

Aging of Polypropylene Using High Oxygen Pressure: Influence of Sample Thickness and Stabilization*

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Synopsis

Thin films (0.05–0.08 mm thick) of stabilized and unstabilized polypropylene were aged under 4.24 MPa (614 psi) of oxygen at 90°C. The oxidation of these films was monitored using transmission infrared spectroscopy. Previously it was shown that embrittlement for the thin unstabilized polypropylene films occurred 3.6 times faster in 4.24 MPa of oxygen than in air at atmospheric pressure. For thick stabilized polypropylene (3.18 mm thick), the oxidative induction time at 120°C and 4.24 MPa of oxygen was drastically reduced compared with conventional air aging at this temperature. Specifically, sample embrittlement occurred in 1 week during the high oxygen pressure aging in stark contrast to 70 weeks for conventional air aging. Consequently, due to the shortening of time to age samples at high oxygen pressures, aging can be conducted at this lower temperature (nearer the service temperature) rather than at the commonly used aging temperature of 150°C.

INTRODUCTION

As part of a study to determine the feasibility of using high oxygen pressure to accelerate the aging of polypropylene, the effects of oxygen pressure and temperature on the aging of this material were studied previously in this laboratory.¹ That initial investigation was confined to thin, unstabilized films. It was determined that conventional transmission infrared spectroscopy could be used to define an oxidation induction time that coincided with a drastic reduction in tensile elongation. It was concluded that aging in air and at high oxygen pressure resulted in virtually identical initiation activation energies, which suggests a similarity of degradation mechanisms. Furthermore, it was determined for the unstabilized system that aging at an oxygen pressure of 4.24 MPa is 3.6 times faster than conventional air aging. Thus, the rationale for using high oxygen pressure for aging is to be able to conduct aging experiments at lower temperatures (nearer the service temperature) than at the commonly used aging temperature of 150°C.

The work described in this paper is an extension of the previous investigation.¹ Attempts were made to characterize and quantify the aging of thicker stabilized polypropylene specimens. While such systems are much more difficult to study systematically, they are, however, more representative of polypropylene parts used in service.

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EXPERIMENTAL

Materials

Hercules' Profax 6501 (powder) and Profax 6523 (pellet) were used in this investigation. The former is generally considered to be unstabilized even though it contains a trace amount of 2,6-di-*t*-butyl-4-methyl phenol (butylated hydroxytoluene or BHT) stabilizer.¹ Other stabilizers subsequently added to Profax 6501 were 1,3,5-tris(4-*t*-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione (Cyanox 1790) and distearyl thiodipropionate (DSTDP) both supplied by American Cyanamid. Profax 6523 is process-stabilized and contains an antioxidant package.²

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was used to characterize the oxidative stability of the stabilized (Profax 6523) and unstabilized (Profax 6501) polypropylenes. The DSC scans were run in air at a rate of 10°C/min until sample decomposition occurred. The results are shown in Figure 1. The unstabilized material melts at 168°C and the stabilized material melts at 170°C. Moreover, the decomposition temperature for the unstabilized polypropylene is 193°C whereas the decomposition temperature for the stabilized material is 244°C.

Sample Preparation

Mixing of Stabilizers with Unstabilized Polypropylene. One-tenth gram of Cyanox 1790 was dissolved in 100 mL of toluene and mixed with 100 g of Profax 6501 to form a slurry. Stirring continued under a nitrogen

