabilizer, perhaps by peroxides.

Figure 2 summarizes results with film F, which contained both a phenolic and a hindered piperidine stabilizer. With our 500-W lamp, in comparison with film I, it has twice the lifetime and absorbs almost twice as much oxygen before it becomes brittle. Film F absorbs appreciable oxygen initially; oxidation then slows but increases again when the oxygen supply is replenished. Such a relationship makes lifetime prediction difficult.

With 2 Mrd of γ radiation, the lifetime of film F was reduced by about two-thirds, but the oxygen absorption at failure and the curve shapes remained similar. It is possible that γ radiation will be useful in shortening the very long test periods required for such stable films.

Film S, containing the same hindered piperidine but also a phosphite ester peroxide decomposer, with 2 Mrd of γ radiation behaved like film F during the first 130 h but then absorbed more oxygen less rapidly, with a 50% longer time to embrittlement.

Effect of Light Intensity. To determine the effect of light intensity with film F, we carried out parallel experiments with a 200-W high-pressure mercury lamp as well as our usual 500-W lamp. In both experiments, the lamps failed at about the same time and were replaced. The acceleration of oxidation after lamp change is thought to be caused by both the lamp change and replenishment of the oxygen supply. The oxygen absorption curves in Figure 2 have similar shapes; at lamp replacement 58% more oxygen has been absorbed in the 500-W run than in the 200-W run. Thereafter, the difference between the two runs becomes greater. The 500-W film became brittle after absorbing 335 mmol of oxygen/g of PP after 610 h, but the 200-W film was still *not* brittle after absorbing 570 mmol of oxygen at 3350 h, the highest oxygen absorption that we measured: 2.4 mol % on the PP units. We propose that at lower light intensity, the peroxide decomposer in the stabilizer package has more time to exert its effect; the implications of these results are discussed in the Summary and Conclusions.

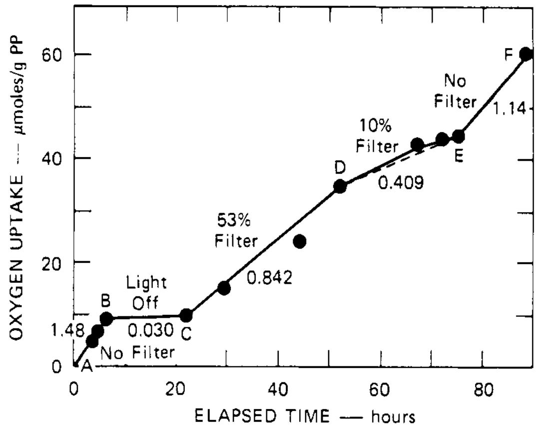

Figure 3. Effects of neutral density filters on rate of photooxidation of film I at 35 °C. Numbers are slopes of indicated line segments.

For a better measure of the effects of light intensity on oxidation rate, we established a steady rate of oxidation on film I with unfiltered light, measured the rate with two neutral-density filters, and checked the rate with no filter.

Figure 3 shows the effects of Oriel Inconel UV-transmitting neutral-density filters 5067 and 5070, which pass 53% and 10%, respectively, of the incident radiation. The slopes of the various line segments, shown in the middle of each segment, correspond to the rates of oxygen absorption in millimoles (g of PP)$^{-1}$ h^{-1}. Inserting the 53% transmission filter at point C reduced the slope from 1.48 between A and B to 0.842 between C and D, a change corresponding to oxidation rate = intensity$^{1.02}$. The rate with the 10% filter between D and E, 0.409, increases to 1.14 with unfiltered light between G and H, a change corresponding to an intensity exponent of 0.444. These results need to be checked and extended, but the film contained a peroxide decomposer (Table I).

Literature results on the effects of light intensity in the absence of a peroxide decomposer are simpler. Vink and Van Veen[7] measured the rates of oxygen absorption and disappearance of 2-hydroxy-4-(octyloxy)benzophenone as a function of light intensity with a high-pressure mercury lamp and Pyrex filter. The stabilizer disappeared in a zero-order reaction during most of the IP. For the stabilized polymer, the IP was proportional to (light intensity)$^{-0.9}$ (−1.0 expected for a good radical scavenger), but for the unstabilized polymer or one containing a light-absorbing benzotriazole stabilizer, the exponent was the expected −0.5. They point out that the different responses of different light stabilizers may account for the poor correlation of artificial and outdoor tests.

