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Non-invasive headspace measurement for characterizing oxygen-scavenging in polymers

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ABSTRACT

A non-invasive headspace analysis method to measure rate and amount of oxygen uptake in oxygen-scavenging polymers is presented. Oxygen uptake data for metal-catalyzed poly(1,4-butadiene) at 30 °C are provided to illustrate the method. These data were obtained by measuring oxygen headspace concentration above the scavenging polymer with an OxySense® 200T non-invasive oxygen sensor, and, for comparison, oxygen uptake was measured with an analytical balance. Excellent agreement was observed between these two independent experiments.

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1. Introduction

Although there is a growing demand for high barrier packaging polymers due to their compelling advantages over glass from weight, safety, and aesthetic viewpoints, conventional polymers do not provide enough oxygen barrier resistance to replace glass and metal in certain applications, such as the packaging of beer, fruit juices, and some pharmaceutical agents [1]. However, recent developments in the area of active packaging have led to improved oxygen barrier properties of polymeric materials by incorporating an oxygen-scavenging polymer (OSP) into the package wall [2]. By reacting with and sequestering oxygen diffusing through the container, catalytically activated OSPs dramatically reduce the amount of oxygen that permeates into the headspace of the package, thereby increasing the shelf-life of the product [3].

Oxygen transmission rates of high barrier materials are commonly measured with an Ox-Tran (Mocon, Inc.) oxygen transmission rate measurement system [1]. This system uses a patented coulometric sensor to detect oxygen transmission through flat films and packages [1]. However, high barrier materials that include OSPs are nearly impermeable to oxygen until the scavenging capacity is exhausted; therefore, oxygen transmission rates can be negligible for long periods of time (e.g., several months) [4]. Scavenging performance is more efficiently characterized via oxygen uptake measurements, and headspace analysis is useful for such studies [5]. The potential evolution of volatile by-products during the oxygen-scavenging process may limit the use of gravimetric or barometric sorption methods to measure oxygen uptake [6].

To measure oxygen uptake via headspace analysis, a polymer sample is first loaded into a vessel of known volume, which is then charged with a gas of known oxygen composition. Then, the gas in the headspace is sampled using an oxygen sensor or a gas chromatograph to determine the headspace oxygen concentration. Based on the known initial amount of oxygen charged to the system and the known volume, temperature, pressure and composition in the headspace, a mass balance is used to determine the amount of oxygen taken up by the film. By sampling the headspace oxygen concentration as a function of time, the rate of oxygen scavenging and total amount of oxygen scavenged can be determined. Because excessive sampling can introduce leaks or contaminants into the headspace, a non-invasive measurement of headspace oxygen concentration is desirable.

This article describes a non-invasive headspace measurement to determine the rate and amount of oxygen uptake of OSPs. In this method, an OxySense® 200T (OxySense, Inc.) non-invasive oxygen sensor is used to measure changes in oxygen concentration inside 1/2 pint Ball® Mason jars loaded with OSP samples. The OxySense® 200T measures the fluorescent radiation released from an oxygen-sensitive film attached to the inside of the Mason jar to determine headspace oxygen concentration. This non-invasive system allows

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for the simultaneous and reliable measurement of the amount and rate of oxygen scavenging of multiple OSP samples. This ability to increase the number of repetitions can be important in quantifying sample variation and identifying spurious data, which could otherwise provide misleading characterization of the scavenging material.

2. Principle of operation

Fig. 1 presents a schematic of the system used for non-invasive headspace measurements. The oxygen analyzer is an OxySense® 200T purchased from OxySense, Inc. (Dallas, TX), and this sensor has been previously used in oxygen-scavenging studies [7]. This analyzer consists of the 200T instrument, a bifurcated fiber optic cable bundle with an infrared detector attached to a reader pen, and oxygen-sensitive films (OxyDot®). The OxySense® measures the oxygen concentration inside a transparent, sealed container by monitoring the fluorescence of the OxyDot® upon illumination with the reader pen. Dynamic quenching by oxygen molecules causes the OxyDot® fluorescence lifetime to decrease in proportion to the oxygen partial pressure in the container. The temperature of the OxyDot® is measured simultaneously via the infrared sensor contained in the reader pen. In the system shown in Fig. 1, the OxySense® 200T interfaces with a Dell 2400 personal computer through a USB port. The OxyDots® are mounted inside the transparent sample container with clear, silicon rubber (GE 284, GE Sealants and Adhesives, Huntersville, NC).