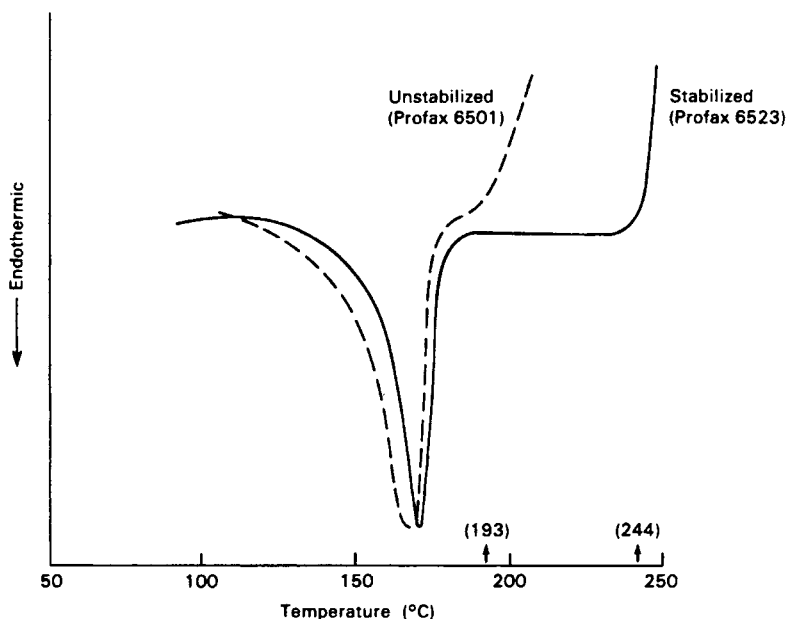


Fig. 1. Differential scanning calorimetry (DSC) traces of stabilized polypropylene (Profax 6523) and unstabilized polypropylene (Profax 6501).

atmosphere until most of the toluene was evaporated. This was followed by drying for 14 h under vacuum at 50°C. The above sequence was repeated with 0.1 g of DSTDP instead of Cyanox 1790, and again using a combination of 0.1 g each of Cyanox 1790 and DSTDP. Thin films of the resulting toluene-free resin systems were subsequently compression-molded as described previously.¹ In later studies Profax 6523 was used to provide a stabilized polypropylene resin.

Molding of Tensile Specimens. Profax 6523 was injection-molded into tensile bars according to the supplier's recommendation. The dimensions of the narrow portion of the tensile bar were 3.05×3.81 mm with a gauge length of 9.53 mm. Samples of various thicknesses were compression-molded using Profax 6501. The sample configuration conformed to type L tensile impact bars as described in ASTM D 1822 test. The compression molding conditions are the same as those used to mold films in the previous study.¹

Aging

Most samples were aged in a forced air circulation oven at 90°C. However, fully stabilized injection-molded samples were aged at 120°C. All samples were either aged in uncovered glass beakers exposed to air or in oxygen atmospheres at 4.24 MPa in high pressure vessels constructed of stainless steel. These vessels were manufactured by Parr Instrument Co. To avoid contact with the metal walls during high oxygen pressure aging, the polypropylene samples were placed inside glass beakers which were then inserted into the vessels for aging. Ultra-pure oxygen (less than 0.2 molar ppm total hydrocarbons and 0.96 molar ppm water), supplied by Air Products and Chemicals, was used.

Tensile Elongation Determination

Tensile elongations were determined using an Instron tensile testing machine at a crosshead speed of 50.8 mm/min. Tensile tests were conducted at the respective aging temperatures to approximate possible application temperatures.

Microtomy

Microtomy was employed to obtain shavings for various depths of an aged polypropylene specimen. These shavings were used to prepare samples for infrared spectroscopy analysis. Specifically, a tensile bar was aged for a given time. After aging a thin layer was microtomed from the sample near the midsection using a razor blade. The thickness of the microtomed section was determined using a micrometer; the shavings were retained for subsequent analysis. This procedure was repeated for successive layers.

Infrared Spectroscopy

A Perkin-Elmer Model 621 Grating Spectrophotometer was used routinely to determine infrared spectra for polypropylene films and for the polypropylene shavings compressed with potassium bromide (KBr) to form pellets. For greater sensitivity, Fourier transform infrared (FTIR) spectra, obtained using a Digilab FTS-20C Spectrometer, were also determined for

polypropylene films cast from hot toluene onto KBr discs. The absorbance of carbonyl end groups was determined from these spectra in order to monitor the extent of oxidation. For predicting the lifetimes of polypropylene, Rose and Mayo have suggested that methods which monitor such end groups appear more promising than traditional methods of oxygen absorption or viscosity changes.³