Kollman and Wood[8] measured times to embrittlement of PP films, some containing an unspecified phenolic

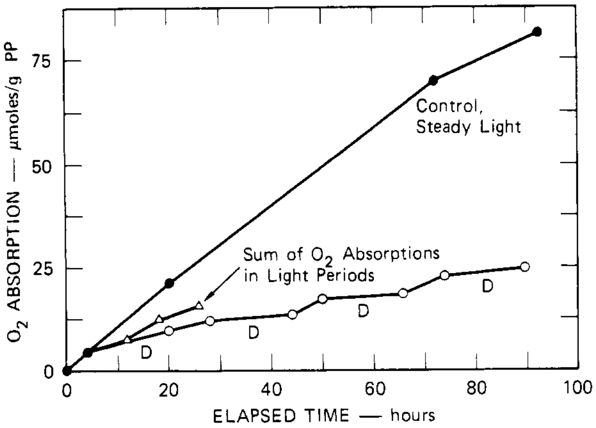

Figure 4. Effects of interrupted illumination on photooxidations of film S at 35 °C. D indicates dark periods. None of these films became brittle.

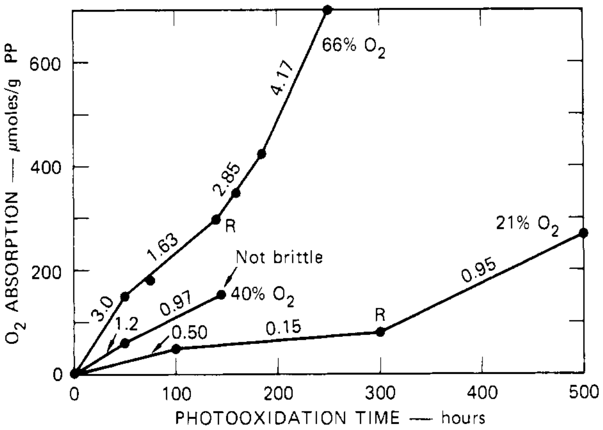

Figure 5. Oxygen absorption by film F in photooxidations at 35 °C at various concentrations of oxygen. R has the same significance as in Figure 1. Numbers on curves are rates of O_2 absorption per gram of PP per hour.

stabilizer. The results are compared in terms of the relation (time to failure)$^{-1}$ = X(light intensity)^{Y}. With 280–400-nm radiation, Y was 0.57 for unstabilized films and 0.87 for stabilized films, thus supporting the conclusions of Vink and Van Veen, but with 254-nm radiation, Y was 0.27 and 0.53. The X and Y values are uncertain: a high Y value is compensated by a high X value, and so on.

Effect of Intermittent Illumination. Figure 4 shows that the oxygen absorption per hour of illumination is decreased substantially with intermittent illumination, probably because the peroxide decomposer is more effective.

Effect of Oxygen Concentration. Figure 5 shows the oxidation rates of film F at three oxygen concentrations in nitrogen at a total pressure of 1 atm. The rate of oxygen absorption increases with the oxygen concentration but the quantitative relations are less clear: there are indications of both experimental error (initial and final rates at 21% O_2) and oxygen depletion. However, as judged by either the initial or overall rates, the dependence on oxygen is at least first order between 21 and 40% oxygen and about 1.5 order between 40 and 66% oxygen. Because no such effects appear in the oxidation of pure hydrocarbons, the stabilizers are apparently involved in oxygen consumption and chain initiation.

The best known effect of oxygen pressure on the oxidation rate of a polymer is the change in termination mechanism from $2RO_2\cdot$ to $RO_2\cdot + R\cdot$ as the oxygen is depleted; the rate of termination increases and the rate of oxidation decreases.[9] The efficiency of initiation in solid PP increases with increasing oxygen pressure.[10] There are also small effects on chain propagation associated with the mobilities of the polymer and oxygen. Shelton[11] showed some time ago that in thermal oxidations of elastomers, "initiation by direct attack of oxygen on the antioxidant appears to be the most important initiation reaction in the first stage of retarded oxidation". We propose that the large effects that we report for the photooxidation of stabilized PP are a new example of a stabilizer in chain initiation.