The sample container, in which the polymer sample is sealed and oxygen is scavenged, is a 1/2 pint Ball® Mason jar. Mason jars are inexpensive and easy to seal, and the jars can sustain subatmospheric pressures for long periods of time. The interiors of hermetically sealed ampoules, which were considered as an alternative to the Mason jars, were difficult to access due to their small diameter opening. As a result, mounting OxyDots® was laborious, and residual adhesive from the mounting process could create pinhole leaks in the ampoule seal. Fig. 2 presents headspace oxygen concentration data for various transparent containers that were initially filled with 100% nitrogen. After approximately two months of storage in air, Mason jars exhibited the slowest rate of oxygen ingress, and the rate of oxygen concentration increase, 0.003%/day, was well below the experimental error observed in the control sample, which was a sample jar open to ambient air. The upward drift in oxygen concentration in the control sample can be attributed to signal drift, which is reported by the manufacturer to be <5% of the reading.

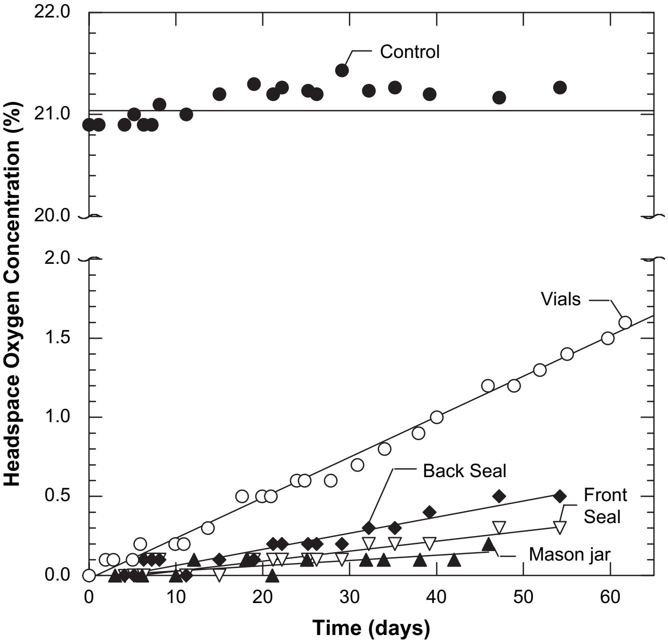

Fig. 2. Oxygen headspace measurements of various nitrogen filled enclosures (○ glass vial with phenolic screw cap; ◆ glass vial with Teflon® plug and back sealing *o*-ring; ▽ glass vial with Teflon® plug and front sealing *o*-ring; ▲ 1/2 pint Ball® regular Mason jar; ● unsealed glass vial, open to atmosphere).

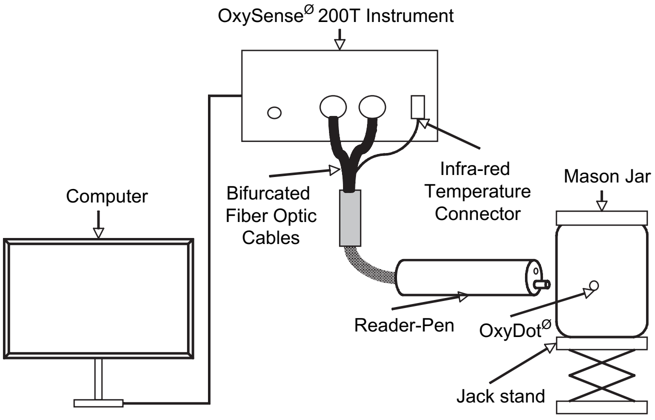

Fig. 1. Schematic diagram of OxySense® non-invasive oxygen analyzer system.