RESULTS AND DISCUSSION

Aging of Stabilized and Unstabilized Polypropylene

Initially it was felt that by directly mixing stabilizers into unstabilized polypropylene more control could be maintained over stabilizer effectiveness through selection of possible synergistic combinations. In Figure 2, aging results are presented for Profax 6501 with added stabilizer. These experiments were performed under 4.24 MPa of oxygen at 90°C and compared with that of an unstabilized control sample. In this figure the relative absorbance for carbonyl formation ($A_{1710\text{ cm}^{-1}}$), from infrared transmission spectra, normalized by a reference absorption band ($A_{974\text{ cm}^{-1}}$), is plotted against aging time. The intensity of the reference absorption band was previously shown to be independent of aging.¹ Typically, as seen in Figure 2, there is an induction period for oxidation followed by a regime of autooxidation.⁴ The results appear systematic and as expected, except in the case where the Cyanox 1790 stabilizer is added alone. This gives the rather surprising result of a sample containing only Cyanox 1790 outlasting a sample containing the same amount of Cyanox 1790 in addition to DSTDP.

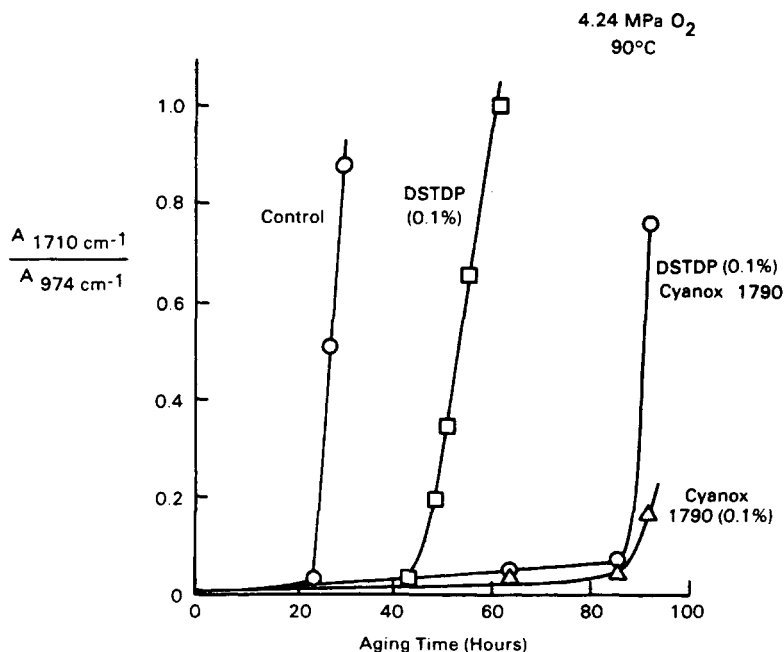


Fig. 2. Effect of stabilizer on the aging of polypropylene (Profax 6501).

Subsequent analysis of the samples indicated that incomplete dispersion of the stabilizer(s) occurred using the solution blending technique. At this point it was decided to use a commercially available polypropylene (Profax 6523) to provide the stabilized system for this study.

Thin films of Profax 6523 were prepared by compression molding. After an extensive accelerated aging period under 4.24 MPa of oxygen at 90°C, relatively little change occurred for the Profax 6523 absorption band at 1710 cm^{-1} , even though the sample began to crumble around the edges after 300 h. Because of this low absorbance, a logarithmic plot was used in order to compare the effect of aging unstabilized polypropylene with Profax 6523 (Fig. 3). The shaded circles and half-closed circles for Profax 6523 are for duplicate runs. It is seen in Figure 3 that the aging kinetics of the stabilized polypropylene (Profax 6523) is significantly slower than the unstabilized material.

Effect of Sample Thickness on Aging

Figure 4 shows the effect of sample thickness on the retention of tensile elongation for unstabilized polypropylene aged at 90°C at 4.24 MPa of oxygen. There is a systematic increase in the time for a drastic reduction in tensile elongation to occur with increasing sample thickness. This is consistent with previously observed diffusion controlled oxidation of polypropylene with samples thicker than 0.1 mm.^{4,5}

