

Characterization of Oxygen Scavenging Films Based on 1,4-Polybutadiene

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ABSTRACT: To better characterize the fundamentals of oxygen scavenging as a means to prepare high oxygen barrier polymer films, the oxidation of 1,4-polybutadiene, in the presence of a transition metal salt catalyst, cobalt neodecanoate, was studied at 30 °C. Oxygen uptake of 1,4-polybutadiene films was measured as a function of cobalt neodecanoate concentration. In these samples, oxygen mass uptake values as high as 15 wt % were observed, and the kinetics of oxidation were of the order of 10 days. Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) analysis suggest that the oxidation was heterogeneous, with the film surface being highly oxidized and the film center being less oxidized. Interestingly, the oxygen uptake exhibited a maximum with catalyst loading, which is believed to be related to the heterogeneous nature of the oxidation process. Since antioxidants are typically added during the industrial scale preparation and the amount of antioxidants would affect the oxygen mass uptake value and oxidation kinetics, the importance of an antioxidant removal method and a normalized purification strategy were determined prior to oxygen uptake experiments.

INTRODUCTION

Although the use of polymers in packaging has grown rapidly, polymers have not replaced glass and metal in a number of applications.¹ One reason for the lack of penetration is that polymer packaging systems based on passive diffusion alone cannot always provide adequate barrier properties to gases such as oxygen. Oxygen must be excluded from some foods and beverages to maintain freshness and avoid changes in flavor and texture. The presence of oxygen at even ppm levels causes certain foods and beverages to experience deleterious oxidation or other aerobic degradation processes.² There is considerable interest in the use of reactive polymer membranes in oxygen scavenging systems,^{3–8} in part because conventional packaging materials, such as poly(ethylene terephthalate) (PET), do not have low enough oxygen permeation properties, by themselves, to meet certain applications, such as the packaging of beer in long-shelf life plastic bottles.⁹ Incorporation of oxygen scavengers into otherwise passive barrier polymers can markedly reduce oxygen transmission and extend the shelf life of oxygen sensitive products to levels rivaling those of glass and metal packaging over time scales of use for food and beverage applications.^{2,10,11}

Oxygen scavenging materials are important in active packaging. The removal of headspace oxygen and providing barriers to environmental oxygen have long been targets in the packaging of oxygen-sensitive products.¹² Early attempts include vacuum packaging and inert gas flushing,¹³ use of sachets containing oxygen scavengers in low oxygen transmission conditions,¹⁴ and introducing salts, such as potassium sulfite or sodium sulfite,¹⁵ and oxidizable metal complexes¹⁶ into barrier polymers.

Oxygen scavenging systems that incorporate reactive hydrocarbon polymers doped with transition metals have been

reported by, among others, Speer et al.¹¹ and Cochran et al.⁹ For example, polyamides, such as poly(*m*-xylylene adipamide), typically known commercially as MXD6 can also be used as oxygen scavenging polymers.^{9,11} Blends of PET with small amounts of MXD6, doped with an appropriate transition metal salt, can be used to prepare oxygen scavenging systems. Such systems are now used commercially in some barrier packaging applications requiring high oxygen barrier.

Polybutadiene is an important synthetic rubbery polymer that is readily oxidized upon exposure to even low levels of atmospheric oxygen at room temperature. Many studies of thermo-oxidation,^{17–21} photo-oxidation,^{22–26} and ozonolysis²⁷ of polybutadiene have been conducted during the last 50 years, and several oxidation mechanisms have been suggested.^{21,23,28} However, most of these studies have focused on preventing oxidation of polybutadiene under processing or use conditions. Only a few studies have examined oxidation rate, mass uptake, or application of polybutadiene in oxygen scavenging materials.^{11,29} In such cases, it is typical to add a small amount of a transition metal catalyst to the polybutadiene to accelerate the oxidation. In this regard, cobalt neodecanoate is a popular choice in the patent literature.^{11,29–31}

This study reports the influence of preparation and reaction conditions on oxidation of 1,4-polybutadiene. Commercial 1,4-polybutadiene samples contain antioxidants that can be largely removed prior to preparing oxygen scavenging films. However, UV tests show that antioxidants are not totally removed in a single purification step, and oxygen sorption experiments

Received: August 25, 2011

Revised: April 30, 2012

Accepted: April 30, 2012

Published: April 30, 2012

confirm that oxygen uptake and oxidation rate are affected by the number of purification steps (i.e., extent of antioxidant removal). Oxygen uptake and oxidation rate stabilize after a sufficient number of purification steps, suggesting that antioxidants can be removed at least to a level that they no longer measurably influence oxygen scavenging, so in this study, we report the influence of extent of antioxidant removal on oxygen scavenging. Cross-linking was detected both before (i.e., in the absence of exposure to oxygen) and during the oxidation process, so we report observations of this phenomenon. Additionally, the effect of cross-linking on oxygen uptake was also studied. In oxygen uptake experiments, oxygen mass uptake by 1,4-polybutadiene was measured using a noninvasive oxygen sensor based system.³² The oxygen uptake experiments show that oxygen uptake can reach values as high as 15 wt %. The effects of catalyst concentration on oxygen uptake rate and amount were determined.