The ability of the 1/2 pint Ball® Mason jars to hold vacuum is verified using a technique illustrated in Fig. 3. A 1/4″ stainless steel tube was routed through a Mason jar lid and affixed with metal epoxy. Pressure inside the Mason jar was reduced with a vacuum pump, and the reduced pressure inside the jar was monitored with the OxySense® and simultaneously confirmed with an external pressure gauge. Using this technique, 1/2 pint Ball® Mason jars are found to maintain pressures below 1 psia for over one month.

Effective OSPs can consume 50 cm^3(STP) O_2/g of polymer (or more) at rates as high as 5.0 cm^3(STP) O_2/g of polymer/day. Therefore, a small amount of OSP (~100 mg) can scavenge substantial amounts of oxygen (~5 cm^3(STP)) at a rate of approximately 0.5 cm^3(STP)/day [2]. The reported oxygen detection limit

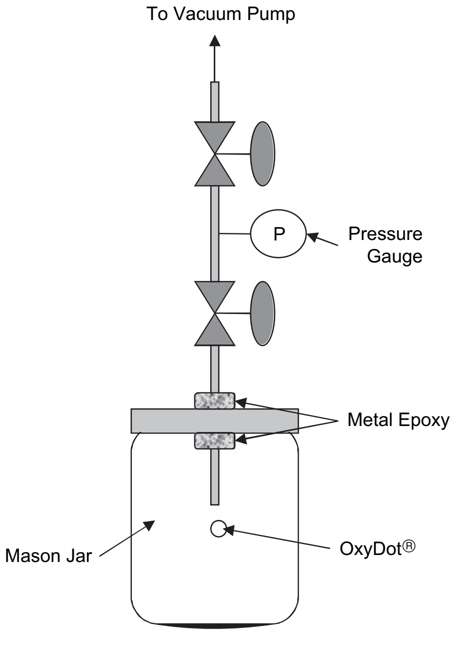

Fig. 3. Schematic diagram of Mason jar vacuum testing apparatus.

of the OxySense® 200T is 0.13 cm^3(STP); therefore, the use of just 100 mg of an OSP generates a measurable change in oxygen concentration inside a 1/2 pint Ball® Mason jar. The small sample requirement also facilitates concurrent testing of many samples since these small Mason jars are conveniently stored and readily available.

Scavenging performance of polymeric materials is often characterized by the amount of oxygen reacted with the polymer, i.e., the amount of oxygen consumed by the polymer. When using the OxySense® system, oxygen uptake (mass of oxygen consumed/mass of polymer) is calculated from measured oxygen partial pressures inside the Mason jars as follows:

1. The number of moles of free oxygen in the Mason jar at time t, n_t, is calculated from the corresponding partial pressure measured at time t, P_t, according to the ideal gas law [8]:

$$n_t = \frac{P_t \times \left(\mathrm{Vol_{jar}} - \mathrm{Vol_{polymer}}\right)}{R \times T} \tag{1}$$

where $\mathrm{Vol_{jar}}$ is the internal volume of Mason jar, $\mathrm{Vol_{polymer}}$ is the volume of the polymer, R is the ideal gas constant, and T is the temperature of the OxyDot®.

2. The mass uptake of oxygen at time t, M_t, is calculated by subtracting n_t from the initial number of moles of oxygen in the jar, n_0. The mass uptake is then normalized by the weight of the film as follows:

$$M_t = \frac{[n_0 - n_t] \times \mathrm{MW}}{m_0} \tag{2}$$

where MW is the molecular weight of oxygen, and m_0 is the initial film mass.