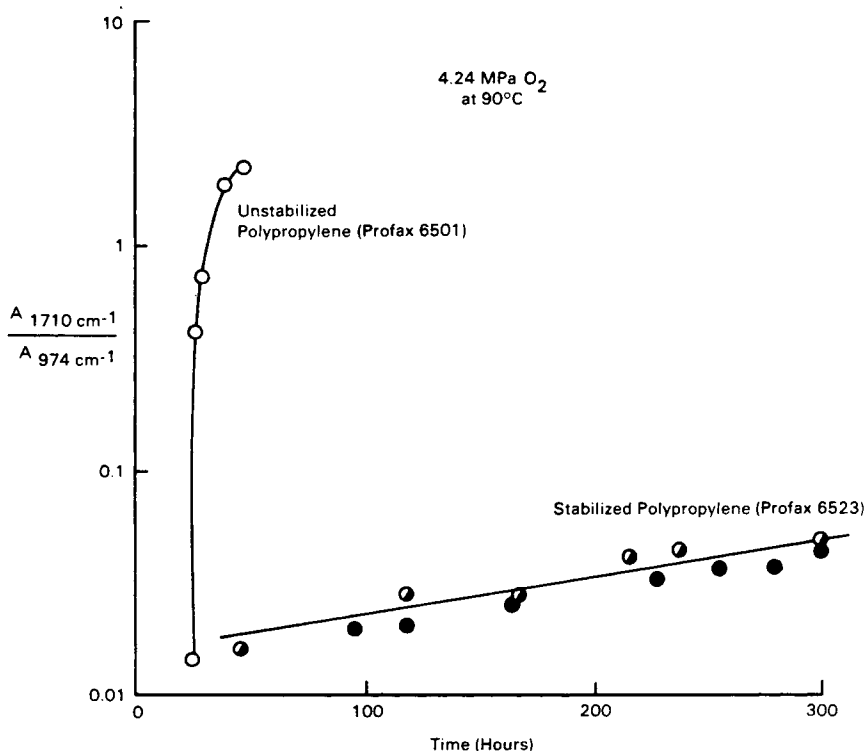


Fig. 3. Aging kinetics of commercial stabilized polypropylene (Profax 6523) and unstabilized polypropylene (Profax 6501).

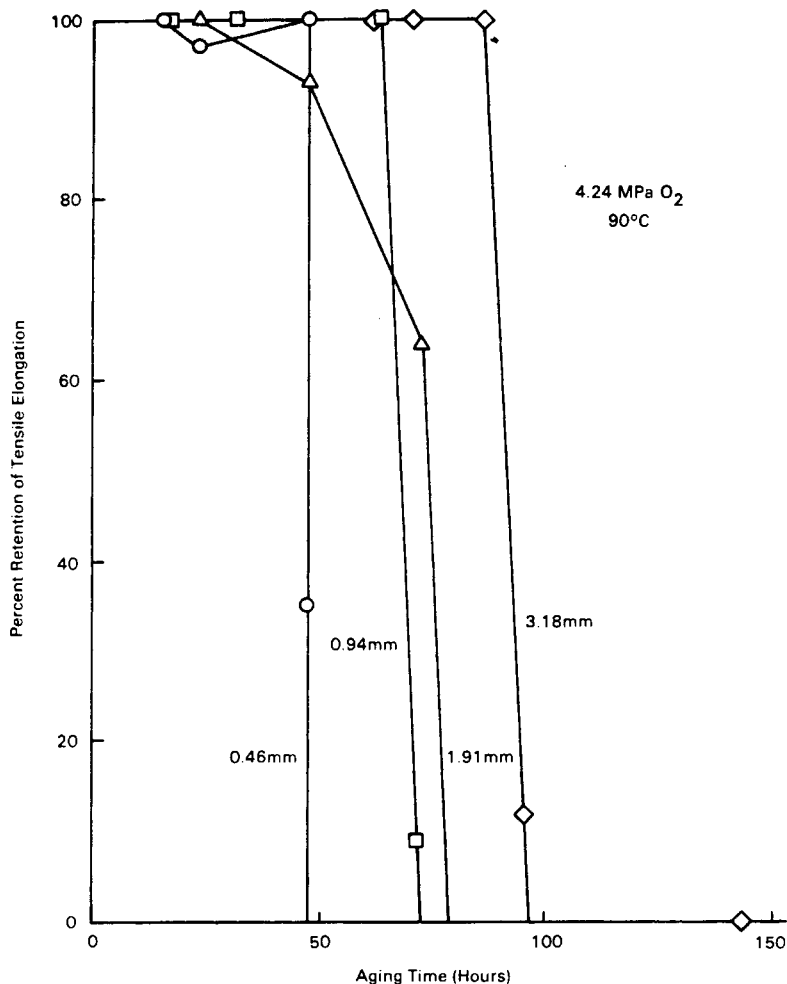


Fig. 4. Effect of sample thickness on tensile elongation for unstabilized polypropylene (Profax 6501).