■ EXPERIMENTAL SECTION

Cyclohexane (anhydrous, 99.5%), toluene (anhydrous, 99.8%), and methanol (anhydrous, 99.8%) were purchased from Sigma-Aldrich Inc. (St. Louis, MO) and used as received. Cobalt neodecanoate liquid (12 wt % in mineral oil) was purchased from Shepherd Chemical Company (Norwood, Ohio) and was diluted 100 times using cyclohexane (volume fraction) in a volumetric flask before use.

1,4-Polybutadiene (36% cis, 55% trans, and 9% vinyl, $M_n = 230\,000$) was purchased from Scientific Polymer Products Inc. (Ontario, New York) and purified as follows: 50 g of 1,4-polybutadiene was dissolved in 450 mL of dry toluene in a 1000 mL three-necked flask equipped with a mechanical stirrer at 65 °C under nitrogen. The polymer was then precipitated from solution by pouring the solution into 2000 mL of methanol at room temperature. The precipitated 1,4-polybutadiene was placed in a seven-speed laboratory blender (Waring Laboratory, Torrington, CT), cut into small pieces, and dried under vacuum in a vacuum oven overnight at ambient temperature to remove residual methanol. These steps were repeated several times, with the exact number of purification cycles being a variable in this study. The purified 1,4-polybutadiene was stored in amber glass bottles filled with nitrogen until needed.

Polymer films were prepared by solution casting. The polymer was dissolved in cyclohexane at 2 wt % solids while stirring in an amber glass bottle. Then, a prescribed amount of the cobalt catalyst, cobalt neodecanoate, was added to the solution while stirring. Once the solution was well mixed, the casting solution was poured into a glass casting ring (2 in. in diameter) on a Teflon plate and kept under nitrogen in a glovebox covered with aluminum foil for 8 h to permit the cyclohexane to evaporate. Then, the films were stored under vacuum at ambient conditions for an additional 6 h to remove residual solvent. To minimize the influence of polymer mass and thickness on oxygen mass uptake, all of the 1,4-polybutadiene films had the same surface area and similar thickness (nominally 100 μm). Film thickness was measured using a Mitutoyo Litematic VL-50A indicator (Mitutoyo Corporation, Japan).

Oxygen mass uptake was measured using an OxySense noninvasive oxygen analyzer system that has been described previously.³² Ball Mason jars (1/2 pint) were used as sample containers. They initially contained air at ambient conditions. The polymer films were placed inside the Mason jars, which were subsequently sealed and placed in a temperature

controlled wooden box, maintained at 30 °C, for the duration of the oxygen scavenging experiment. Oxygen uptake (mass of oxygen consumed/mass of polymer) was calculated indirectly from the decrease in the oxygen partial pressure in the headspace of the Mason jars over time.³² The size of the polymer samples was small relative to the size of the Mason jar to ensure that the oxygen partial pressure did not decrease extensively during the course of the scavenging measurement. The majority of the uncertainty in determining oxygen uptake of scavenging materials comes from uncertainties in the oxygen partial pressure and container volume. The uncertainty in oxygen uptake ranges from $\pm 3\%$ to $\pm 14\%$ depending on the measurement conditions.³² Previous studies have identified conditions under which oxygen uptake measured in the sealed Mason jars is essentially equal to that measured by leaving the samples exposed to ambient air, providing an essentially infinite sink of oxygen for the sample to oxidize, and these studies were conducted under such conditions.³²

The amount of residual antioxidant in the polymer was characterized by ultraviolet (UV) spectroscopy. UV spectra were recorded on a Shimadzu Mini UV spectrometer (Columbia, MD). Untreated and purified polybutadienes were dissolved in cyclohexane to prepare 5 wt % solutions. Solutions were filtered through a 0.1 μm Whatman PURADISC Teflon syringe filter to remove any solid impurities. Then, the polybutadiene solutions were transferred to quartz cuvettes using glass pipettes for UV tests. Pure cyclohexane was used as reference background before each sample test.

