Polymer 53 (2012) 4211–4221

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Characterization of the oxygen scavenging capacity and kinetics of SBS films

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ARTICLE INFO

Article history:
Received 21 June 2012
Received in revised form
6 July 2012
Accepted 14 July 2012
Available online 20 July 2012

Keywords:
Butadiene
Oxidation
Permeation

ABSTRACT

Butadiene-containing polymers such as styrene-butadiene-styrene (SBS) block copolymers are of a potential use as oxygen scavenging polymers (OSP) in barrier applications. To evaluate their use in such applications, oxygen uptake was measured for films made of an SBS copolymer and four cobalt catalyst loadings with various thicknesses. The oxygen uptake was found to be kinetically limited for thin films while diffusion controls the uptake at long times for thick films. The thickness of the oxidized region at long oxidation times is termed the critical thickness L_c and was quantified by various analyses. Thin films (i.e.,$L \leq 2L_c$) oxidize fully and homogeneously, whereas heterogeneous oxidation typically occurs in thicker films (i.e., $L > 2L_c$). A thin film model was used to extract the reaction rate parameters and a stoichiometric oxidation coefficient that describe oxygen uptake in the absence of diffusion limitation. An approximate moving-boundary model was developed to describe thick film oxidation behavior at long times and was found to be in semi-quantitation agreement with the measured uptake.

1. Introduction

Polymers are often favored as barrier materials because they are easily formed into films, sheets or bottles and are lighter in weight than alternatives like glass or metal [1]. However, for some foods and beverages, or even electronic components [2–4], there is a need for polymeric formulations that limit the ingression of oxygen into the contents of a package to a much greater extent than simple polymeric barrier materials can provide. An approach that has attracted interest in recent times is to include oxygen scavenging components into a polymeric film or bottle wall [5,6]; temporarily, this can greatly reduce the amount of oxygen reaching the package contents. This can be an effective strategy when the duration of this retarded oxygen influx is greater than the anticipated shelf life of the product. Implementation of this technique requires a judicious combination of experimental development of formulations, mathematical modeling and determination of model parameters by matching models to experiments; this has been a focus of recent research in this laboratory [7–14].

The concept envisioned requires one polymer chosen for its structural characteristics, which could also be a reasonably good barrier material like poly(ethylene terephthalate) by virtue of its low oxygen permeability, and an oxygen scavenging polymer, OSP, that chemically reacts with oxygen. The latter might be incorporated as a dispersed phase in a blend film [7,9] or layers in a multilayer film [13,14] made by coextrusion. Butadiene-containing polymers are attractive materials for oxygen scavenging since the carbon–carbon double bonds provide sites for significant oxygen reaction [15–20]; this rate can be regulated by the addition of certain catalysts [12,21,22].

The rate and extent of oxygen uptake by the scavenging component can be measured experimentally as described in numerous publications [10–12]. The extent of oxygen uptake in such experiments appears to plateau to an asymptotic value at times of the order of weeks or months [12]. The plateau value is essentially independent of film thickness when below a certain "critical thickness", but for thicker films the plateau value decreases with increasing thickness [23–25]. This is a complex process involving the physical dissolution of oxygen into the polymer, oxygen diffusing through the polymer, and reaction of the polymer with oxygen [26,27] with physical parameters being significantly affected by the chemical state of the OSP. There is ample evidence that the oxidation process is spatially heterogeneous involving a moving front in thick films [9–12,23–25]. The apparent plateau in oxygen uptake for thick films does not really mark a true end-point of the process but simply a greatly reduced rate of uptake limited by a much lower rate of diffusion through the oxidized layer owing to the changes in the intrinsic transport characteristics of the polymer resulting from the formation of polar structures by the oxidation reactions and, of course, the growing thickness of this region.

Prior analyses of the oxygen uptake by the scavenging polymer [12,28] have not adequately reduced the results to fundamental

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http://dx.doi.org/10.1016/j.polymer.2012.07.028

parameters that can subsequently be used to model the oxygen flux emerging from a blend or layered film during its functional life time, i.e., prior to the eventual breakthrough of oxygen when all the OSP has reached its scavenging capacity [7–9,13,14]. The purpose of this paper is to explore the oxygen uptake by an attractive oxygen scavenging system, viz., a styrene-butadiene-styrene, SBS, block copolymer containing varying amounts of a cobalt catalyst, for a wide range of film thicknesses. It will be shown that for thin enough films, the rate of oxygen uptake is not limited by diffusion and the results can be analyzed by a simple chemical kinetic model to obtain stoichiometric and reaction rate parameters. For thicker films, oxygen diffusion becomes limiting and the results can be understood semi-quantitatively in terms of a moving-boundary model. The "critical thickness" dividing the two regimes deduced from long term oxygen uptake data agrees well with post-mortem microscopic inspection of the partially oxidized film. The parameters deduced here should be useful for future design and modeling of blend and laminate barrier films based on this SBS/cobalt catalyst system.

2. Experimental

2.1. Materials

Styrene-butadiene-styrene block copolymers are a more convenient oxygen scavenging polymer than polybutadiene used in previous studies [10–12] owing to ease of handling and processing plus their potential compatibility, i.e., interfacial tension and adhesion, with the selected structural polymer. The SBS used here is a commercial product of Kraton Polymers, Inc., D1102, containing 28 wt.% styrene and 72 wt.% butadiene, of which 92 wt.% is 1,4 polybutadiene, with an overall $M_n = 100{,}000$.