Infrared spectroscopy was considered as a method to independently characterize the oxidation of thick unstabilized polypropylene. Unlike thin polypropylene films where oxidation can be conveniently monitored by conventional transmission infrared spectroscopy, thicker samples pose more of a problem. Several techniques were tried including attenuated total reflectance (ATR) spectroscopy to analyze surface oxidation. However, poor contact of the sample with the crystal led to inadequate reproducibility of the ATR spectra. Another technique employed consisted of dissolving the aged polypropylene in hot toluene and casting films from the resultant solution onto KBr discs. FTIR spectra were obtained for these aged samples and for the corresponding unaged samples prepared using this method. In these experiments, two thicknesses were considered: 0.46 and 3.18 mm. In Figure 5, spectra for the aged and unaged thinner sample are compared.

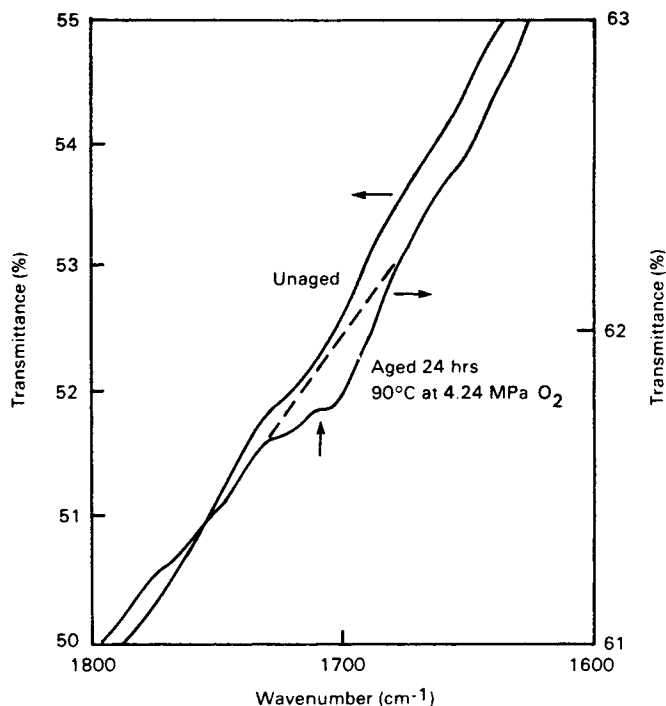


Fig. 5. Fourier transform infrared (FTIR) transmission spectra of aged and unaged unstabilized polypropylene (Profax 6501) cast onto KBr discs (original sample thickness = 0.46 mm).

There is a significant absorbance in the vicinity of 1710 cm^{-1} of the sample which was aged for 24 h at 4.24 MPa of oxygen in contrast to the unaged specimens. In Figure 6, spectra of aged and unaged thicker polypropylene samples are compared for the same aging conditions as the thinner specimens. In this case there is virtually no detectable difference in the spectra of the aged and unaged sample. Presumably, the difference for the detection of oxidation of the two thicknesses is due to there being a smaller percentage of oxidized material in the thicker sample than in the thinner one.

These results suggest that surface oxidation occurred before oxidation of the core. Successive layers were microtomed from an unstabilized polypropylene sample (3.18 mm thick), which had been aged for 1 week in air at 90°C , to confirm that oxidation occurred first at the sample surface. These layers were dissolved in toluene, precipitated from the solution, mixed with KBr powder, and compressed to form pellets for infrared analysis. Figure 7 shows the results for three successive layers. As expected, these results show that any detectable oxidation is confined to the outer (surface) layer, with no oxidation in the successive layers. As a control, an infrared spectrum of the outer layer of an unaged sample was also determined. In this control no evidence of oxidation was detected. These results are consistent with those reported by Wyzgoski, who found a systematic decrease in the extent of oxidation of polypropylene with removal of successive outer layers.⁶