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was performed using a Thermo Nicolet Nexus 470 FT-IR spectrophotometer (Madison, WI) equipped with an ATR Smart Avatar Miracle attachment (Zinc Selenide crystal). The measurements were conducted at 1 cm^{-1} nominal resolution, 256 scans, and the region from 675 to 4000 cm^{-1} was recorded for each spectrum. The data were collected and analyzed using Omnic software from the spectrometer manufacturer.

X-ray photoelectron spectroscopy (XPS) was used to characterize oxidation of the $\alpha\text{-C}$ next to the $\text{C}=\text{C}$ double bonds in the polymer main chain as well as monitor changes in the carbon and oxygen atomic percentage change in film. XPS spectra were obtained using a Kratos Axis Ultra Electron Spectrometer (Kratos Analytical Inc., Chestnut Ridge, NY) equipped with a monochromatic Al $K\alpha$ ($h\nu = 1456.6\text{ eV}$) X-ray source. Operating conditions were: 1×10^{-9} Torr background pressure; 15 KV; 200W X-ray power. For XPS analysis of the center of an oxidized film, the film was fractured by bending. A sandwich structure was readily visible across the cross section of the film, consisting of a brittle, highly oxidized surface layer and a softer, less oxidized core layer. A razor blade was used to cut through the sample to expose the surface of the center of the film, and XPS analysis was conducted immediately on the newly generated surface (i.e., the film center of an oxidized 1,4-polybutadiene film). This step was undertaken just before loading the sample into the XPS apparatus to limit any additional oxidation of the sample prior to performing the XPS measurements.

■ RESULTS AND DISCUSSION

UV spectroscopy is one method to characterize antioxidant concentration in 1,4-polybutadiene since many common oxidation antioxidants are strongly UV-active. Figure 1 presents the UV spectra of purified and unpurified (i.e., as-received)

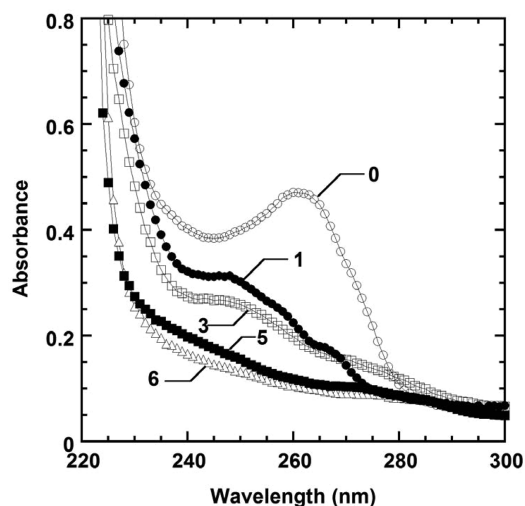


Figure 1. UV spectrum of unpurified and purified 1,4-polybutadiene; ○: unpurified 1,4-polybutadiene (i.e., 0 purification cycles); ●: 1,4-polybutadiene after 1 purification cycle; □: 1,4-polybutadiene after 3 purification cycles; ■: 1,4-polybutadiene after 5 purification cycles; △: 1,4-polybutadiene after 6 purification cycles. The numbers shown next to the spectra indicate the number of dissolution/precipitation purification cycles that the sample was subjected to prior to acquiring the spectrum.

polybutadiene samples. The peak between 240 and 280 nm is ascribed to the antioxidant. After one purification cycle, the peak height decreases, as shown in Figure 1. The peak decreases to the point that it is no longer resolvable after five purification cycles. However, even very small amounts of antioxidant can influence the oxidation of 1,4-polybutadiene.³³ In our experiments, we made one additional cycle of purification (i.e., a sixth cycle) and compared the oxygen mass uptake from samples with various numbers of purification steps.

Other than purification cycles, vacuum storage time is also essential to oxygen uptake experiments. During the film preparation, after the evaporation of cyclohexane in a nitrogen-filled glovebox, polybutadiene films were stored in a vacuum oven to remove residual solvent. However, experiments showed that the observed oxygen mass uptake values depend on the length of time of vacuum storage. To study this effect, 1,4-polybutadiene films were stored under vacuum for various periods of time beyond the 6 h stated in the Experimental Section before being transferred to the Mason jars for oxidation. The results of this study are presented in Figure 2. This experiment used 1,4-polybutadiene samples that had been subjected to 6 purification cycles and contained 200 ppm of cobalt neodecanoate. The films were prepared as described in the Experimental Section except they were stored under vacuum for different amounts of time, from 6 to 168 h. They were then transferred to Mason jars, where their oxygen mass uptakes were measured. On the basis of the results presented in Figure 2, the maximum oxygen mass uptake decreases as vacuum storage time increases. For the sample stored under vacuum for 6 h, oxygen uptake reaches a maximum, after about 7 days, of approximately 15 wt %. Samples stored under vacuum for longer times show less oxygen uptake. For example, for the sample stored under vacuum for 168 h, the maximum oxygen uptake is only about 9 wt %.

