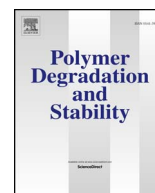




Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Overview of DLO modeling and approaches to predict heterogeneous oxidative polymer degradation

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ARTICLE INFO

Keywords:

Polymer degradation
Accelerated aging
Diffusion limited oxidation
Finite element method
Oxidative material fraction

ABSTRACT

Accelerated polymer aging under thermal oxidative conditions often involves heterogeneous degradation processes due to diffusion limited oxidation (DLO). DLO depends on geometrical shape and size, intrinsic oxidation rate and oxygen permeability of the material and occurs through the competition of simultaneous diffusional transport and reaction of oxygen. Definitions of the many parameters that describe polymer aging under DLO conditions are summarized for several applicable situations, which include the average oxidation rate, the oxidizing material fraction (i.e. fraction of the material oxidizing at a reference oxidation rate), and the depth of a specific flux reduction (i.e. generalized total oxidized layer (TOL)). Analytical and numerical solutions are derived for the prediction of spatially dependent oxidation behavior within a systematic framework for 1D to 3D geometries, multi-material situations and for a range of boundary conditions. Traditional mathematical approaches are expanded to embrace an arbitrary reaction domain through the finite element method (FEM). Concepts are also developed that address time dependent DLO profiles when the underlying oxidation rate or permeability may in itself depend on the evolving oxidation level. Understanding the occurrence of DLO and having the ability to predict spatially resolved oxidation reactions in polymers is critically important to determine when DLO (i.e. non uniform degradation) will interfere as part of accelerated aging studies, or to predict the aging behavior of multi-material polymer components of any geometry. This overview wishes to guide the polymer aging community towards embracing DLO phenomena and share newly developed computational approaches that facilitate comprehensive predictive modeling capabilities.

1. Introduction

The degradation of polymeric materials affects all industries that rely on the mechanical integrity and chemical stability of polymers in real world applications. The mechanical and chemical degradation of polymeric components may be critical to the overall function of engineered assemblies, thus resulting in the need to study and accurately predict the effects of polymer degradation from exposure to common environments.

Polymer aging under thermal oxidative conditions, particularly under accelerated conditions, often involves heterogeneous degradation processes subject to diffusion limited oxidation (DLO) phenomena [1,2]. Depending on depth, intrinsic oxidation rate and oxygen permeability of the material, oxidation reactions may transition from fully homogeneous to heterogeneous degradation at elevated temperatures. The resulting spatial distribution of polymer degradation can be theoretically described and predicted by reactive-transport relationships that combine depth dependent oxygen availability (Fickian diffusion)

with competitive reaction kinetics.

The polymer aging community has long understood that oxidation reactions are a major factor for polymer degradation, which, in general agreement, involves a free-radical mechanism with peroxides as intermediates. The mechanism for free-radical oxidation of hydrocarbons, now refined and referred to simply as the basic auto-oxidation scheme (BAS), was initially proposed in the 1950's by Bolland [3] and Bateman [4], and they showed the oxygen partial pressure dependence of the oxygen consumption rate that is generally acknowledged today. Cunniffe and Davis later used a succinct form of the oxygen consumption rate, which is given in equation (1) from the BAS, to generate the spatial profile of oxygen concentration using a Taylor Series approximation of Fick's Laws in equilibrium [1], thus publishing the first diffusion limited oxidation (DLO) prediction within a material for the photo-oxidation of thick samples.

