

Oxidation of Gamma-Irradiated Ultrahigh Molecular Weight Polyethylene

CHRISTOPHER F. COOTE,¹ JOHN V. HAMILTON,^{*2} W. GRANT MCGIMPSEY,³ ROBERT W. THOMPSON¹

¹ Department of Chemical Engineering, Worcester Polytechnic Institute, Worcester, Massachusetts 01609

² Johnson & Johnson Professional, Inc., 525 Paramount Drive, Raynham, Massachusetts 02767

³ Department of Chemistry & Biochemistry, Worcester Polytechnic Institute, Worcester, Massachusetts 01609

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ABSTRACT: Ultrahigh molecular weight polyethylene (UHMWPE), the current polymer of choice in orthopedic prosthetic devices, is typically sterilized by exposure to Co-60 gamma irradiation prior to packaging for long-term storage. However, the exposure to Co-60 irradiation generates free radicals along the polymer chain that can participate in a series of reactions commencing with the oxidation of the free radicals to form reactive peroxy radicals. This study was undertaken to identify the role of hydroperoxide species in shelf-aged and accelerated aged UHMWPE samples by using a nitric oxide derivatization technique. It is shown that the concentration of hydroperoxides did not change appreciably with shelf aging. However, during accelerated aging the hydroperoxide concentration increased to a plateau and then decreased, suggesting its role as an intermediate in the process. By contrast, the concentrations of carbonyl species continued to increase during shelf aging and accelerated aging. The effects of several packaging materials on the oxidation characteristics were also investigated. A vacuum foil package is shown to be effective in preventing oxidation to a significant extent during accelerated aging. However, accelerated aging after removal from the foil pack resulted in oxidative degradation. Extended vacuum to remove dissolved oxygen and a 5-week room-temperature healing process in the foil pack were shown to be ineffective in reducing oxidative degradation. It also was shown that increased moisture content in the aging environment did not affect the degradation process. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2525–2542, 2000

INTRODUCTION

There are approximately 200,000 total hip and knee replacement operations performed annually worldwide.¹ In many of these operations, an ultrahigh molecular weight polyethylene (UHMWPE) piece is used as the load-bearing cushion-

ing component, in a sense acting as replacement cartilage.

It is common for the UHMWPE pieces to be manufactured in bulk quantity in a variety of sizes and remain in storage at hospitals until a surgeon requires a piece of a specific size. Consequently, a shelf life of up to 10 years may be required for each piece prior to its use, and, obviously, it must be sterile at the time of use.

UHMWPE pieces are typically sealed in plastic packaging, sterilized, then placed in cardboard containers for shipment and storage. Although the plastic wrap is permeable to air, it does seal out microorganisms. In the past, ethylene oxide

* *Current address:* Molecular Geodesics, 20 Hampden St., Boston, MA 02119.

Correspondence to: R. W. Thompson.

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was used to sterilize UHMWPE pieces, but has been substantially replaced by exposure to Co-60 gamma irradiation, because ethylene oxide posed unacceptable health hazards for manufacturing personnel.

However, gamma radiation induces the formation of free radicals along the UHMWPE polymer chain and results in some chain scission. These free radicals can then participate in oxidation reactions by reacting with dissolved oxygen present at the time of irradiation and with oxygen that diffuses into the sample as the reactions proceed. It is desired to minimize the extent of oxidation, because these reactions ultimately lead to degradation of the polymer component, which in turn accelerates wear and can lead to the need for replacement.²⁻⁴ Therefore, a vacuum-sealed foil packaging system has been developed in which the Co-60 irradiation can be carried out and which is impermeable to oxygen. The elimination of oxygen should extend the shelf-life of UHMWPE pieces, but the system is too new to have much historical data on which to evaluate its effectiveness. Therefore, part of the goal of this study involved understanding how to compare the effects of accelerated aging at high temperatures to shelf aging at ambient conditions.

The tensile strength of UHMWPE can be reduced from ca. 65 MPa for a fresh sample to approximately 21 MPa for a heavily oxidized piece.⁵ Fatigue life is a material's ability to withstand exposure to repeated stresses before failure. Raw UHMWPE can withstand a bending stress of 35.7 MPa for about 8 million cycles prior to fatigue failure, whereas oxidized samples can withstand only about 1.5 million cycles.⁶ A typical person performs a walking gait cycle one million times per year,⁷ and the abrasion associated with this wear results in weight loss of about 15-30 mg.⁸ In short, progressive oxidation of UHMWPE implant pieces has been associated with changing physical properties⁹ and high levels of damage, cracking, and delamination in vivo,¹⁰⁻¹² thus making it essential that details of the oxidation process be well understood.

UHMWPE and Oxidative Degradation. UHMWPE is a linear polymer having molecular weights in the range of 2-6 million g/mol and a mass density in the range of 0.930-0.945 g/mL.¹³ UHMWPE is partially crystalline, with the crystalline regions separated by amorphous regions. It is inert in the body and resistant to alkali and weak acids, but is susceptible to attack by oxygen

and oxidizing acids. Moisture and many gases are soluble in UHMWPE, the extent and rate of transport being partially dependent on temperature. Its low coefficient of friction is an additional beneficial property that makes it suitable for these applications.

The absorption of gamma irradiation generates free radicals in UHMWPE during sterilization according to either of the reactions (where R represents the polymer chain)¹⁴:

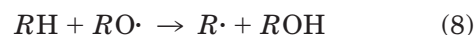
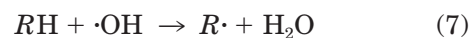
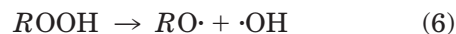


Reaction (1) involves breaking a C-H bond, whereas (2) results in chain scission. It is expected that the $H\cdot$ radicals are short-lived because they are relatively mobile and may terminate readily. Thus, the important radicals are those on the polymer chain.

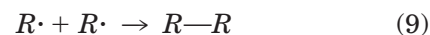
In the presence of oxygen, both initially dissolved and that which diffuses in, the following sequence of initiation reactions are reported to occur¹⁵:



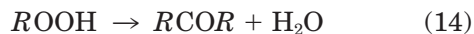
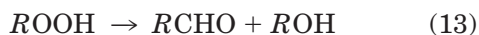
These reactions are followed by propagation reactions¹⁵:



Chain termination or hydroperoxide formation can occur to eliminate free radicals¹⁶:



Finally, carbonyls form as the end product of the sequence¹⁵⁻¹⁷:



Superimposed on these reactions, and complicating the kinetic picture, is the diffusion of oxygen from the air outside of the piece toward the interior. The oxygen solubility and diffusivity are functions of temperature,¹⁸ such that the solubility decreases slightly, whereas the diffusivity increases as the temperature of the piece increases. Temperature is, therefore, an important consideration when attempting to compare shelf-aging and accelerated aging effects.

Prior Oxidation Studies. There have been numerous reports on studies of oxidative degradation of UHMWPE.¹⁹⁻²⁹ It has been common to report an oxidation index (OI), which in some way reflects the change in the carbonyl region of the IR spectrum (i.e., around the 1720 cm⁻¹ wavenumber region). It also has been common to report a depth profile of the OI and report how that changes as a function of aging time. It has been found that changes in the OI profile with depth into the sample occur on the time scale of years at room temperature. Furthermore, it has been reported previously that a subsurface peak of the OI arises at a depth of approximately 2 mm from the surface after 2-5 years of room temperature aging.^{22,24-27} The extent of oxidation at the surface, measured by the carbonyl concentration, appears to remain essentially constant at a low level over the aging period. However, Flynn²⁷ noted that, at a constant depth of 2 mm, which coincided with the location of the subsurface peak, the rate of production of carbonyl species accelerated with aging time, that is, an apparent autocatalytic effect was observed at that fixed depth.

Sun et al.²² suggested that molecular oxygen has ample time to diffuse into the sample, because diffusion is faster than the slower oxygen-consuming reactions. Thus, they suggested that [O₂] should be at its saturation value. Donohue and Apostolou²¹ suggested, by contrast, that the oxidation reactions were so rapid that oxygen was consumed upon arrival within the bulk sample. Others^{19,20} have suggested that the diffusion and reaction rates were of comparable magnitude and that a quasi steady-state oxygen concentration

profile should exist in the sample. This matter can be addressed by the data reported in this study.