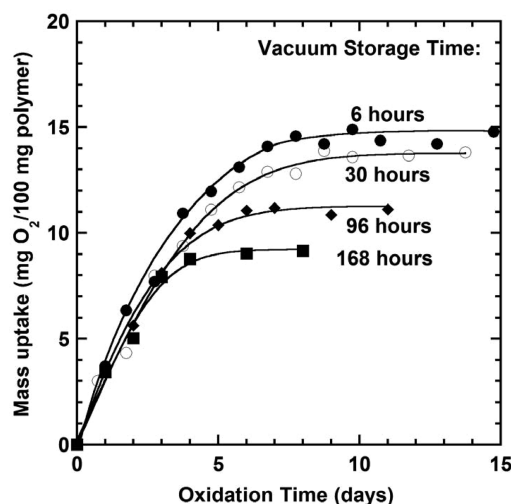


Figure 2. Effect of vacuum storage time on oxygen mass uptake. The abscissa (oxidation time) is measured from the moment that the films were initially exposed to air following removal from the vacuum oven.

Since there was no oxygen in the vacuum oven, no oxidation reaction (and, therefore, no mass uptake) would occur inside the vacuum oven. Adventitious oxygen could be present during the film-making process, but the small amount of oxygen would not lead to large differences in the subsequent oxygen uptake experiment. Obviously, some changes in the film occur during vacuum storage. Although a complete understanding of this phenomenon is not available, we believe there could be several reasons for this behavior. Cross-linking can occur between the double bonds without the presence of oxygen, or it could be initiated by radicals produced by the adventitious oxygen present during the film preparation process.^{22,23} However, swelling experiments only showed a light extent of cross-linking in samples that were stored in vacuum for 96 and 168 h. The oxygen mass uptake values are very sensitive to cobalt catalyst concentration (see Figure 4 in the later discussion); change in catalyst activity during vacuum storage time could affect the observed oxygen uptake. Catalyst activity might be affected by either chemical or physical processes. For example, the state of dispersion of cobalt catalyst in the polymer film might change due to the loss of some of the mineral oil into which the catalyst was originally dispersed. Since vacuum storage is required for residual solvent removal, this step cannot be eliminated before oxygen uptake experiments. To standardize the oxygen uptake experiment, the vacuum storage time during the film preparation process was fixed. All films (except those discussed in Figure 2) were stored under vacuum for six hours before testing.

FTIR was used to characterize the chemical changes occurring in the polymer during oxidation, and the results are presented in Figure 3. Several new peaks were observed in FTIR spectra after 2 weeks of oxidation in air at room temperature. On the basis of their positions, the peak at 3450 cm^{-1} is assigned to hydroxyl groups, the one at 1715 cm^{-1} is consistent with the presence of carbonyl groups,²² and peaks at 1250 and 805 cm^{-1} indicate the generation of epoxides.³⁴ The disappearance of the sharp peak at 965 cm^{-1} indicates the consumption of C=C bonds in the trans-1,4 structure.³⁵ These groups have been reported in other polybutadiene oxidation studies.^{22–24}

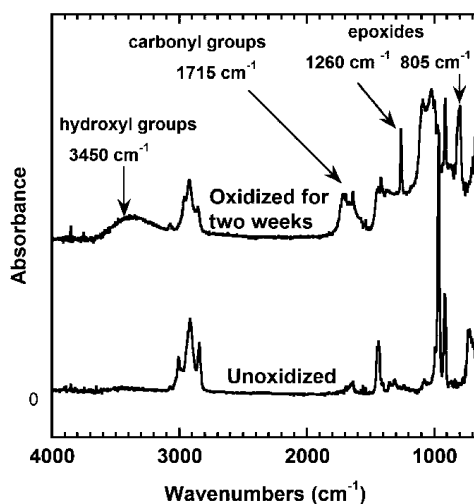


Figure 3. ATR-FTIR spectra of oxidized and unoxidized 1,4-polybutadiene films.

In commercial 1,4-polybutadiene, antioxidants are added to prevent oxidation and cross-linking.³⁶ If there are antioxidants

in cobalt-catalyzed 1,4-polybutadiene films, the free radicals generated at the beginning stages of oxidation will be consumed by the antioxidant, leading to an induction period in oxygen uptake. That is, there will be a period of time at the beginning of the experiment when there is no measurable oxygen uptake (i.e., oxidation), followed by a period where oxygen uptake increases as the sample oxidizes. Figure 4 presents oxygen mass uptake data as a function of the number of purification cycles. For each fixed number of purification cycles, three or four different cobalt neodecanoate concentrations were used in preparing the polymer membranes.