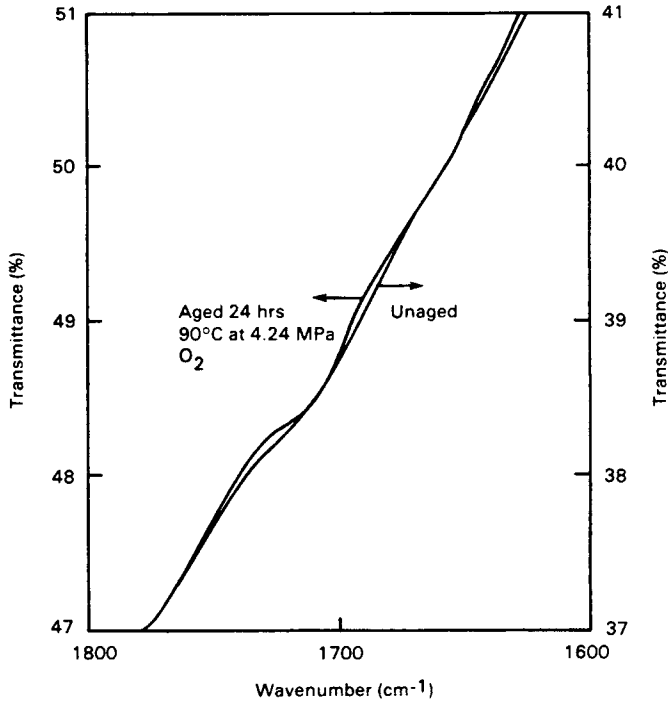


Fig. 6. Fourier transform infrared (FTIR) transmission spectra of aged and unaged unstabilized polypropylene (Profax 6501) cast onto KBr discs (original sample thickness = 3.18 mm).

Aging of Thick Stabilized Samples

Previously, it was shown that an acceleration factor, defined as the ratio of the induction time obtained by conventional air aging to that of a sample aged at high oxygen pressure, could be obtained for thin unstabilized films

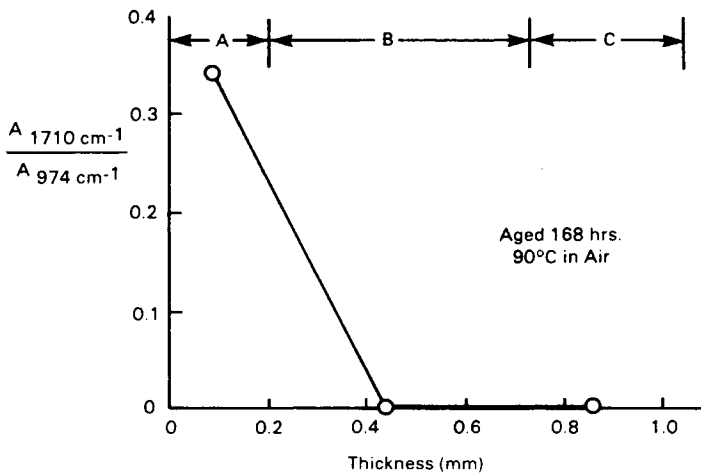


Fig. 7. Relative absorbance of three successive layers (A, B, and C) for unstabilized polypropylene (Profax 6501) (original sample thickness = 3.18 mm).

using infrared spectroscopy.¹ In that study the acceleration factor was determined to be 3.6 over a range of 60–90°C for 4.24 MPa of oxygen. Simply put, the unstabilized films age 3.6 times faster in oxygen at 4.24 MPa than in air, at atmospheric pressure.

For reasons already discussed it is difficult to use infrared spectroscopy to obtain induction times for thick polypropylene samples. However, in earlier work, it was noted that the time for a significant reduction of tensile elongation to occur coincided with the induction time.¹ Thus, the induction times for thick stabilized polypropylene were defined using this criterion. The results for reduction in tensile elongation for stabilized samples plotted against aging time for samples aged at 120°C (in contrast to the 90°C previously used) in air and 4.24 MPa of oxygen are shown in Figure 8. For samples aged in air, the elongation drops dramatically after 70 weeks of aging. In stark contrast to the air aging, samples aged at high oxygen pressure experience a significant reduction in tensile elongation in 1 week. Consequently, the acceleration factor is 70, which is markedly greater than the 3.6 value obtained for unstabilized films.