Sun et al.²⁴ conjectured that the cause of the subsurface peak in the OI was due to the initial distribution of free radicals generated by the Co-60 treatment, coupled with the decreasing oxygen concentration as a function of depth into the sample. In that reference, it was speculated that [O₂] decreased with depth into the sample due to the combined effects of oxygen consumption and diffusion, whereas the initial free-radical concentration was suggested to increase with depth into the sample due to backscattering of the radiation. The assumed oxygen profile can certainly be justified and modeled as a normal diffusion/reaction process.^{19,20} However, Sun's assumption of the free-radical profile increasing with depth into the sample cannot be supported. Figure 1³⁰ shows an Electron Spin Resonance (ESR) depth profile immediately after irradiation and illustrates that the initial free-radical concentration was essentially uniform.

Flynn tested the oxidation of UHMWPE samples subjected to elevated temperatures and elevated oxygen partial pressures in an attempt to simulate shelf aging, but in shorter times.²⁷ She reported the OI profiles (ratio of IR peaks at 1720 and 1370 cm⁻¹, i.e., the carbonyl and the methylene regions, respectively) with accelerated aging times at various aging conditions. There was no subsurface peak in the OI and the oxidation levels at the surface increased with time for all conditions tested. The conditions tested did not represent the shelf-aging conditions, nor were the resulting OI profiles representative of the shelf-aging OI profiles. The absolute extent of oxidation in the accelerated conditions also exceeded those reported in the shelf-aged samples.

Prior Modeling Studies. Several investigators have reported on the results of modeling the simultaneous oxygen diffusion and oxidation reactions as a function of depth and time.^{19,20,28,29} Several investigators have assumed that the oxygen profile reaches a pseudo steady state in a relatively short time and remains constant thereafter,^{19,20} thus simplifying the problem. This assumption is probably reasonable, because the time scale of oxygen diffusion is somewhat shorter than that for the reaction sequence (discussed further below).

In a very recent study, Daly and Yin²⁸ simplified the reaction sequence shown in eqs. (2)-(14)

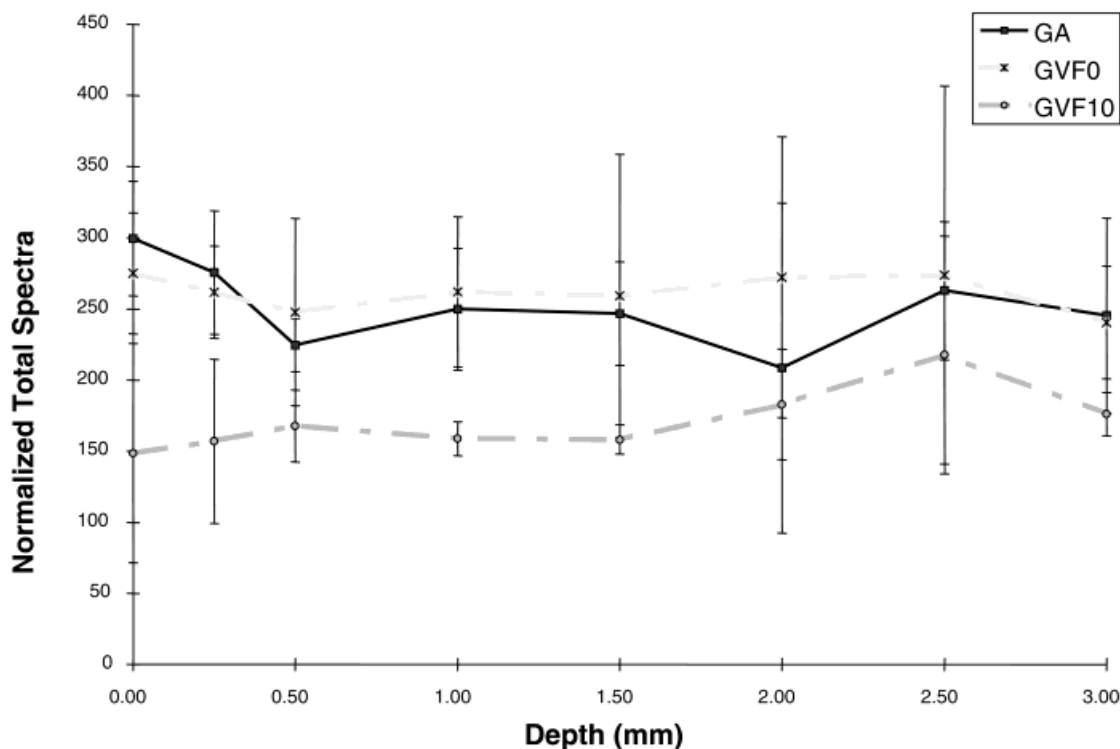


Figure 1 Depth profile of ESR measurements showing the uniformity of the initial free-radical concentration immediately after Co-60 irradiation.²⁷

by assuming that certain reactions were rapid and ignoring others (i.e., several species concentrations were low), resulting in:



Daley and Yin solved the time- and position-dependent differential equations, coupled with the oxygen diffusion equation, to generate depth profiles of the key species remaining in their model as a function of time. Their measured value of oxygen diffusivity was close to the value reported in Ref. 18. Their two reaction-rate parameters were determined to give a best fit for a 10.9 years' aged sample, and the same parameters were used to generate a reasonable fit to their data for a 5.8 years' aged sample. They assumed that the sample had no oxygen dissolved initially, which is probably not realistic.

In our own simulations using the Daley and Yin²⁸ model, we have noted that it is inconsistent with several measured results. These include predicting a shifting subsurface peak with aging,

which has not been observed in most reports, and predicting a constant rate of production of carbonyl species rather than an accelerating (auto-catalytic) rate as observed by Flynn.²⁷ It also did not include any means of computing the time- or position-dependent hydroperoxide species concentrations, which we shall show can be observed experimentally. Those species were in fact one group that was assumed to be present as an intermediate in quite low concentrations.

EXPERIMENTAL

Samples were obtained from tibial inserts machined from compression-molded sheets of UHMWPE with molecular weight in the range of 2–4 million D. The inserts were packaged in air-permeable plastic packaging, and shelf-aged for up to 8 years. Additionally, samples were obtained for accelerated aging studies. Some were sealed in plastic packages, whereas others were sealed in aluminum packages at a pressure of 18 mbar (absolute) prior to irradiation. Co-60 irradiation was carried out at dosage levels of between 30.0

and 44.1 kGy, typical levels for sterilization of components. There was a 1–2 days' delay between packaging and irradiation, and about a 48-h delay between irradiation and the beginning of the accelerated aging treatments.

Accelerated aging was carried out in a closed Parr Series 4520 bench-top reactor (Parr Instrument Co., Moline, IL, USA) at 70°C or an open-air oven at 80°C for periods extending up to 13 weeks. Most environments used in the accelerated aging tests were dry (ambient), with no added O₂. Liquid water was added to the bottom of the reactor in one test in the Parr reactor to evaluate the effect of humidity on the oxidation reactions. Some tests were performed with samples kept in their packages to evaluate the integrity of the package to elevated temperatures and the permeability of air through the packaging material.

One-inch-thick UHMWPE samples (cubes) were sliced in half for analysis of the core material. Skivings (thin slices) were prepared by microtoming these cut pieces into sheets on the order of 100–200- μm thick. Skivings were taken from the exposed interior faces of the cut samples to study the oxygen penetration and subsequent degradation reactions in the bulk rather than examining the edge effects on the original aged samples. IR spectra were collected at the midpoint of the skivings at specified depths away from the surface up to about 5000 μm into the piece.

Hydroperoxide species concentrations were monitored by derivatizing skivings with NO at dry ice temperature prior to measurement by IR spectroscopy, as previously reported by Carlsson and Lacoste.³¹ Several samples were placed in a sealed polytetrafluoromethylene (PTFE) reactor, which was then placed in a dry-ice and isopropanol bath. The reactor was purged at least 15 min with N₂ prior to passing NO over the sample. The –78°C bath was replenished with NO periodically over the 48-h period used for the derivatization. (This derivatization process also separated alcohol groups from carbonyls, so that they could be quantified more clearly.)