The unpurified 1,4-polybutadiene film exhibited an induction period approximately 4 days long in a sample containing 1000 ppm of cobalt neodecanoate. Even more time was required to initiate measurable oxidation in a sample containing less cobalt neodecanoate (e.g., 400 ppm) (cf., Figure 4A). The sample containing 200 ppm of catalyst did not exhibit measurable oxygen uptake even after 1 month, suggesting that the sample was stable against oxidation, due to the presence of the oxidation antioxidants, for at least 1 month at this catalyst concentration.

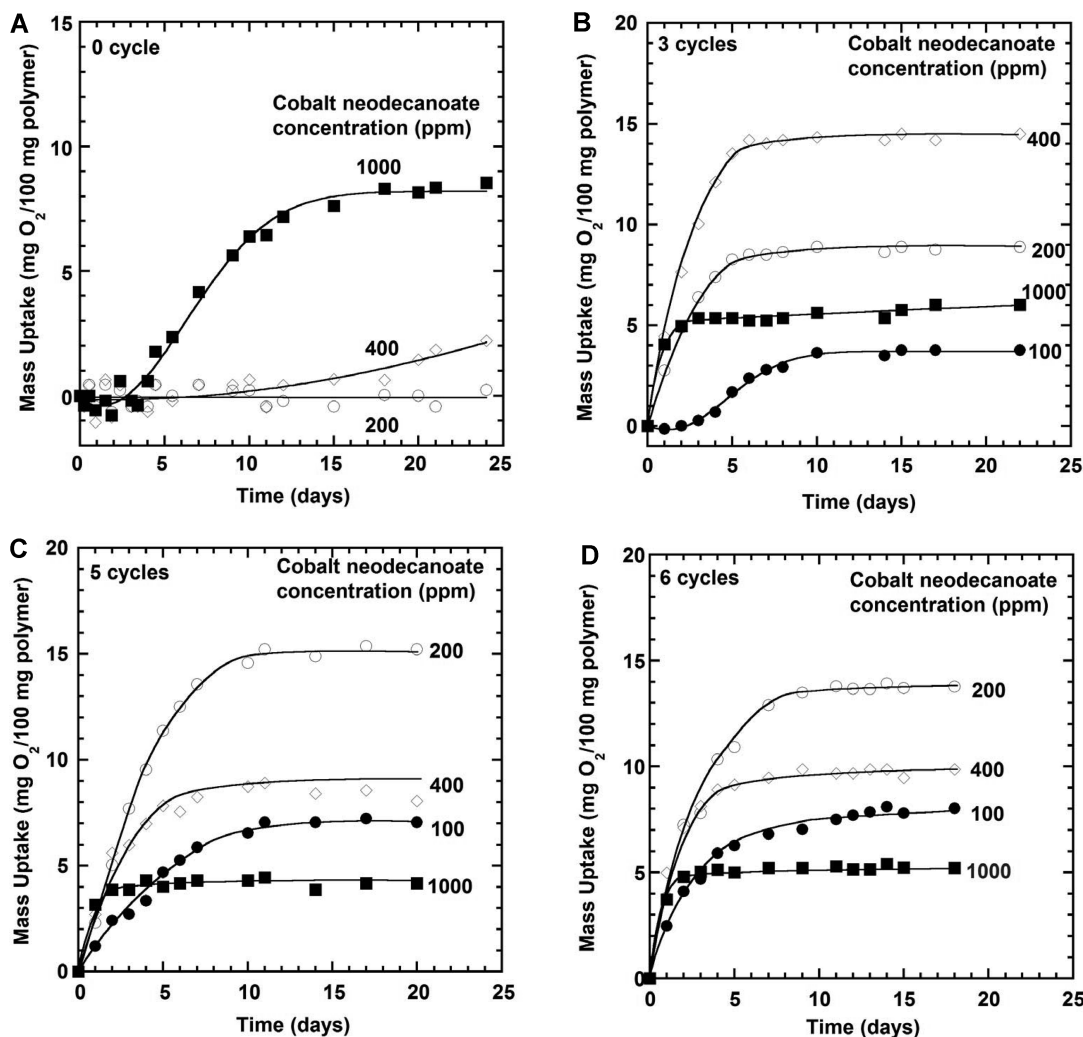
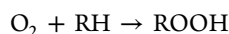


Figure 4. Influence of cobalt neodecanoate concentration and number of purification cycles on oxygen mass uptake. The cobalt neodecanoate concentrations are the numbers beside each data set (e.g., 100 ppm cobalt neodecanoate): (A) unpurified, (B) three cycles, (C) five cycles, and (D) six cycles.