Benzophenone (>99%), used as a photoinitator to produce radicals that triggers oxidation given a proper source of UV energy [15,17,19,28–32], was purchased from Sigma–Aldrich and used as received. The oxidation catalyst [12,33] was purchased from Shepherd Chemical Company (Cincinnati, OH) in the form of blue solid pastilles that contains 20.5 wt.% cobalt neodecanoate. The cobalt catalyst was diluted 100 times (by volume), using cyclohexane, in a volumetric flask. Cyclohexane (99.9%) was purchased from Fisher Chemical and used as received. Silicon wafers (5-in and 2-in diameter) were purchased from Addison Engineering Inc. (San Jose, CA).

2.2. Film preparation

Reactive films were made by both solution casting and spin coating techniques [11]. In solution casting, the polymer was dissolved in cyclohexane to make a 2 wt.% solution in an amber glass bottle. Predetermined amounts of cobalt neodecanoate solution and benzophenone were added to the stirred solution. After the additives were fully dissolved, the homogeneous solution was poured into a glass ring (5.1 cm in diameter) resting on a glass plate. The nacent film on the glass plate was held under nitrogen in a glove box covered with aluminum foil to allow the cyclohexane to slowly evaporate. The resulting films were stored in a vacuum oven at room temperature for an additional 6 h to fully remove the solvent. Film thicknesses were determined using a Mitutoyo Litematic VL-50A instrument (Mitutoyo Corporation, Japan) specially designed to measure the thickness of rubbery films. In this study, solution casting was used to form films with thicknesses ranging from 50 to 250 μm.

In spin coating, SBS solutions were filtered through a 5.0 and 0.2 mm Whatman® PURADISC™ Teflon syringe filter before use. From the filtered SBS solution, thin films were spin coated onto a clean, polished, native-oxide silicon (100) wafer using a Laurel WS–400B–8NPP/LITE model spin coater (North Wales, PA) at 1000 rpm for 60 s. In this study, spin coating was used to form films with thicknesses ranging from 1 to 15 μm. For oxygen mass uptake experiments, these films were left on the silicon wafers to oxidize. Since silicon wafers are impermeable to gases, the SBS films were oxidized from only one surface.

To prepare film samples for permeation experiments, 3 cm × 3 cm pieces of the thin films were cut with a razor blade and then detached from the wafer surface by immersing the wafer-film composite in deionized water. A thin wire frame described earlier [12] was used to transfer the films into a vacuum oven, where they were dried at room temperature for 1 h before use.

While the thin films were on the silicon wafer, their thicknesses were determined using a KLA-Tencor Instrument Alpha-step 200 profilometer (Mulpitas, CA). First, a small nick was cut on films using a razor blade. Physical contact of the profilometer tip with the film and the wafer gives a measure of the nick depth or the thickness of the spin-coated film.

2.3. Oxygen uptake measurement

A UV light source providing a predetermined amount of energy was used to irradiate the SBS films containing benzophenone as a photoinitator to initiate oxidation. The overall UV energy provided is a function of UV light intensity, film distance from the light source, and exposure time. To prevent premature oxidation, polymer films were kept free of oxygen by storing under an inert atmosphere (nitrogen) until the oxygen uptake experiments began. The irradiated films were kept in a temperature controlled chamber at 35 °C for the duration of the oxidation experiment. Oxygen mass uptake was tracked by monitoring weight changes of the films on a Mettler Toledo AB54-S/FACT analytical balance (accuracy to 0.1 mg); oxygen uptake is taken as the difference between the film mass at any given time and its initial mass before the start of sorption experiments. Film samples were oxidized in ambient air, ~21% oxygen, as a function of time.

The oxidation of butadiene units under the conditions of interest here involves rather complex chemistry, and the details of the reaction are beyond the scope and the interests of the current study. The butadiene units can be imagined as reactive sites that consume oxygen [10,11,17]. Since SBS D1102 has a density of 0.94 g/cm^3 and contains 72 wt.% butadiene, the concentration of butadiene units is approximately 12.2 $mmol_{PB}/cm^3$. For subsequent analysis, the initial concentration of unreacted butadiene units will be designated as n_0 and a stoichiometric coefficient $\hat{\nu}$ defines the ratio of moles of butadiene units that reacts with each mole of O_2 and will be determined experimentally. In order to make the reaction rates fast enough for practical use in barrier systems, the cobalt catalyst mentioned must be added.

2.4. Gas transport properties measurement

The permeability of SBS films to nitrogen and oxygen was measured using a constant volume/variable pressure apparatus [34]. Because conventional packaging is usually designed to minimize oxygen permeance, oxygen is a gas of direct interest in characterizing these new oxygen scavenging materials. Nitrogen is an inert, non-oxidizable gas molecule similar in size to oxygen that can be used to determine and confirm changes in gas transport properties in samples without furthering oxidation.

Solution cast thick films were masked, with openings on their upstream and downstream sides, using impermeable aluminum tape. Spin-coated thin films mounted on the copper wire frame were carefully placed at the center of a Whatman Anodisc® for