The OI reported in this study was the ratio of the carbonyl peak height (1720 cm⁻¹) relative to the methylene peak (1370 cm⁻¹), which was assumed to be constant throughout the tests. A new index, the hydroperoxide index, or HI, was defined as the ratio of the peak heights of the secondary nitrate peak (1630 cm⁻¹) to the methylene peak (1370 cm⁻¹). This measurement was done on the NO derivatized skivings. The depth profiles of

Table I Values of Oxygen Solubility and Diffusivity in UHMWPE

$T = 23^\circ\text{C}$
Oxygen solubility = 7.23×10^{-5} (mol/L) ¹⁸
Oxygen diffusivity = 1.14×10^{-7} (cm/s) ²⁸
Activation energy for oxygen solubility = -1.7 (kJ/mol) ¹⁸
Activation energy for oxygen diffusion = 36.8 (kJ/mol) ¹⁸

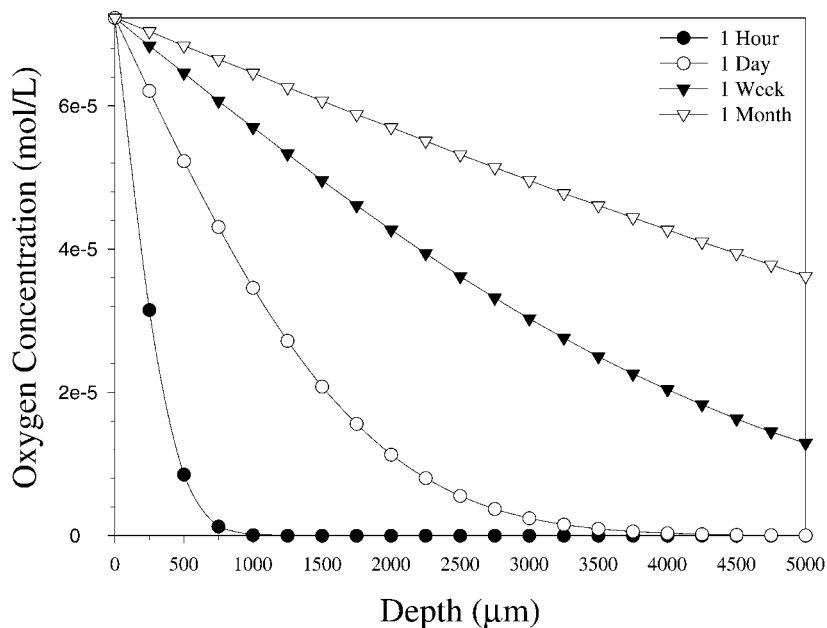
the OI and the HI were collected for each sample, and multiple samples were analyzed to ascertain the uncertainty associated with the procedure.

RESULTS AND DISCUSSION

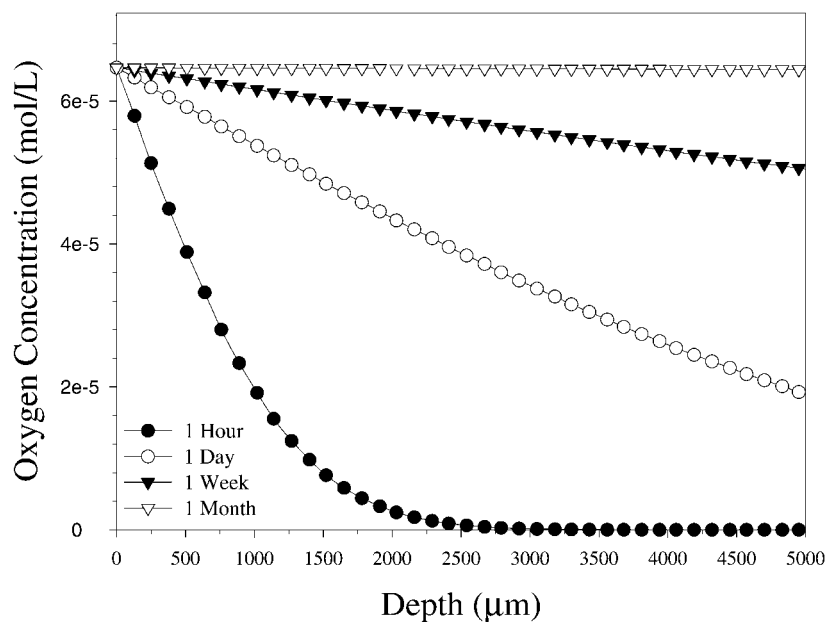
Results of shelf-aging and accelerated-aging experiments will be presented in the context of the reaction sequence discussed above, and oxygen transport rates will be simulated by using parameters from the literature.

Oxygen Transport Rates. Prior to evaluating the shelf-aged or accelerated-aged samples, it is worthwhile to understand the time scale of oxygen diffusion in UHMWPE. Several simulations were carried out, assuming one-dimensional transport in a slab having no dissolved oxygen present initially, and with no chemical reactions occurring. The measured value of the diffusivity obtained by Daly and Yin²⁸ was used at 23°C, whereas the activation energy reported by Pauly¹⁸ was used to adjust the diffusivity for elevated temperatures. Additionally, values for oxygen solubility reported by Pauly were used to estimate saturation values at the sample surface. The values used in these simulations are listed in Table I.

Figure 2(a,b) shows the results of these simulations. In Figure 2(a), it is shown that at room temperature, oxygen can be expected to penetrate to about 3000 μm in a week and to 5000 μm by the end of the first month. Considering that shelf-aged samples take several years before evidence of the oxidation reaction sequence to be manifested, oxygen diffusion is apparently relatively rapid compared to the time scale of the degradation reactions. The predictions of oxygen penetration at 80°C are shown in Figure 2(b) and illustrate the much more rapid transport of oxygen at that elevated temperature. The oxygen-concen-



(a)



(b)

Figure 2 Results of simulations of one-dimensional oxygen diffusion into UHMWPE sample with no oxygen present initially: (a) transport at 23°C, and (b) transport at 80°C.

tration profile after 1 day (24 h) at 80°C looks very much like the 1-week (7 days) profile at 23°C, keeping in mind that the oxygen solubility at 80°C is marginally lower than that at 23°C, as noted by the surface concentrations. The piece would be essentially saturated to a depth of 5000

μm within 4 weeks. The accelerated aging tests showed significant changes over a period of 5–13 weeks, suggesting that oxygen transport is somewhat more rapid than the evolution of oxidation species.

The oxygen diffusion simulations, although in-

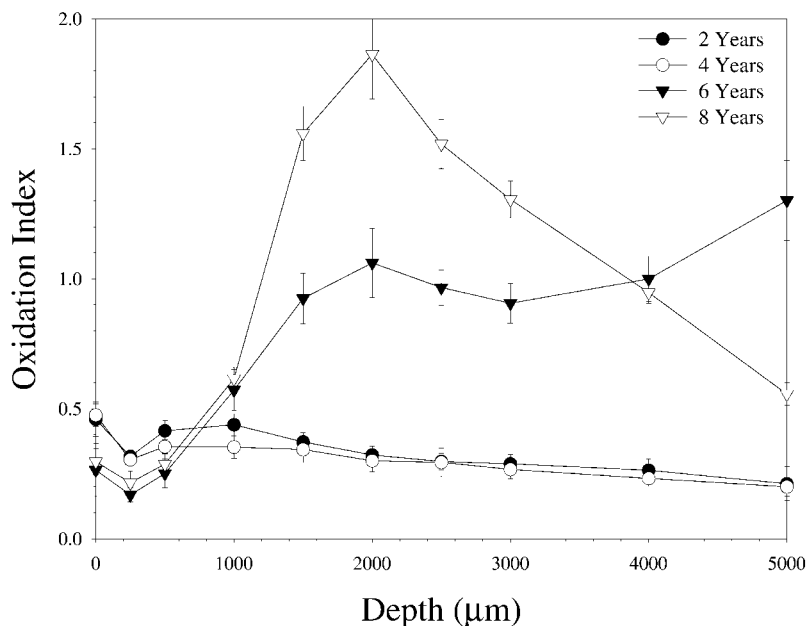


Figure 3 The oxidation index for UHMWPE samples aged for 2, 4, 6, and 8 years in plastic packaging.

dicative of transport rates, were performed assuming no oxygen was present in the piece initially. This was clearly not the case in the irradiated samples used in this study. However, as will be reported below, the oxygen present initially when the piece is irradiated is low compared to the oxygen needed to degrade the piece by a measurable amount (i.e., the oxygen present initially may be consumed rather quickly on the time scale of the aging process), and the profiles obtained appeared to be the same as those in pieces that had essentially no oxygen.