Both Co^{2+} and Co^{3+} species are reported to participate in the steps of oxidation and help generate free radicals. More specifically, the oxidation reactions proposed in the literature are³⁷



where RH is a section of the 1,4-polybutadiene molecule susceptible to oxidation. Typically, the allylic carbon–hydrogen bonds would be the most susceptible linkages to undergo oxidative degradation, because of their lower bond energy (85 kcal/mol) compared with the tertiary C–H bond energies in saturated hydrocarbons (90–103 kcal/mol) and vinylic C–H bond energy (105 kcal/mol).³⁸ Of course, oxidation of the double bonds to form epoxides²² and generation of carboxylic acid from aldehydes,²⁴ etc., are other potential sources of oxygen uptake.

Upon increasing cobalt neodecanoate concentration, the free radical generation rate will increase. Simultaneously, antioxidants in the polymer consume free radicals and terminate the reaction before chain transfer occurs, preventing the polymer film from being oxidized before all the antioxidants are consumed.³³ After the antioxidant has been consumed, the reactions noted above can occur to a greater extent. Then, significant oxidation begins to be observed and continues until the surface of the film is highly oxidized.²² At this point, the rate of oxygen mass uptake slows, since presumably the highly oxidized surface is much less permeable to oxygen, the oxidation rate decreases sharply, and oxygen mass uptake stabilizes.^{39,40}

An induction period is also observed in the sample prepared with three purification cycles and 100 ppm of catalyst (cf., Figure 4B), but the induction time is shorter than in the unpurified samples. In films with higher catalyst concentration (200, 400, and 1000 ppm), the induction period disappears altogether.

Some studies suggest that an induction period followed by acceleration is typical of an autoxidation reaction,¹⁹ because chain transfer reactions occur after photo initiation⁴¹ as part of an autocatalytic reaction. This behavior was not observed in the present work. The induction period disappears in Figure 4B (samples undergoing 3 purification cycles) at higher catalyst concentrations, and the induction period does not appear at all in Figure 4C,D, which presents results from samples that have undergone 5 and 6 purification cycles, respectively. The disappearance of the induction period does not mean that antioxidants no longer affect the oxidation reaction. If one compares Figures 1 and 4B,C, there is a still significant difference in oxidation as well as in the UV spectra. One potential hypothesis to explain the disappearance of the induction period is that the samples may still be exposed to a small amount of oxygen during the film-making process, and this adventitious oxygen may generate enough peroxide free radicals to consume the residual antioxidant before the oxygen uptake measurements were started.

Figure 4B shows the highest oxygen mass uptake in samples containing 400 ppm of cobalt neodecanoate, while Figure 4C exhibits the highest oxygen mass in samples containing 200 ppm of cobalt neodecanoate. The oxygen mass uptake of a sample containing 100 ppm of cobalt neodecanoate in Figure

4B is lower than that in Figure 4C. While UV tests show a significantly reduced peak at 250 nm for the sample having three purification cycles relative to the as-received polymer, the oxygen mass uptake data show obvious effects of residual antioxidants on the oxidation kinetics and uptake.

The oxygen mass uptake of 1,4-polybutadiene subjected to six purification cycles is presented in Figure 4D. The highest oxygen mass uptake (14.5 wt %) is obtained in the sample containing 200 ppm of cobalt neodecanoate. This result is similar to that in the sample subjected to five purification cycles (cf., Figure 4C), which exhibited maximum oxygen uptake (15 wt %) in a sample containing 200 ppm of cobalt neodecanoate. Additionally, the oxygen mass uptake values at 100, 400, and 1000 ppm of cobalt neodecanoate are similar in the samples that were subjected to either five or six purification cycles. Thus, it appears that the antioxidants are removed to the point that they have little effect on the oxidation kinetics and uptake after five purification cycles. To put the oxygen uptake values in perspective, the solubility coefficient for oxygen in 1,4-polybutadiene is $0.957 \times 10^{-6} \text{ cm}^3(\text{STP})/(\text{cm}^3\text{Pa})$.⁴² This value, corresponding to 0.003 wt % oxygen uptake at ambient conditions, is negligible compared to the total amount of oxygen scavenged by 1,4-polybutadiene, which according to Figure 4C,D, is on the order of 15 wt %.