An accurate value of $\mathrm{Vol_{jar}}$ is obtained from the difference in weight before and after the addition of deionized water to a sealed Mason jar. Water is added to the jars via a small hole drilled through the lid, and the weight of water at room temperature is readily converted to volume using tabulated density data of water [8]. $\mathrm{Vol_{polymer}}$ is found by dividing the polymer film mass by the film density, ρ. The polymer film density is determined by hydrostatic weighing using a Mettler Toledo balance (Model AG204, Switzerland) and a density determination kit [9].

Fig. 4 presents an example of the conversion of oxygen partial pressure data to mass uptake values for a model scavenging polymer. The solubility of oxygen in typical polymers is very low compared to the amount of oxygen that can react with an oxygen-scavenging polymer. For example, the solubility of oxygen in poly(1,4-butadiene) is 0.957×10^{-6} cm^3(STP)/cm^3 Pa, and this value, corresponding to 0.003 wt% at ambient conditions, is negligible compared to the total amount of oxygen scavenged by poly(1,4-butadiene), which, according to Fig. 4, is on the order of 14 wt% [10].

3. Method validation

The oxygen uptake kinetics of poly(1,4-butadiene) (36% *cis*, 55% *trans*, and 9% vinyl) doped with 200 ppm of cobalt were determined at 30 °C in several independent and complementary experiments. The polymer was purchased from Scientific Polymer Products, Inc. (Cat# 052, Ontario, NY). The films, approximately 100 μm thick, were cast from 2% (w/v) methylene chloride solutions into Teflon casting rings. After drying under nitrogen for 24 h, films were stored under vacuum to assist in removal of residual solvent. Cobalt was added to the pre-cast solutions in the form of cobalt neodecanoate from Shepherd Chemical Company (Norwood, OH).

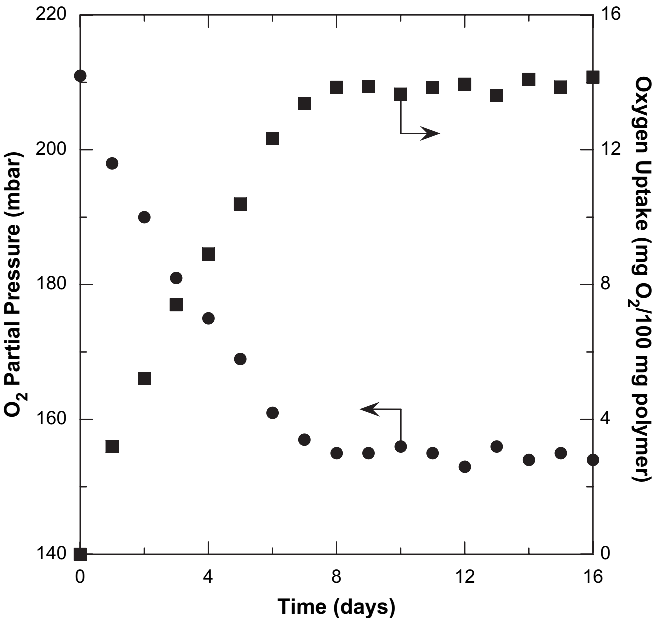

Fig. 4. Conversion of raw headspace measurements to mass uptake values for poly(1,4-butadiene) doped with 200 ppm cobalt at 30 °C. Film mass and film thickness are 124.9 mg and 100 μm, respectively. Cobalt was added as cobalt neodecanoate.

Three uptake experiments were conducted with the cobalt doped, poly(1,4-butadiene) films, and the results from these experiments are shown in Fig. 5. The first experiment, referred to as "Integral OxySense®", tracked the mass uptake of a film stored in a single Mason jar over a period of 16 days. This experiment followed the operation procedures outlined previously.