Room-Temperature Shelf Aging. Figure 3 shows the results of IR spectra measured along the depth of skivings taken from the center of UHMWPE samples shelf aged at room temperature in sealed plastic containers. The depth profiles of the OI showed that the carbonyl species remained at fairly low levels throughout the region of testing (i.e., 5000 μm) for at least 4 years. Between 4 and 6 years a dramatic change occurred, increasing the carbonyl concentration throughout the depth of the sample. In addition, a subsurface peak in the OI developed at a depth of about 2000 μm (the increase at 5000 μm in the 6-year sample is an artifact; that sample was narrower than the others and effects from the opposite side of the piece interfered with the measurements). After 8 years of aging, the subsurface peak in the OI was quite

dramatic, and the measurable OI, above the 2–4 years level, extended well into a depth of 5000 μm . Note that in all samples shown, the change in the OI at the surface was negligible. These effects also were observed by Flynn.²⁷

Figure 4 shows the depth profile of the HI for skivings taken from the same samples and derivatized with NO. In those samples, it is clear that hydroperoxides were present early in the aging process, but that their concentrations did not vary with depth, except at the surface, and that changes did not occur over the aging time of 2–8 years. That is, the hydroperoxides formed quite quickly compared to the time scale of the carbonyl species formation, and they remained at essentially a constant level throughout the aging period. Again, the slight increase in the 6-year sample at around 5000- μm depth is an artifact resulting from a smaller sample size. Alcohols were not observed in the IR spectra of the NO derivatized skivings, at least not at a level greater than the noise in the spectra in the NO–alcohol region.

The tailing effect with depth into the sample in the carbonyl species was undoubtedly due to the reduced oxygen concentration. The relatively low, and constant, OI values deep in the piece stemmed from the oxidation which occurred early in the aging from the dissolved oxygen present at the time of the irradiation. The same tailing can be seen in the HI index, except in the smaller

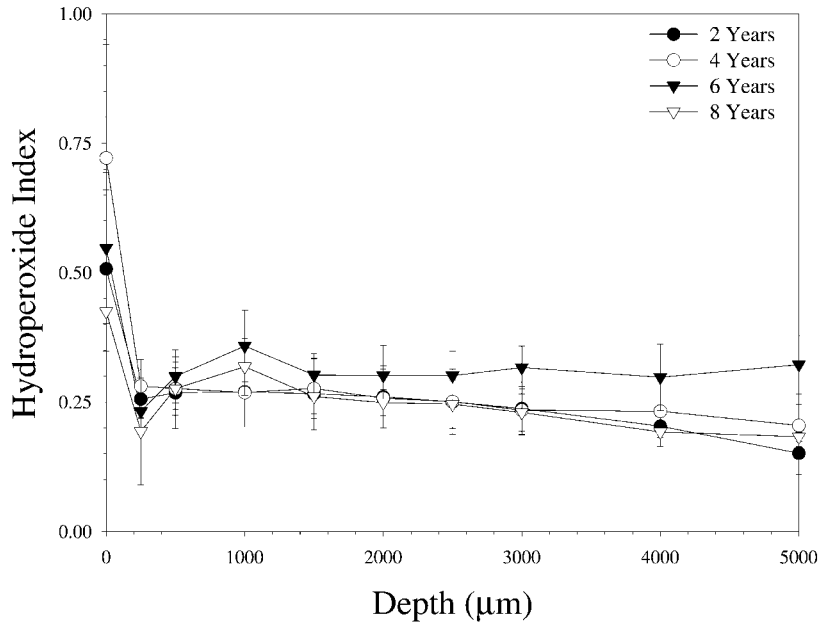


Figure 4 The hydroperoxide index for NO-derivatized UHMWPE samples aged for 2, 4, 6, and 8 years in plastic packaging.

6-year sample, although not to as great an extent, because the HI did not change with aging time.

70°C Autoclaved Aged Samples. Several fresh UHMWPE samples were autoclaved at 70°C to test the integrity of the foil pack in excluding

oxygen and to test the effects of moisture on the oxidation reaction sequence. These tests were conducted in a sealed autoclave, so the temperature and absolute oxygen pressure were both elevated, although no extra oxygen was added.

Figure 5 shows the OI for samples autoclaved

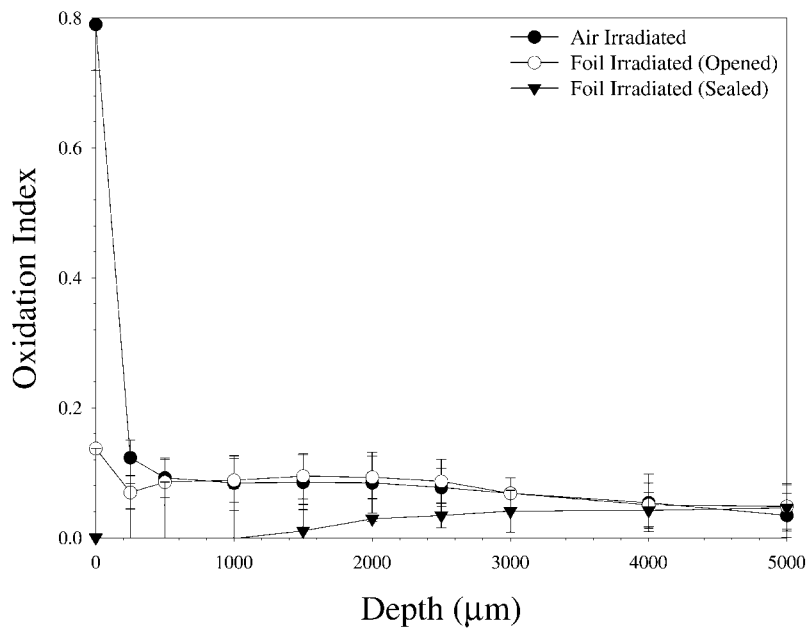


Figure 5 The oxidation index for UHMWPE samples aged 2 weeks in a sealed autoclave at 70°C.

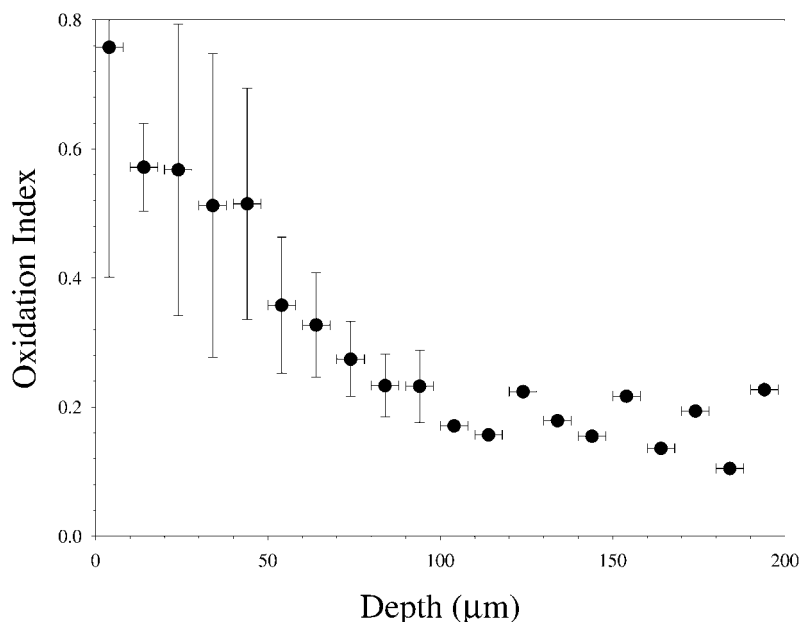


Figure 6 Depth profile of the oxidation index near the sample surface.