The oxidation half-life is defined, in these studies, as the time required for the oxygen mass uptake to reach 50% of its ultimate value. It provides a crude, model-independent way to characterize the oxidation kinetics. The half-lives of the oxidation reactions are presented in Figure 5. The half-life

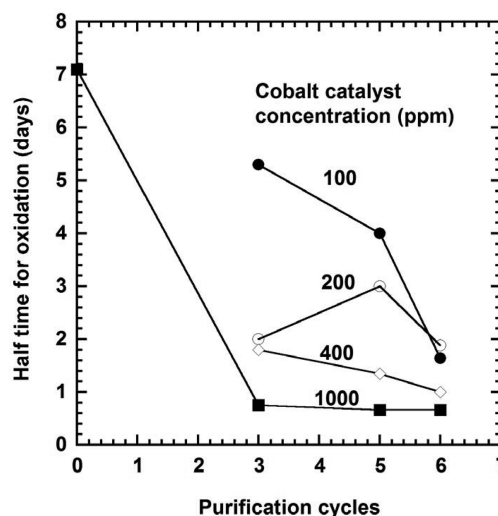


Figure 5. Effect of purification cycles on half-life of oxidation in 1,4-polybutadiene films containing ●: 100 ppm; ○: 200 ppm; ◇: 400 ppm; and ■: 1000 ppm of cobalt neodecanoate. The half-life values (i.e., the time at which half of the final oxygen mass uptake is reached) were obtained from Figure 4.

values show the effect of purification cycles and catalyst loading on oxidation reaction rates. As the number of purification cycles increases from three to six, the half-life of the reaction decreases, and the half-lives of samples with low catalyst loading (i.e., 100 ppm) are more sensitive to the number of purification cycles than that of samples with high catalyst loading (i.e., 1000 ppm). For example, the half-life for oxidation decreases to a low value that is independent of the number of purification cycles after only 3 purification cycles when a catalyst loading of 1000

ppm is used. For a sample containing 100 ppm of catalyst, the half-life is higher than that in the 1000 ppm sample and still decreases even after 6 purification cycles. This is one of the samples which showed negligible oxygen uptake after 30 days when polymer that was not subjected to any purification steps is used (cf. Figure 4A), so presumably the half-life for this sample at zero purification steps would be well above the upper limit of Figure 5.

XPS analysis was also utilized to study the chemical changes during oxidation and was shown in Figure 6. Tests were

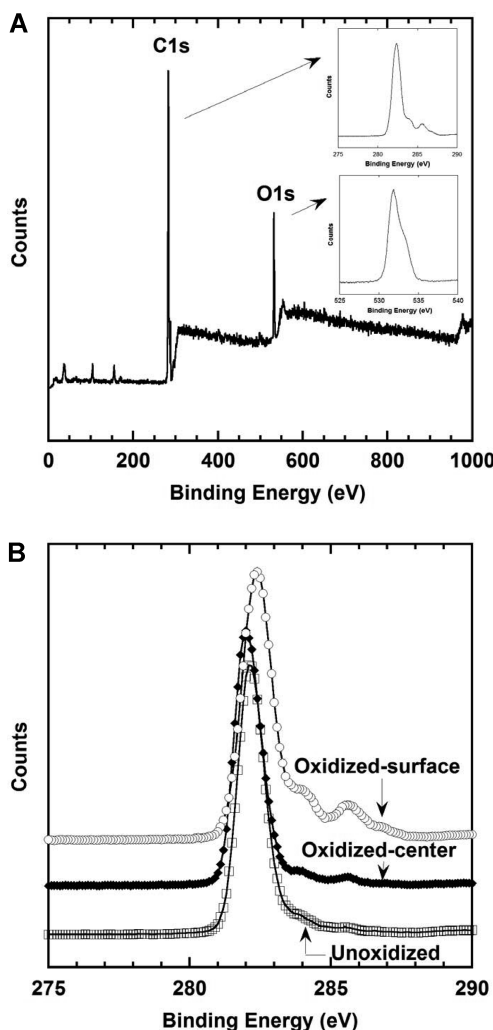


Figure 6. XPS spectra of oxidized and unoxidized 1,4-polybutadiene films. (A) Survey spectra of oxidized film surface. (B) C 1s high-resolution spectrum of oxidized and unoxidized films; □: unoxidized 1,4-polybutadiene film; ♦: oxidized 1,4-polybutadiene film center; ○: oxidized 1,4-polybutadiene film surface.

performed both on the film surface and the center of the film. In these studies, 1,4-polybutadiene was purified as described above. Cobalt neodecanoate (200 ppm) was added to the casting solution, and the films were prepared by the process described above. The films were oxidized in air for 2 weeks at 30 °C. The carbon and oxygen spectra were obtained by XPS both on the surface and at the film center. To detect the oxygen content at the film center, the film surface layer was removed using a clean razor blade.