Table II
TGA at 176 °C of Films Aged at 150 °C

film	aging time at 150 °C, h	IP at 176 °C, min indicated aging at 150 °C	 with no aging at 150 °C
G	1.0	0	9.2
F	33.0	2	18
H	9.0	0	55
D	400	0	311
C	640	0	340
I	1700	0	360

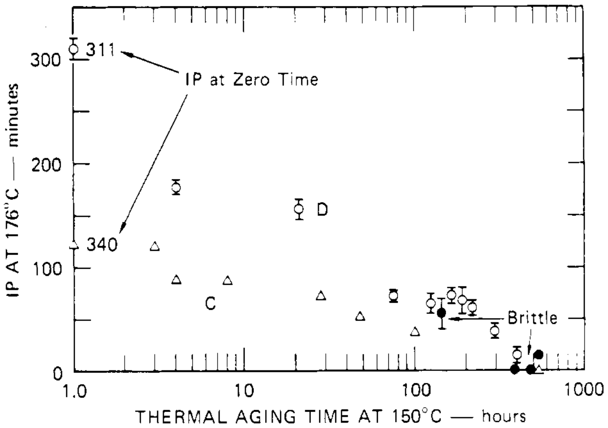

Figure 6. Induction periods at 176 °C vs. aging times at 150 °C for stabilized films C and D.

B. Thermal Oxidations. Thermal Analyses. Table II compares IPs of six films at 176 °C as measured by thermogravimetric analyses (TGA). The films are arranged in order of their IPs at 176 °C without any previous aging; the periods before steady weight loss begins range from 9 min for unstabilized film G to 6 h for the most thermally stable film I. The first column of figures shows the number of hours of aging at 150 °C required to embrittle the films. The IPs at 176 °C were then reduced to zero or a low value. These times to brittleness are in nearly the same order as the initial IPs at 176 °C.

The IP at 176 °C for unstabilized film G decreased almost linearly from 9 to 0 min during the 60-min aging time at 150 °C. Films C and D were so stable that the results are plotted on a semilogarithmic scale in Figure 6. On aging at 150 °C, film D revealed an initial abrupt decrease in IP at 176 °C and then a slow decrease to zero, without the final curvature shown on the log scale. The data suggest that a fair extrapolation to failure might be made on both films C and D, after 10% of the time to failure has elapsed.

Figure 7 compares IPs for film I by differential scanning calorimetry (DSC) at 176 °C after aging at 90, 120, and 150 °C. The IPs at 176 °C decrease rapidly during the initial aging period and then slowly and more regularly. Useful predictions may be possible from the slower changes. As far as they go, the 90 °C data are remarkably

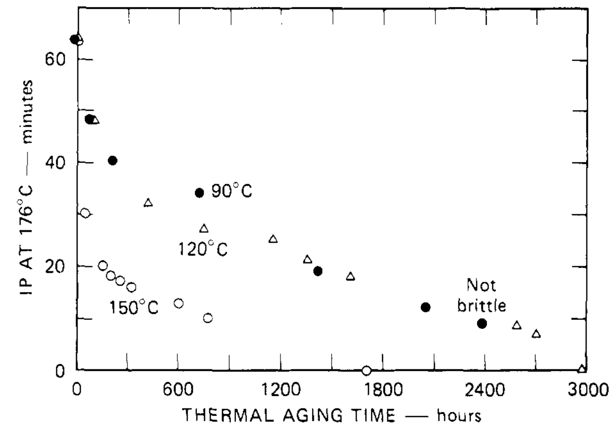

Figure 7. IP for film I by DSC at 176 °C after aging at 90, 120, and 150 °C.