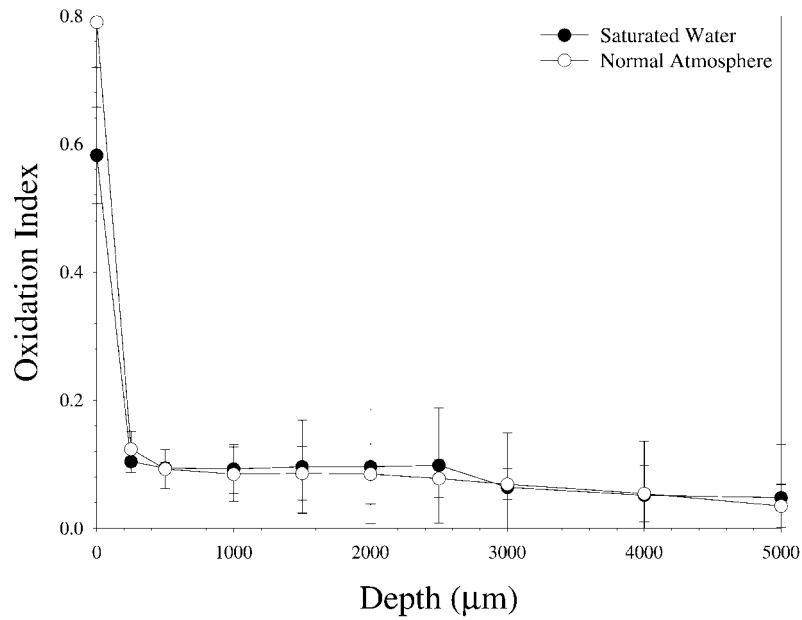
together at 70°C for 2 weeks and illustrates that the sample left in its vacuum-sealed foil pack showed no presence of carbonyls after the treatment. By comparison, the sample irradiated in a plastic container and the sample removed from its foil pack prior to autoclave aging at 70°C both showed noticeable levels of carbonyl formation in the 2-week test. However, note that the sample removed from the foil pack had a much lower OI at the surface than the air-irradiated sample, due to the lower oxygen concentration or some surface stabilization. The lower OI near the surface in the foil pack sample left in the pack reflects the fact that the vacuum-packing process removed some of the oxygen near the surface, further reducing the formation of carbonyls. The very small amount of carbonyl formation in the bulk of that piece reflected the presence of a small amount of residual oxygen. In the aggregate, these OI levels are somewhat below the values shown for the shelf-aged pieces in Figure 3.

Figure 6 is a more detailed analysis of the OI for the sample irradiated in a plastic package, looking more closely at the region near the surface. The results show a more gradual decrease over the 200 μm below the surface and clearly show what would be expected to be patterned after an oxygen depth profile due to its concentration gradient into the piece as reactions consume oxygen in the bulk. The periodic OI oscillations at depths $> 100 \mu\text{m}$ resulted from striations along

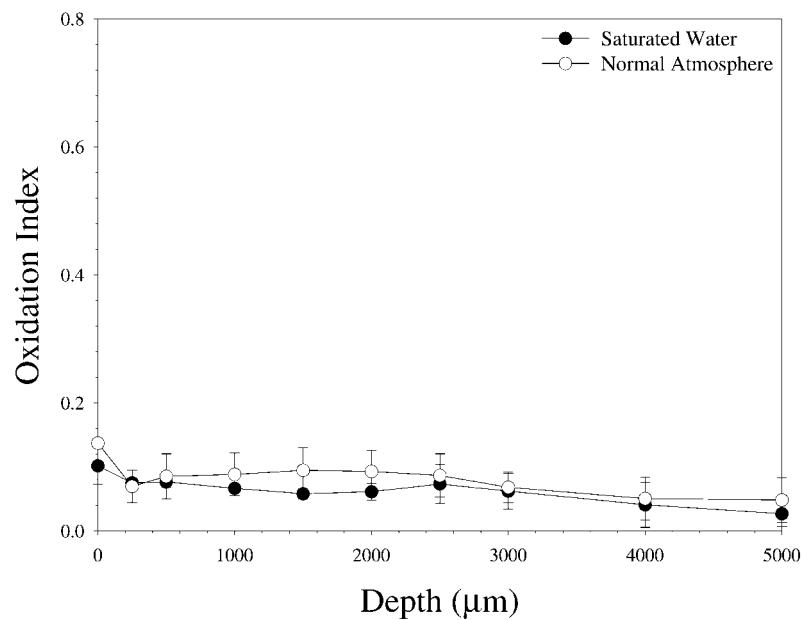
the direction of cut after the skivings were made. These striations could be observed by light microscopy.

Figure 7(a–c) shows the depth profile of the OI for samples autoclaved for 2 weeks in a dry (ambient) environment and an environment saturated with water vapor at 70°C. In all three cases the presence of water vapor had no effect on the development of carbonyl species in the samples, because the profiles were the same with or without added moisture. It appears from the results of the air-irradiated samples that the presence of moisture in the environment around the shelf-aged samples was *not* responsible for the apparent stabilization of the surface against the formation of carbonyl species with shelf-aging time.

Figure 8 shows the depth profile of the HI for the air-irradiated sample removed from its plastic pack with water added to the autoclave. After 2-weeks aging at 70°C, the HI increased more than the OI (relative to the constant methylene peak in the IR) to a depth of about 3000 μm , beyond which it decreased significantly. The HI at the surface was higher than the value between 200 and 3000 μm , very much like the profiles shown for the shelf-aged samples in Figure 4. The lower levels beyond 3000 μm would suggest that oxygen had not penetrated to beyond that depth by diffusion within 2 weeks at 70°C, and the HI beyond that depth was due to the dissolved oxygen present at the time of irradiation. Interest-



(a)



(b)

Figure 7 The oxidation index for UHMWPE samples aged 2 weeks in a sealed autoclave at 70°C with and without water vapor present: (a) irradiated in plastic packaging, (b) irradiated in foil packaging and removed prior to aging, and (c) irradiated in foil packaging and left in the pack during aging.

ingly, the HI after 2 weeks at 70°C was of comparable magnitude to the HI values for the shelf-aged samples after 2–8 years shown in Figure 4. However, the HI at depths beyond 3000 μm was lower than the shelf-aged values, again suggest-

ing that it was limited by the oxygen present at the time of irradiation.

Accelerated Aging at 80°C. Samples were aged at 80°C in an atmospheric oven, that is, at ambient

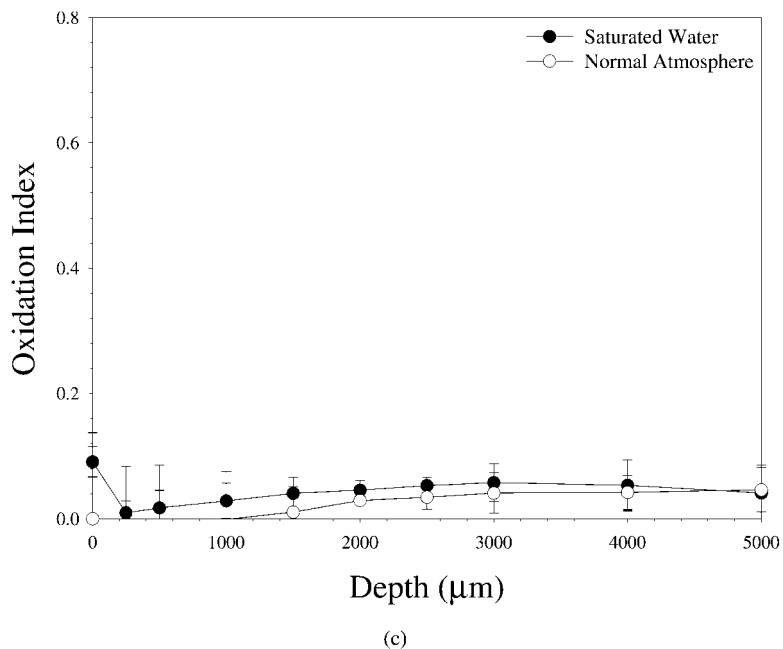


Figure 7 (Continued from the previous page)

pressure rather than in a sealed autoclave. Additionally, two schemes for reducing the oxidation of UHMWPE samples were tested in this environment: extended time under vacuum to remove more oxygen from the sample, and extended room-temperature aging in the foil package to

promote termination of the free radicals prior to accelerated aging after removal from the foil package.