The precise reason for the much greater acceleration factor for the thick stabilized samples than for the thin unstabilized films was not determined in this investigation. The results presented in Figure 4, which show the effect of sample thickness, are undoubtedly related to diffusional effects.^{4,5} In thin films diffusional effects are minimized. Boss and Chien derived an expression showing that the rate of oxidation is proportional to the oxygen concentration gradient and presented data at relatively low oxygen pressures showing a linear increase in the reaction rate with oxygen pressure.⁵

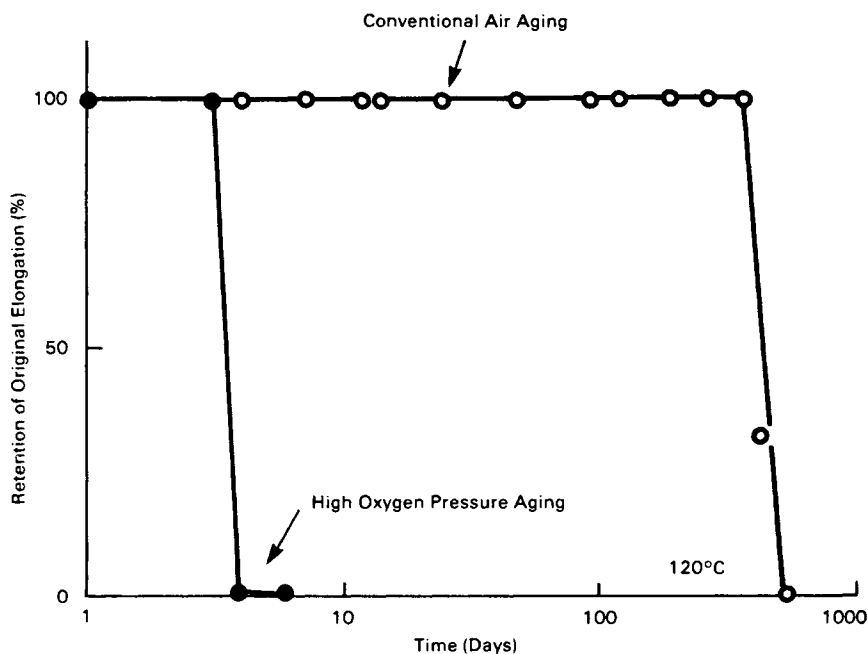


Fig. 8. A comparison of the retention of elongation for stabilized polypropylene (Profax 6523) aged in air and at 4.24 MPa (614 psi) O₂ (sample thickness = 3.18 mm).

However, the magnitude of the difference in acceleration factors appears too large to be explained solely in terms of oxygen diffusion.

Another element of this process may be related to the reaction of the stabilizer with oxygen. In 1972, Shelton concluded for the thermal oxidation of stabilized elastomers that the reaction of the antioxidant with oxygen was the most significant reaction in the initiation step.⁷ Rose and Mayo recently extended this concept to explain the increase in oxidation rate with increasing oxygen concentration for the photooxidation rates of stabilized systems with that for pure hydrocarbons, they suggested that the reaction of oxygen with the stabilizer increased the rate of free radical production; this, in turn, accelerated oxidation.⁸ More work is required in this area to separate the effects of the two elements on the acceleration factor for the oxidation of polypropylene.

It is concluded that using high oxygen pressure to accelerate polypropylene aging is more effective than conventional air aging. From the standpoint of being able to use lower temperatures (such as 120°C), which are closer to the service temperature for a moderate time, this method may be more realistic than the traditional method. Most polypropylene oven aging tests are commonly performed at 150°C. At this higher temperature the aging results are less likely to correlate with the oxidative stability at lower temperatures encountered in service. In addition, it is possible to use high oxygen pressure aging to cause failure of the stabilized polypropylene in a reasonable time at 120°C. Thus, comparative failure data can be obtained on different materials rather than noting only whether the materials pass a given time-temperature exposure. Further study is needed to clarify the relative roles of oxygen diffusion and the effect of oxygen concentration on the overall degradation process (including the possible direct oxidation of the stabilizer system) in order to establish the relationship between aging under high oxygen pressure and the lifetimes of actual parts in service.

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