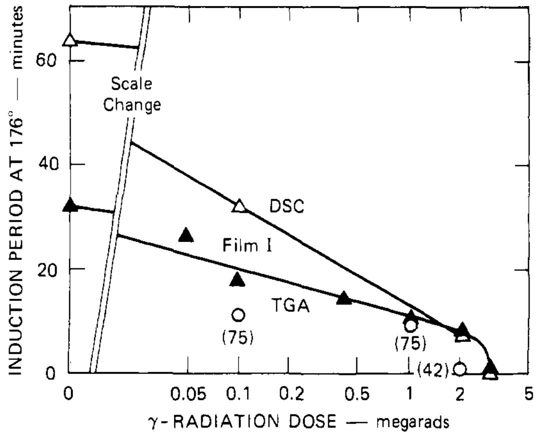

Figure 8. Induction periods of film I at 176 °C after γ irradiation. Numbers in parentheses indicate heating times in hours in air at 120 °C after γ irradiation but before test at 176 °C.

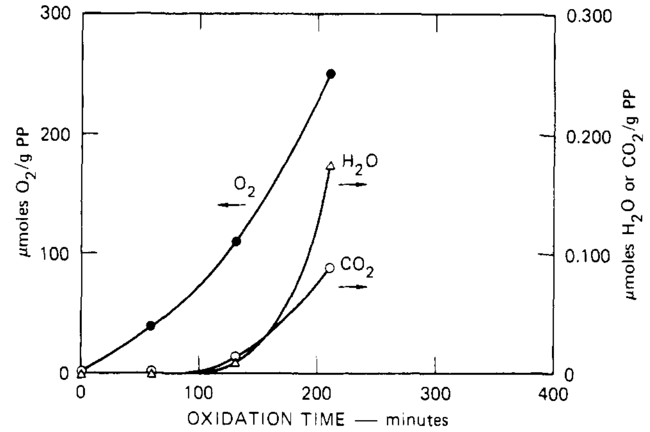

Figure 9. Absorption of oxygen and formation of water and carbon dioxide in thermal oxidation of film H at 150 °C.

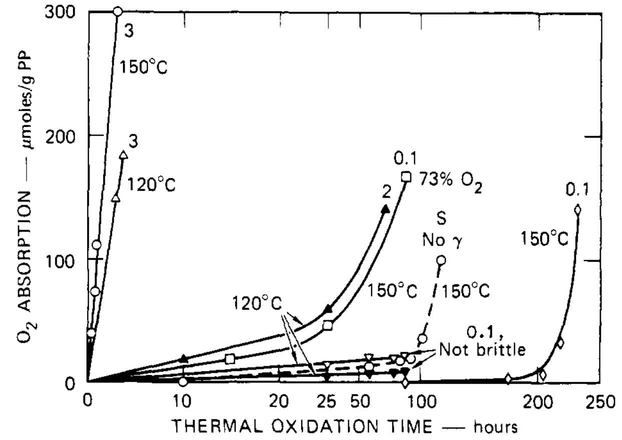

Figure 10. Thermal oxidations of film I (and film S as noted) at 120 and 150 °C. Oxidations were in air, except as noted. Doses of γ radiation in megarads before oxidation are indicated on each curve. With no γ radiation, O_2 absorption was <10 μmol/g of PP at 250 h at 150 °C and unmeasurable at 120 °C.

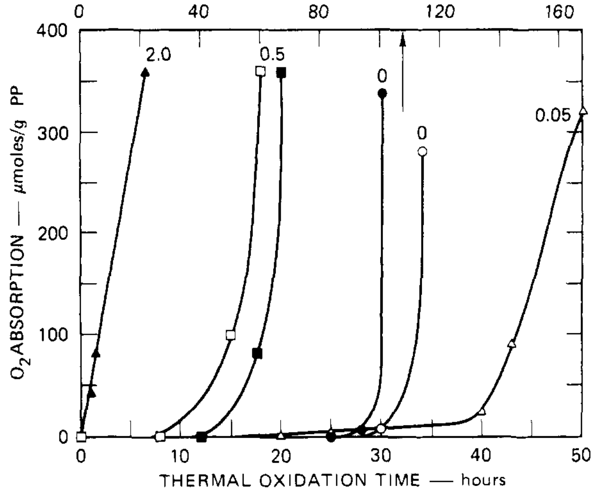

Figure 11. Thermal oxidations of film J at 150 °C. Doses of γ radiation in megarads before oxidations are indicated for each curve. Upper time scale applies for no γ radiation only.

similar to the 120 °C data: aging at 90 °C of film I might be predicted from 120 °C experiments; conversely, aging at 90 °C might as well be measured directly. The initial rapid decreases in IP at 176 °C suggest that the original stabilizer is ineffective but is converted to something that is more effective over a long period.