The use of the OxySense® technique to measure mass uptake requires a change in oxygen partial pressure inside the Mason jar,

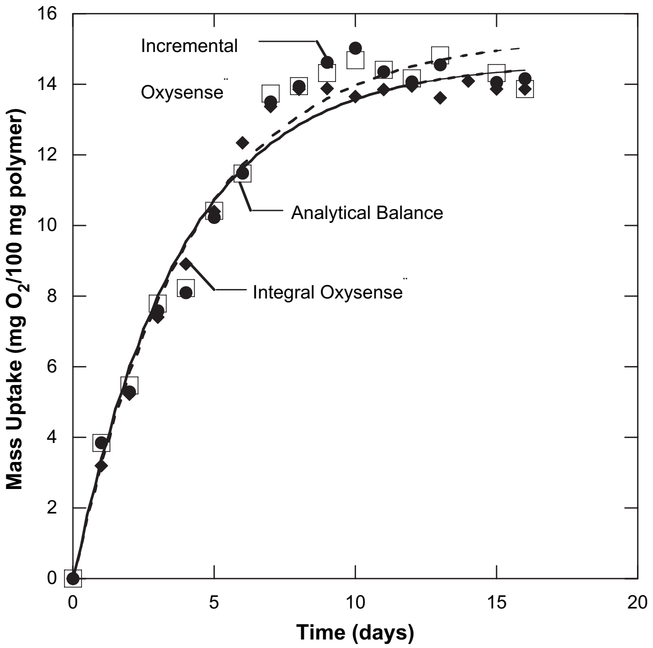

Fig. 5. Comparison of analytical balance and OxySense® data for oxygen uptake of poly(1,4-butadiene) doped with 200 ppm cobalt at 30 °C (☐ Analytical Balance, $k = 0.23 \pm 0.04$ $days^{-1}$, $M_f = 15.6 \pm 0.8$ mg O_2/100 mg polymer; ● Incremental OxySense®, $k = 0.24 \pm 0.03$ $days^{-1}$, $M_f = 15.4 \pm 0.4$ mg O_2/100 mg polymer; ◆ Integral OxySense®, $k = 0.27 \pm 0.04$ $days^{-1}$, $M_f = 14.6 \pm 0.5$ mg O_2/100 mg polymer). The solid and dashed curves represent the least-squares fit of the Integral OxySense® and Analytical Balance data, respectively, to the first order kinetic model given in Eq. (4). Cobalt was added as cobalt neodecanoate.

Table 1
Summary of oxygen uptake methods and experimental results

Method	Description	k (days)	M_f (mg O_2/100 mg polymer)
Analytical Balance	• OSP sample removed from jars on each of their scheduled test day and manually weighed • Each of the 16 data points is a separate sample	0.23 (±0.04)	15.6 (±0.8)
Incremental OxySense®	• OxySense® measurement of "Analytical Balance" sample prior to removal of the sample from the jar • Each of the 16 data points is a separate sample	0.24 (±0.03)	15.4 (±0.4)
Integral OxySense®	• Repeated OxySense® measurement of the same OSP sample, without opening jar • All 16 data points are from a single sample	0.27 (±0.04)	14.6 (±0.04)

but if mass uptake is determined gravimetrically, then no change in oxygen partial pressure is required. The mass uptake can simply be tracked by recording changes in sample mass using an analytical balance in ambient air. However, oxygen partial pressure can have a significant effect on polymer scavenging kinetics [11]. Therefore, in order to validate the OxySense® method using a gravimetric technique, samples must be stored in Mason jars so the films are exposed to oxygen partial pressures similar to those in the OxySense® experiments.

Therefore, in the experiment referred to as "Analytical Balance," 16 samples of poly(1,4-butadiene) films were prepared, ranging in mass from 107 to 126 mg, and these samples were sealed in separate Mason jars (labeled Jar 1, Jar 2, etc.). Mason jars were exposed to air at ambient temperature before loading with poly(1,4-butadiene) films, so the original total pressure inside Mason jars is 1 atm. The original oxygen partial pressure inside Mason jars was determined by measuring with OxySense® instrument. After one day, the film in Jar 1 was removed, and the film mass at time t, m_t, was recorded with an analytical balance. The oxygen uptake, M_t, was calculated as follows:

$$M_t = \frac{m_t - m_0}{m_0} \tag{3}$$

where m_0 is the initial film mass. On day two, the oxygen uptake in Jar 2 was measured using the analytical balance, and on day three, Jar 3 was measured, etc. This process continued until the oxygen uptake of all 16 samples was determined. The use of individual samples during the "Analytical Balance" experiment ensured that the mass uptake measured with the analytical balance on day 16, for example, would account for a change in oxygen partial pressure similar to the change observed in the "Integral OxySense®" experiment.