Plastic Packaging. Figure 9 shows the depth profiles of the OI for plastic-packaged irradiated

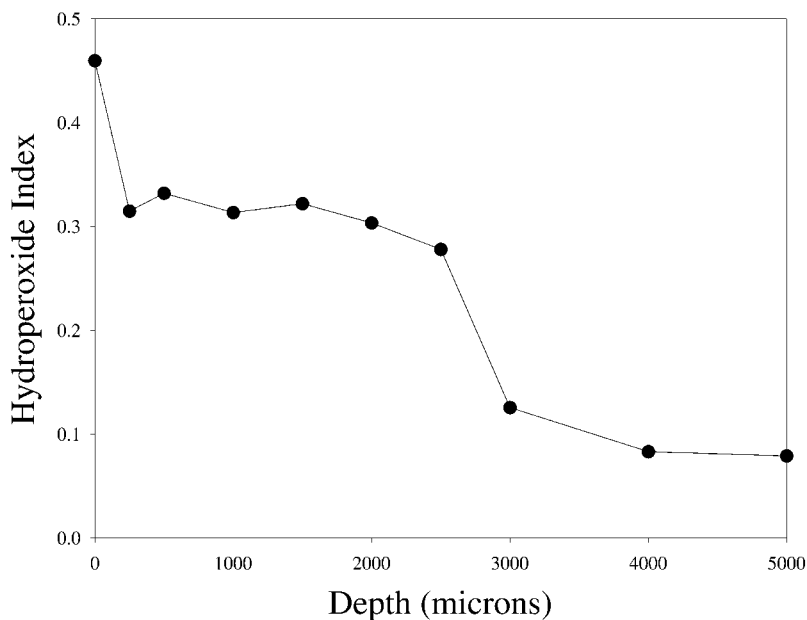


Figure 8 Hydroperoxide index for air irradiated sample autoclaved at 70°C for 2 weeks saturated with water vapor.

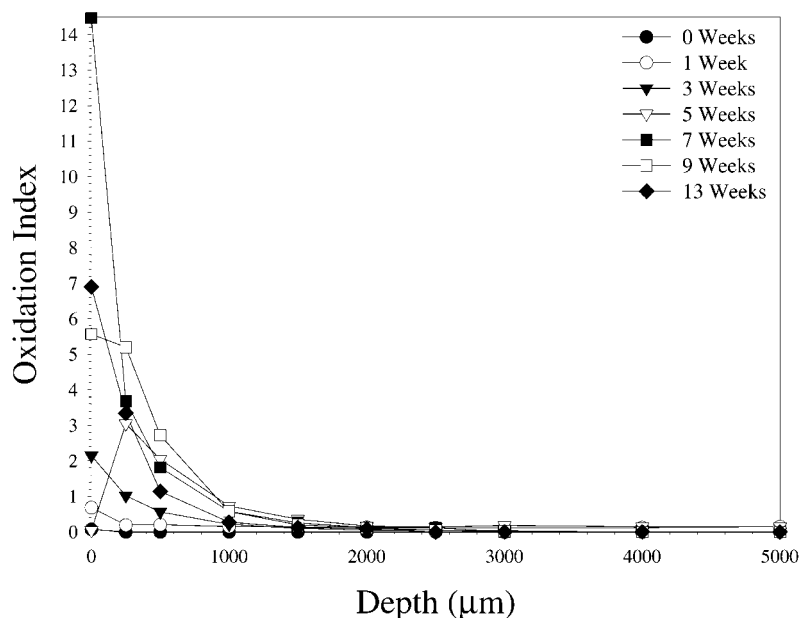


Figure 9 The oxidation index for UHMWPE samples irradiated in plastic containers, then removed and aged at 80°C.

samples aged at 80°C for up to 13 weeks in the atmospheric oven. The profiles were very different in shape than the shelf-aged samples, because there was virtually no evidence of a subsurface peak. Only the profile after 5 weeks of accelerated aging may be judged to have developed a subsurface peak, although not at 2000- μm depth, and only because the surface value appeared to have $\text{OI} = 0$. The zero value at the surface may have been an artifact, because the IR spectra at the surface were sometimes difficult to obtain due to the finite width of the sample window. (Flynn²⁷ also observed nonzero surface values consistently in her accelerated-aging studies at both 70 and 80°C.) The development of the carbonyl species was much more rapid at 80°C (Fig. 9) than at room temperature (Fig. 3), in part due to the much more rapid diffusion of oxygen at 80°C compared to the transport rate at 25°C. The very low, but measurable, OI levels beyond 2000 μm arose from oxygen present at the time of irradiation.

Figure 10 shows the HI profiles for the same samples as in Figure 9. As in the 70°C aging study, the HI profiles were observed to have some relatively high values, comparable to the shelf-aged samples, to a depth of about 3000 μm . Beyond 3000 μm , the HI values were low and probably resulted from only oxygen present at the time of irradiation.

One interesting feature of the time variation of

the HI within the first 3000 μm from the surface was the increase up to ca. 5 weeks of accelerated aging, followed by a decrease in HI values. This observation is consistent with the reaction scheme, which shows that the hydroperoxides form first, then decompose to produce carbonyls. Petruj and Marchal reported observing a similar effect in 1980³² for low-density polyethylene undergoing thermo-oxidation at 95°C. In their study, they induced oxidation reactions thermally at 95°C, but did not indicate that samples had been irradiated previously. Additionally, they irradiated samples at 25°C, but implied that the irradiation continued for up to 50 days. Thus, although their systems were not exactly like those reported here, it is interesting that they observed a maximum in the hydroperoxide concentration in time, with a simultaneous autocatalytic acceleration of the carbonyl production. These observations were explained by assuming that ketones were produced by a chain reaction in which the consumption of hydroperoxides followed by their regeneration takes place.³¹

Vacuum Foil Packaging. Figure 11 shows the OI depth profiles for UHMWPE samples irradiated in the vacuum foil packages, and subsequently removed from the packs prior to accelerated aging at 80°C. Differences in the OI between these samples and identically aged samples from the plastic

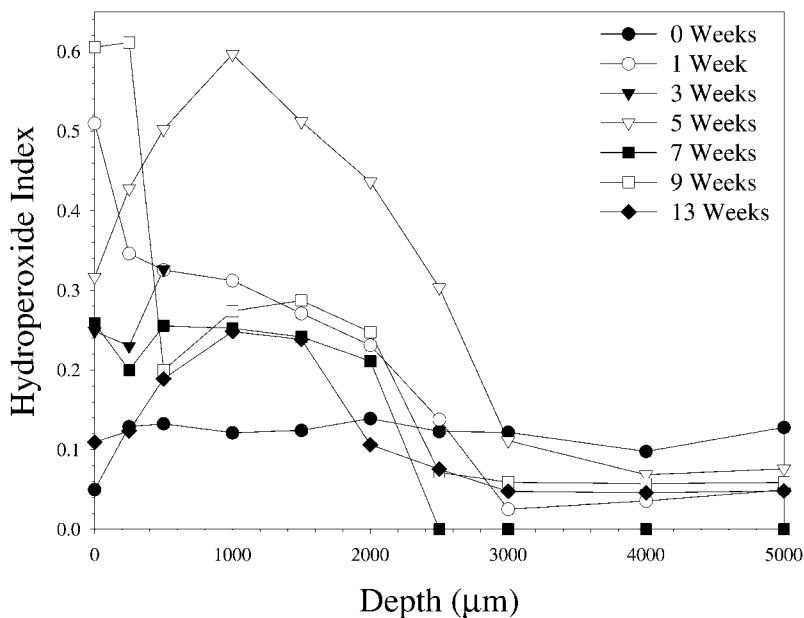


Figure 10 The hydroperoxide index for UHMWPE samples irradiated in plastic containers, then removed and aged at 80°C.

packs would show that either oxidation was due primarily to oxygen present within the piece at the time of irradiation, or that free-radical termination had occurred within the 48-h delay between irradiation and aging.

Careful examination of Figures 9 and 11 indi-

cate that there was little difference in the oxidation profiles of the two sets of samples in the core of the samples. However, it was noted that the OI at the surface of the foil-irradiated sample remained quite low until 5 weeks of aging. It also was observed that a large increase in the OI oc-

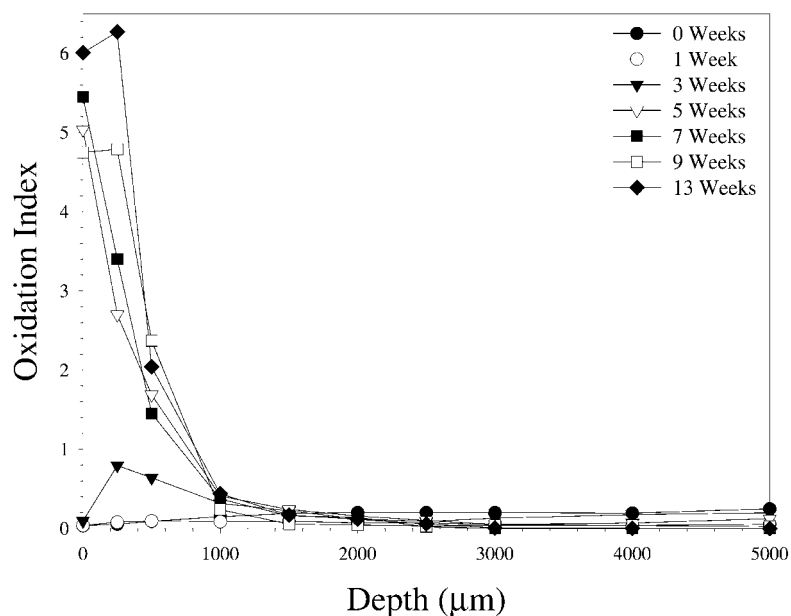


Figure 11 The oxidation index for UHMWPE samples irradiated in vacuum foil packs, then removed and aged at 80°C.