Figure 8 shows the effects of γ radiation on IPs for film I as measured by both TGA and DSC at 176 °C. A log scale is used for most of the wide range of radiation doses, but a scale change is necessary to represent points at zero dose. The length of the IP with film I decreases with increasing radiation dose, as expected. Thermal aging at 120 °C (open circles) further decreases the IP at 176 °C, with the greatest decrease at the lowest dose. The difference between the DSC and TGA is unexpected and unexplained, but we cannot make any further TGA measurements.

However, TGA and DSC give nearly the same results with film S. With this film, there was no significant effect of either 0.1 or 1.0 Mrd of γ radiation on the IP at 176 °C as measured by either DSC or TGA. The stabilizer system in this film may therefore provide good protection against radiation.

Determination of H_2O and CO_2 by Gas Chromatography. In addition to TGA of thermally aged films at 150 °C , O_2 absorption (see below) and H_2O and CO_2 formation were measured by gas chromatography. Figure 9 shows the results with film H, stabilized with only 0.05% BHT. Although oxygen is absorbed from the beginning, the formation of H_2O and CO_2 is delayed and in the interval shown never reaches 0.1% of the oxygen absorbed. Measurements of these byproducts are therefore unsuitable for following thermal oxidations. No measurable H_2O or CO_2 was found in the thermal aging of film I after 1700 h at 150 °C.

Oxygen Absorptions. Figures 10 and 11 show the effects of prior γ irradiation on oxygen absorption of 120 and 150 °C. With films I and J at 150 °C, with low or no γ irradiation, there is no measurable oxygen absorption during the IP; then rapid oxygen absorption and brittleness are observed. Film I is the most stable film. With in-

Table III
Oxygen Absorptions by PP Films during Oxidations

film	γ dose, Mrd	O_2 absorption in μmol/(g of PP)[a] at embrittlement
Photooxidations at 35 °C with 500-W Lamp		
I	0	173 at 150 h
I	0.1	155 at 78 h
I	0.1	171 at 42 h
I	1.0	133 at 27 h
I	2.0	158 at 22 h
I	3.0	170 at 18 h
I	3.0	131 at 10 h
F[b]	0	570 at 3350 h[c]
F	0	335 at 610 h
F	2.0	307 at 250 h
S	2.0	485 at 420 h
Thermal Oxidations at 120 °C		
I	2.0	131 at 48 h
I	3.0	178 at 3.5 h
Thermal Oxidations at 150 °C		
I	0	12 at 750 h
I	0.1	130 at 230 h
I	3.0	300 at 6 h
J	0	475 at 105 h
J	0.05	320 at 49 h
J	0.50	480 at 18 h
J	2.0	300 at 8 h
S	0	64 at 125 h

[a] Not including the oxygen absorbed during radiation. [b] 200-W lamp. [c] Test stopped before failure.

creasing γ irradiation the time to brittleness decreases; the IP ends less abruptly and eventually disappears. With film S at 150 °C, the IP is indistinct even without γ irradiation. These results are not promising for predicting service lives by initial rates of oxygen absorption at 150 °C.

However, with film I at 120 °C, increasing but low levels of prior γ irradiation result in increasing steady rates during the IPs. This effect may be useful in predicting or comparing the very long lifetimes of polymers at 120 °C or lower temperatures. Higher doses eliminate the IP at 90 and 120 °C as well as at 150 °C.

The two 0.1-Mrd oxidations with film I in Figure 10 show that increasing the oxygen concentration from 21% to 73% at a total pressure of 1 atm reduces the time to brittleness from 230 to 90 h. Thus, increased oxygen pressure during aging will shorten the test, perhaps predictably. These experiments were run with irradiated samples because the test times would be excessive without irradiation.