A survey spectrum of the surface of oxidized 1,4-polybutadiene is shown in Figure 6A, and it shows the presence of carbon and oxygen. Because of the low concentration of cobalt neodecanoate catalyst, no cobalt peaks are observed in the survey spectrum. High resolution spectra were also taken of the C1s and O1s regions. The binding energy for C1s is between 280 and 288 eV. For O1s, the binding energy is around 533 eV.⁴³ The peak at 286 eV is assigned to the carbon–oxygen double bond. High resolution C1s spectra of an unoxidized film, an oxidized film surface, and an oxidized film center are presented in Figure 6B. The main peak at 282 eV remained fundamentally unchanged before and after oxidation. Two new peaks appeared in the spectrum of the oxidized film surface. The shoulder peak around 284 eV beside the main peak is assigned to the C–O binding, and the peak at 288 eV is attributed to the C=O binding, indicating the presence of a large amount of hydroxyl and carbonyl groups.

These two peaks can also be observed in the spectrum of the oxidized film center. However, the peak strength is much weaker. This result is consistent with the film surface being more highly oxidized than the film center. Carbon and oxygen atomic percentage were also calculated from the XPS analysis, and the results are recorded in Table 1. On the basis of the data

Table 1. XPS Results from Surface and Center of Oxidized and Unoxidized 1,4-Polybutadiene Films

atomic %	unoxidized 200 ppm cobalt neodecanoate	oxidized 2 weeks, center	oxidized 2 weeks, surface
carbon	96.1	89.7	75.2
oxygen	3.9	10.3	24.8

in Table 1, there is a much higher concentration of oxygen in the oxidized film surface sample than at the film center. On the film surface, there is 24 mol percent of oxygen, while at the film center, the oxygen content is only 10%.

On the basis of these results, a highly oxidized layer is generated at the film surface during oxidation. Further studies, to be reported separately, demonstrate that the highly oxidized layer has more than 2 orders of magnitude lower oxygen permeability than the unoxidized polymer.⁴⁴ Oxidation and cross-linking lead to an increase in polymer density, which would tend to decrease fractional free volume (FFV), thereby decreasing the diffusion coefficient and permeability of polymer films toward all gases.⁴⁵ Additionally, as samples oxidize, the glass transition temperature, T_g , increases remarkably, which suggests much more restricted chain motion in highly oxidized films, and this effect would also tend to reduce penetrant transport through the polymer film; in fact, unoxidized polybutadiene had a T_g of −92 °C, but highly oxidized polybutadiene showed no glass transition events whatsoever in differential scanning calorimetry (DSC) scans from −180 °C to +250 °C, suggesting a marked rigidification of the polymer backbone as a result of the oxidation process.⁴⁴

The formation of this highly oxidized, impermeable crust on the outside of these samples appears to markedly impede the transmission of oxygen to the center of the film and oxidation at the film center is, correspondingly, much lower than at the film surface. That is, the oxidation proceeds in a heterogeneous fashion, with a highly oxidized surface protecting (from oxygen penetration) a much less oxidized core. Of course, the extent of oxidation of the core versus the surface of the films should be sensitive to film thickness, among other variables, and a future

study will report the influence of film thickness on the heterogeneity of oxidation.⁴⁴

CONCLUSIONS

Catalyst-promoted oxidation of commercially available 1,4-polybutadiene was studied as part of a project aimed at characterizing the oxygen scavenging properties of this material. The influences of the polymer purification protocol (i.e., number of purification cycles and time under vacuum) on oxygen uptake and uptake kinetics were explored. These films eventually sorb up to 15 wt % oxygen; for the thickness used here, the oxidation process occurs over approximately 1 week. FTIR and XPS studies show the presence of hydroxyl and carbonyl groups after oxidation. The films have a highly oxidized surface and a less oxidized film center, suggesting that the oxidation is heterogeneous.

The ability to be easily oxidized makes 1,4-polybutadiene among the simplest of oxygen scavenging systems that can be readily studied, from a fundamental perspective, in reasonable time frames. In real packaging applications, melt processability would also need to be considered. In this regard, block copolymers containing butadiene units may be more useful because of their ability to be blended and melt processed with conventional barrier packaging materials. Studies of oxygen scavenging properties in solution cast and melt extruded SBS films will be discussed elsewhere.⁴⁵

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research is based upon work supported by the National Science Foundation under Grant No. DMR #0423914. The authors also gratefully acknowledge the financial support provided by Eastman Chemical Co. (Kingsport, TN).

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