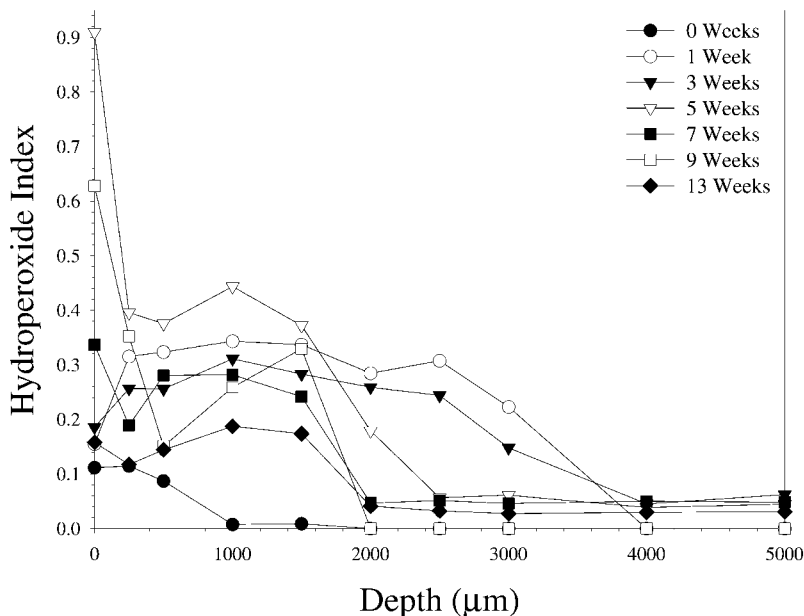


Figure 12 The hydroperoxide index for UHMWPE samples irradiated in vacuum foil packs, then removed and aged at 80°C.

curred between 3 and 5 weeks of aging in the 500 μm closest to the surface in the foil-irradiated samples. The fact that there were no differences in the OI profiles beyond ca. 1000 μm indicated again that the major contributors to sustaining the reactions were the elevated temperature and the oxygen that diffused into the samples. The concentration of oxygen present in the pieces initially was small compared to that needed to cause the observed degradation.

Figure 12 shows the HI as a function of depth into the same samples. Again, other than some differences at the surface, the depth profiles shown in Figures 10 and 12 for plastic- and foil-packed samples were essentially the same. After increasing for 5 weeks, the HI began to decrease slightly with longer accelerated aging times, consistent with their role as precursors to the carbonyls.

Reduced Oxygen Level. Several samples were left in the vacuum chamber for an additional hour in an attempt to remove some of the oxygen present at the time of irradiation. These samples were then sealed in the vacuum packs and irradiated as usual. Computer simulations of the oxygen profile after these treatments suggested that the oxygen concentration was reduced within the first 2000 μm from the surface by about 10%. The samples were then removed from their foil packs

after irradiation and placed in the 80°C oven as before.

Figure 13 shows the OI profiles of those samples after different accelerated aging times. These data can be compared to the aging data in Figure 11 up to 7 weeks of aging. It is clear that the profiles were about the same, even including the rather large increase in the OI, which occurred between 3 and 5 weeks of aging at 80°C. The values near the surface, where the oxygen concentration was somewhat lower, were essentially the same in both experiments, as was the depth to which the OI was noted to increase beyond the background level. The OI below about 2000 μm was almost imperceptible. These data again indicated that, after about 3 weeks, the oxygen diffusion rate at 80°C was sufficiently rapid to provide ample oxygen near the surface region for carbonyl formation, to a depth of about 2000 μm , and that residual oxygen at the time of irradiation was almost insignificant and present in the hydroperoxides.

Figure 14 shows the HI depth profile for the same samples, which had some oxygen removed. They were essentially the same as those in Figure 12, which were processed in the normal way, again showing the decrease of the HI after 5 weeks of aging. It appeared that oxygen transport was sufficiently rapid at 80°C in these pieces to

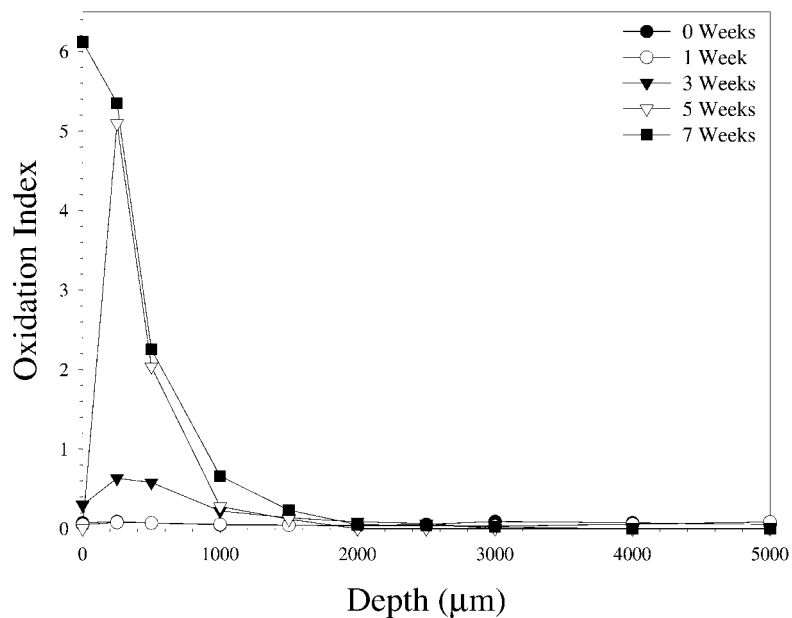


Figure 13 The oxidation index for UHMWPE samples held in vacuum for 1 h prior to sealing in vacuum packs, then removed and aged at 80°C.

make up for the reduced oxygen concentration due to the extended vacuum time.

5-Week Healing Experiment. Eyere and Federo³³ noted that withholding oxygen from irradiated UHMWPE samples for about 20 days was

sufficient to heal the broken polymer chains by free-radical termination (i.e., by crosslinking). Consequently, several samples were left in their vacuum packages at room temperature for 5 weeks after irradiation. Subsequently, the samples were removed from their vacuum packages

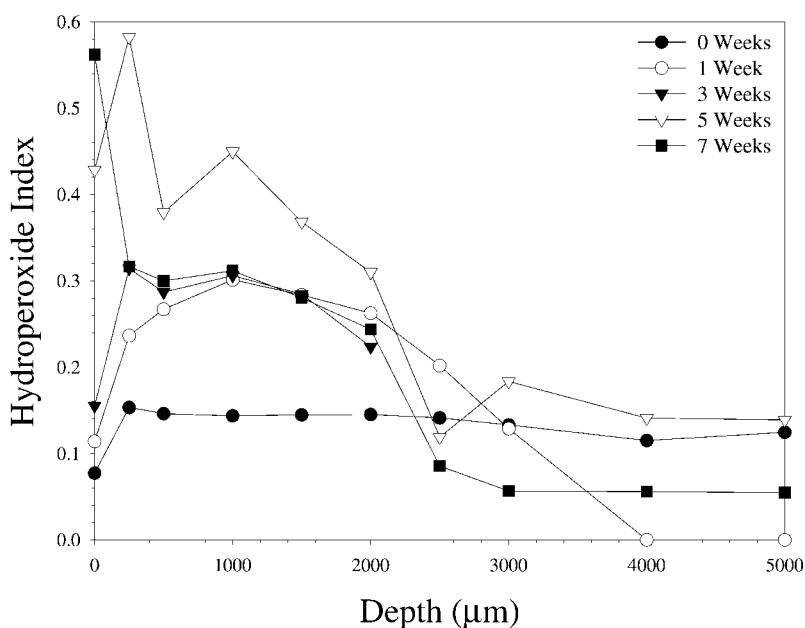


Figure 14 The hydroperoxide index for UHMWPE samples held in vacuum for 1 h prior to sealing in vacuum packs, then removed and aged at 80°C.