Summary and Conclusions

Our results are now summarized, with emphasis on the relation between oxygen absorption and polymer lifetime (to brittleness). In photooxidations of unstabilized and some stabilized PPs, the oxidation rates increase regularly with time and can be fitted to empirical equations so that predicting lifetimes appears possible from early measurements. However, with the hindered piperidines alone and with combinations of stabilizers, changes in oxidation rates during the IP appear to preclude predictions.

Table III summarizes our data on oxygen absorption at embrittlement. Most of the experiments involved prior γ radiation, to be discussed later. The most interesting feature is that in the two experiments with film F with similar 200- and 500-W lamps, oxygen absorption with the 200-W lamp was greater in a much longer time but the film had not yet become brittle. Compared with film I, film F lasts much longer, even though it absorbs more oxygen. We think that these differences in oxygen absorption depend at least partly on the peroxide decomposer in the stabilizer package. This agent presumably converts hydroperoxide groups to stable and inert tertiary alcohol groups, without generating free radicals, thus rendering this oxygen absorption harmless. Peroxide decomposers are therefore most effective at low light intensities and in intermittent illumination, and continuous radiation in testing will underestimate the effect of a peroxide decomposer.

In the dark at 150 °C, films I, J, R, and S, without γ radiation, display greatly different oxygen absorptions at greatly different times to embrittlement. Film I has the longest life with the least oxygen absorption. Data with all films suggest quite different relations between rate of radical formation, rates of chain propagation and termination in oxidation, and rates of peroxide decomposition.

It thus appears that oxygen absorption is unsuitable for comparing aging and making lifetime predictions for polypropylenes with different kinds of stablizer combinations. Failure depends on chain cleavage in the amorphous portions of the polymers. The problems might be attacked by measuring changes in viscosity or molecular weight during aging but these changes will be obscured by the major fraction of inert, crystalline polymer. Measurements of new end groups (methyl ketone or carboxyl or their colored or labeled derivatives) or of new soluble material appear more promising.

Experiments with γ radiation were undertaken to accelerate testing without compromising life prediction under service conditions. In general, γ radiation before exposure to heat or light results in some oxygen absorption and peroxide formation.[6] With films I and F, less oxygen absorption in the light is then required for embrittlement. In most experiments in Table III, the IPs decrease with increasing γ radiation; the effect on oxygen absorption at embrittlement is less clear. There may be some use for γ radiation in aging tests at 90 and 120 °C, but no useful application is apparent in experiments at 150 °C or in the light.

Our finding that oxygen absorption by stabilized PP in the light increases with oxygen concentration may be useful in testing. The effect is apparently caused by an increased rate of free radical production from oxygen and stabilizer. Similar effects have long been known in the thermal oxidation of rubber.[11]

The contrast between the measurable rates of oxidations during IPs in photooxidations (Figures 1 and 2) and the immeasurably low rates in thermal oxidations (Figures 10 and 11, without γ radiation) deserves comment. In photooxidation, chain initiation (radical production) appears to be relatively fast; these radicals consume some oxygen. In addition, the high viscosity of PP at 35 °C, the tendency toward intramolecular propagation,[12] and possibly the low activity of soome scavengers used as photostabilizers[13] combine to permit measurable oxygen consuption. The IPs at 150 °C suggest low rates of initiation in the dark and prompt interruption of kinetic chains by more active scavengers in the softer polymer. When these scavengers are exhausted, fast oxidation sets in abruptly. The synergistic effect of a peroxide decomposer requires that hydroperoxides are both formed and then decomposed efficiently enough to extend the IP, but if any peroxide decomposer survives, it has relatively little effect on the rapid formation of hydroperoxides after the IP. These relationships and our data at 120 °C indicate that γ radiation may be useful in expediting aging tests at 120 °C or below, where acceleration is badly needed.

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Ethylene–Vinyl Bromide Copolymers by Reductive Debromination of Poly(vinyl bromide). A Carbon-13 NMR Study

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ABSTRACT: We have prepared a series of ethylene–vinyl bromide copolymers (0–100 mol % vinyl bromide) by reductive debromination of poly(vinyl bromide) with tributyltin hydride. The compositional and stereosequence microstructures have been determined by ^{13}C NMR. Removal of bromine is a random process with respect to compositional sequence, and meso stereosequence dyads are slightly more reactive than racemic dyads. Minor structural irregularities have been assigned in PVB after its complete reduction to polyethylene. The major chain defect (ca. 1%) is a hydroxyl branch caused by S_N2 displacement of bromine in the presence of water. The chain end groups are an olefin and a *cis*-1-methyl-2-alkylcyclopentyl group. Some internal cyclopentyl groups are observed also. The concentration of *n*-alkyl branches is negligible in the reduced material owing to steric inhibition of head-to-head monomer addition and chain-radical back-biting steps during vinyl bromide polymerization.