Prior to removal of each film in the "Analytical Balance" experiment, oxygen partial pressure inside the jar was recorded with the OxySense® system, and the corresponding oxygen uptake, M_t, was calculated according to Eqs. (1) and (2). These data constitute the "Incremental OxySense®" curve shown in Fig. 5, and these data agree very well with the "Analytical Balance" values. Little deviation is also observed between the "Integral OxySense®" and "Incremental OxySense®" experiments. Close agreement between these experimental data is expected since similar changes in oxygen partial pressure were maintained throughout the three independent experiments.

The rate of oxygen uptake follows first order kinetics in the presence of excess oxygen; therefore, the first order rate constant k and final oxygen uptake M_f are obtained from a best fit of the data to the following equation [12]:

$$M_t = M_\mathrm{f}\left(1 - \mathrm{e}^{-kt}\right) \tag{4}$$

The values of k and M_f determined from these independent experiments are listed in Table 1, and these values are in excellent agreement. The rate constants determined from the 16 jar, "Analytical Balance" and "OxySense® Incremental" experiments are 0.23 ± 0.04 and 0.24 ± 0.03 days^{-1}, respectively. The final oxygen uptake is 15.6 ± 0.8 mg O_2/100 mg polymer in the "Analytical Balance" experiment and 15.4 ± 0.4 mg O_2/100 mg polymer in the "Incremental OxySense®" experiment. For the "Integral OxySense®" experiment, the rate constant is 0.27 ± 0.04 days^{-1}, and the final oxygen uptake is 14.6 ± 0.5 mg O_2/100 mg polymer. Parameter uncertainties were estimated using a nonlinear least-squares method, where the uncertainty in the parameters corresponds to a change of 1 in χ^2 from its minimum value [13]. Therefore, within the precision of this technique, all three experimental protocols yield the same results.

There are several sources of uncertainty in determining the oxygen uptake of scavenging polymers with the OxySense® system: uncertainty in measuring P_t (±1 mbar), uncertainty in measuring $\mathrm{Vol}_\mathrm{jar}$ (±1 cc), uncertainty in measuring $\mathrm{Vol}_\mathrm{polymer}$ (±0.001 cc), uncertainty in measuring T (±0.1 °C), and uncertainty in measuring m_0 (±0.5 mg). The uncertainty of determining oxygen uptake is dominated by the uncertainty in measuring P_t and $\mathrm{Vol}_\mathrm{jar}$, and the uncertainty in measuring these values is about ±0.5%. Using a standard propagation of errors' analysis, uncertainties in oxygen uptake, M_t, were estimated, and these values ranged from ±3% to ±14%, depending on the uncertainty in the OxySense® measurement. Uncertainties in OxySense® measurements are highest when the total amount of oxygen consumed is smallest, i.e., at the beginning of the experiment, and lowest when the total amount of oxygen consumed is high, usually towards the end of the experiment.

4. Discussion

A non-invasive headspace measurement has been described to measure the rate and amount of oxygen uptake of oxygen-scavenging polymers. Non-invasive headspace measurements are particularly useful when studying systems where repeated measurements are needed, and data collection may occur over long periods of time. oxygen-scavenging data for metal-catalyzed poly(1,4-butadiene) at 30 °C have been provided to illustrate the method. Excellent agreement was observed between the oxygen uptake data from the OxySense® method and results collected with an analytical balance. The proposed experimental technique could be useful in active packaging applications, where it is desirable to know oxygen-scavenging amount and kinetics.

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instrument for testing of oxygen scavengers and providing valuable advice on its use.

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