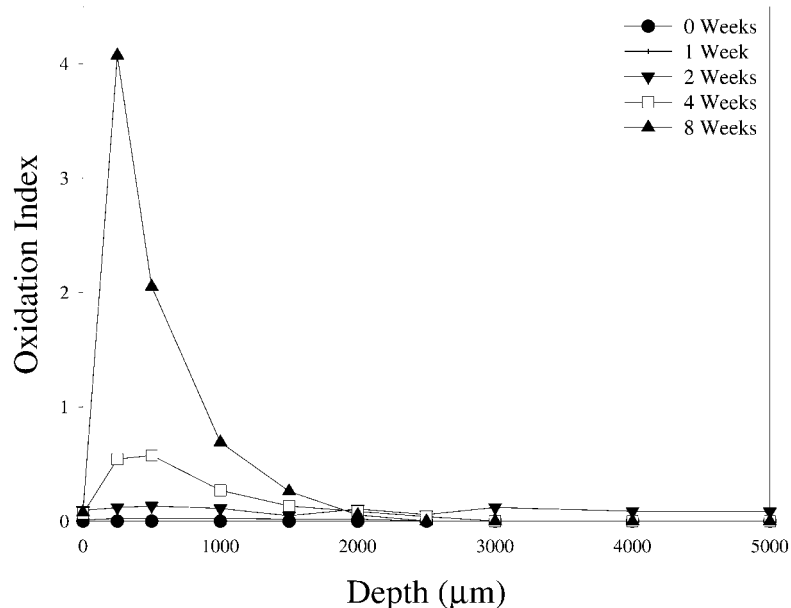


Figure 15 The oxidation index for UHMWPE samples healed for 5 weeks in vacuum packs at room temperature, then removed and aged at 80°C.

and subjected to accelerated aging to ascertain whether the free radicals had undergone crosslinking and oxidative degradation would be reduced.

Figure 15 shows the OI profiles for these samples and indicated that oxidation had occurred to a depth of at least 2000 μm , and perhaps a bit further. The OI appeared to be somewhat lower in the first 4 weeks than the OI profile for the unhealed samples shown in Figure 11. However, after 8 weeks of accelerated aging, the OI increased to levels comparable to those for similar aging times without the healing step. The significant increase in the OI in the 1000 μm closest to the surface between 4 and 8 weeks of aging was observed as before.

The HI depth profiles shown in Figure 16 show similar trends as those for the unhealed samples shown in Figure 12. The HI increased almost uniformly over a depth of about 3000 μm over the first 4 weeks of accelerated aging, but then decreased between weeks 4 and 8 of aging. Very little change occurred deeper than 3000 μm .

One thing that was noted in the 5-week healed samples was that the OI and the HI both had lower values at the surface than the comparable unhealed samples. Whether this observation was an artifact, due to the difficulty in accurately measuring the surface values, is uncertain at this time. However, it was interesting that in ex-

tended shelf-aged pieces the OI at the surface remained essentially at its very low initial value, in spite of the presence of oxygen during the aging step. The healing step, on the other hand, was performed with the sample isolated in a vacuum (i.e., without oxygen). Thus, there appeared to be some stabilization of the surface with the 5-week healing step, but not beyond the surface. Evaluating longer healing times may be suggested.

CONCLUSION

Oxygen plays a significant role in the degradation of orthopedic implants after sterilization with Co-60 irradiation. Depth profiles of an OI, which reflected the level of carbonyl species present, and an HI, which accounted for the hydroperoxide species, were measured in samples which had been either shelf aged at room temperature, or accelerated aged at 70 or 80°C. Carbonyl species were monitored by the change in the IR peak at 1720 cm^{-1} compared to the methylene peak at 1370 cm^{-1} , whereas the hydroperoxides were monitored in NO-derivitized samples by taking the ratio of IR peaks at 1630 cm^{-1} to the methylene peak at 1370 cm^{-1} .

A subsurface peak in the OI was shown to develop in shelf-aged samples after sufficient aging time had elapsed, which in these samples was

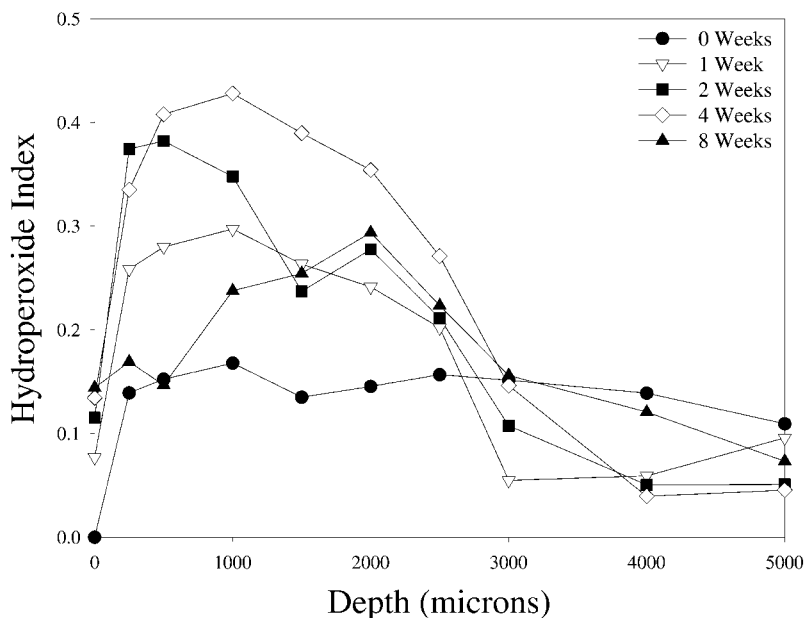


Figure 16 The hydroperoxide index for UHMWPE samples healed for five weeks in vacuum packs at room temperature, then removed and aged at 80°C.

on the order of 4–6 years. The OI continued to increase at all depths below the surface to a depth of ca. 5000 μm . By contrast, the HI depth profiles were shown to reach a constant level within about 2 years and did not change substantially thereafter. Thus, it appeared that the hydroperoxides reached a pseudo steady-state level, whereas the carbonyls continued to form.

Accelerated aging in a sealed reactor at 70°C demonstrated that removing the samples from their plastic and vacuum-sealed packages prior to the aging tests produced similar OI profiles, although air-irradiated samples had noticeably higher surface OI values than the samples removed from the vacuum foil packs. Virtually no oxidation was noted in samples that were left in their vacuum packs, suggesting that oxygen diffusion into the piece was responsible for sustaining the degradation reactions, and residual oxygen still in the piece at the beginning of accelerated aging was not a significant contributing factor to oxidation. Additional moisture in the aging environment did not affect the oxidation process.

No differences were noted in the OI and HI profiles beneath the surface between plastic-pack and vacuum-pack irradiated samples when aged at 80°C after removing the pieces from their packages. Removing some dissolved oxygen by leaving the piece under vacuum for an additional hour

prior to vacuum sealing made essentially no difference in the OI and HI profiles in the core of the samples. Very little difference was noted in the OI and HI profiles below 1000 μm for samples that had been left in their vacuum packs for 5 weeks at room temperature to promote free-radical termination by crosslinking. These results suggested that free-radical termination did not occur, and that the majority of the carbonyl and hydroperoxide formation resulted from oxygen that diffused into the pieces during the accelerated aging process. Keeping the irradiated samples in oxygen-lean environments for increasingly longer periods of time produced some surface stabilization leading to reduced carbonyl formation (Figs. 11, 13, and 15) and ultimately toward reduced hydroperoxide formation (Fig. 16).

Alcohols were not observed at levels above the noise in the IR spectra of any of the NO-derivatized shelf-aged samples or the accelerated aged samples. This suggested that either the alcohol-forming reactions did not occur to any great extent, or that alcohols decomposed as fast as they formed. However, it should be noted that alcohol-degradation reactions are not common under these rather mild conditions. Therefore, it is reasonable to assume that alcohols were not a by-product of the reactions that occurred in the UHMWPE samples.

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