Recently, we characterized the stereosequence microstructure of poly(vinyl bromide) (PVB)[1] and its model compounds[2] by ^{13}C NMR. Other microstructural features of interest in the PVB chain include end groups, branches, unsaturation, and possible head-to-head linkages. In view of the success of ^{13}C NMR in examining analogous details in poly(vinyl chloride) (PVC) after complete reductive dehalogenation by organometallic hydrides,[3] we have adopted this approach in the present work.

Alternatively, if PVB is incompletely reduced, a material equivalent to an ethylene–vinyl bromide (E–V) copolymer is obtained. To our knowledge this material has not been synthesized by the direct copolymerization of ethylene with vinyl bromide. Its study by ^{13}C NMR would provide useful data on bromine substituent effects[4] in spectra of polymers and allow a statistical analysis of the course of the reduction of PVB to be made if the distribution of reacted units could be ascertained.

In this paper we analyze 50.3-MHz ^{13}C NMR spectra of PVB's at stages of reduction varying from 0 to 100% debromination. The above aspects of polymer microstructure are considered and compared with results from published studies on PVC.

Experimental Section

Materials. Commercial PVB (Polysciences, Inc.; prepared at 50 °C in aqueous suspension with lauroyl peroxide) and PVB prepared in our laboratory[1] were used as starting materials. The commercial sample was dissolved in carbon disulfide–acetone, precipitated in cold methanol, and vacuum-dried at room temperature overnight. Its molecular weight averages were $\bar{M}_n$ = 10600 and $\bar{M}_w$ = 28700 according to GPC analysis.

Reductive Debrominations. Reductions by tri-*n*-butyltin hydride (Alfa Products, Ventron Division) were carried out under a nitrogen atmosphere in tetrahydrofuran or 2-methyltetrahydrofuran that had been passed through basic alumina. Recrystallized azobis(isobutyronitrile) was used as the initiator at a concentration of about 1 mol % of polymer. Low levels of reduction were achieved overnight by a one-pass procedure at 50 °C with about 10% excess hydride over the amount calculated for the desired level of reduction. Complete reduction required a two-pass procedure with excess hydride and a second stage at 80 °C in 2-methyltetrahydrofuran.

NMR Spectra. ^{1}H NMR spectra were obtained at 60 MHz on a Varian T-60 A spectrometer. Polymer solutions were prepared in 5-mm sample tubes at 5% by volume concentration in methylene-d_2 chloride or chloroform-d and observed at ambient temperature.

A Varian XL-200 spectrometer was used to acquire ^{13}C NMR data at a frequency of 50.3 MHz. Typically, 10000 transients were accumulated from a 25% by volume polymer solution in a 10-mm sample tube, with a delay from 4.0 to 10.0 s (depending on sample T_1 values) between 90° pulses (14.0-μs duration). A sweep width of 8000 Hz was used with 32K computer locations (acquisition time 2.0 s).

The solvent was dictated by polymer composition. Samples with over 50% reduction were dissolved in either 1,2,4-trichlorobenzene or hexachlorobutadiene with sufficient perdeuteriobenzene or dioxane to maintain field lock and observed at 110 °C. Some samples with high bromine content dehydrobrominated at elevated temperatures and were therefore observed as solutions in either chloroform-d or tetrahydrofuran-d_8 at 50 °C, where this problem was not as acute.

Results and Discussion

1. ^{1}H NMR Spectra. The ^{1}H NMR spectra of PVB at various stages of reduction are shown in Figure 1. The methine or CHBr proton gives a broad, featureless resonance with a maximum that shifts gradually upfield from 4.6 to 4.0 ppm as the bromine content of the polymer decreases.

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