$$\phi \equiv -\frac{d[O_2]}{dt} = \frac{k_1[O_2]}{k_2[O_2] + 1} \quad (1)$$

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The derivation of equation (1) from the BAS mechanism relied on a number of key assumptions. Most importantly, a steady-state condition for radical formation and termination rates is imposed granting the overall oxidation rate time independence and the oxidation proceeding in equilibrium (i.e. where the oxygen consumption rate and permeability are non-varying with oxidation exposure allowing a constant DLO spatial profile to develop). The other main assumptions in deriving (1) from the BAS are imposing a sufficiently long the kinetic chain length leading to a simplified expression for hydroperoxide formation, the concentration of oxidizable hydrocarbon material is in excess and regarded as constant, and the rate of radical termination between alkyl and peroxy radicals is twice as large as either bi-molecular alkyl or peroxy radical terminations [1,5,6]. These assumptions allow for a simplification of the total oxygen consumption rate, as derived from the specific chemical reactions steps that define the most concise BAS mechanism, resulting in the overall rate constants k_1 and k_2 (these can be easily traced back to the underlying chemistry, please see Refs. [7] and [6]). The BAS mechanism also does not account for more complex hydrocarbon oxidation chemistry with for example reactions linked to free radical additions to double bonds or stabilization processes. There are ongoing discussions in the polymer aging community whether polymer oxidation and a refined BAS scheme should be best described by latent hydroperoxide [8–10] or direct hydrocarbon initiation [6,7], and whether a closed loop oxidation model [9–12] has specific advantages over the existing BAS approach. There is little benefit focusing further on the exact details or minor variations of the BAS scheme as DLO modeling has shown that the combination of overall oxidation rate and permeability is the most dominant factor. Only subtle differences exist in the resulting DLO profiles when small variations or side reactions in the BAS scheme are taken into account.

Gillen later questioned the approximate solution to the BAS mechanism, due to the inherent difficulty of validating some of the underlying assumptions, by solving for the general solution of the oxygen consumption rate through the BAS mechanism [7]. Without using the traditional BAS assumptions (e.g. long kinetic chain length and radical termination equivalences), the general solution of the oxygen consumption rate from the BAS resulted in spatial profiles that are similar to those produced with equation (1) [7]. Gillen also experimentally validated the accuracy of the derived form of the pressure dependence of the oxidation rate, referred to presently as the hyperbolic oxidation rate function (1), verifying the usefulness of this relationship to provide accurate predictions of DLO spatial profiles [2].

The method outlined by numerous publications for predicting DLO [1,2,5,7,13–18] requires reformulating equation (1) to be the oxidation rate referenced at a particular concentration of oxygen (i.e. the ambient concentration of O_2 in air), denoted as ϕ_0 . This oxidation rate is then referenced to the effective oxygen concentration at the surface of the polymer $[O_2]_0$, but, since the low concentration of oxygen gas in a solid polymer allows for the applicability of Henry's Law [2] granting algebraic simplicity, the derivations in this work will use the referenced oxygen partial pressure (e.g. denoted as p_0) as the reference analogue of the oxidation rate, where $[O_2]_0 = Sp_0$ (S is oxygen solubility). Referencing the oxidation rate and subsequent variables to the oxygen partial pressure instead of concentration, as done previously [2,6,18], will allow for simpler algebra when considering the oxygen consumption in composite materials. This leads to the definition of θ as the relative O_2 partial pressure normalized by the reference partial pressure ($\theta \equiv p/p_0$), as opposed to the relative oxygen concentration that has been used previously [2], which is the direct solution of the DLO differential equation allowing for a variety of newly derived oxidative predictions that will be discussed.

Throughout the traditional formulation of DLO [1,2,18,19], it was convenient to combine material and kinetic parameters in order to reduce the degrees of freedom that are out of range for experimental quantification. The first term in the denominator of (1) was defined as the referenced value β , ($\beta \equiv k_2[O_2]_0 = k_2Sp_0$) [1]. From the definition of

θ , it is then useful to derive the relative oxidation rate normalized by the oxidation rate referenced at the pressure p_0 , denoted presently as $\hat{\phi}$, and given in equation (2) [1].

$$\hat{\phi}(\theta) \equiv \frac{\phi(\theta)}{\phi_0} = \frac{\theta(\beta + 1)}{\beta\theta + 1} \quad (2)$$

Starting from equation (1) and multiplying by the factor $\frac{L^2}{Pp_0}$ (i.e. L is a reference thickness of the material sample and P is the oxygen permeability which has the correlation to oxygen diffusivity (D) and oxygen solubility (S) ($P = DS$), which effectively eliminates all units in (1), allows for the definition of the normalized and unit-less value α (defined as $\alpha \equiv \frac{k_1L^2}{D}$) [1,2]. The resulting equation leads to the correlation between the kinetic parameters k_1 and k_2 (combined rate constants from the BAS mechanism [1,2]) to the measurable quantities ϕ_0 and P , given in equation (3) [1]. It is then convenient, for algebraic simplicity, to define the right side of the correlation in (3) as a new value denoted as ν , which is easily computed with the experimentally available values of oxidation rate and oxygen permeability. This definition allows for the separation between experimentally available parameters from the underlying rate constants of the free radical mechanism, which are difficult to accurately and independently measure.

$$\frac{\alpha}{\beta + 1} = \frac{\phi_0 L^2}{Pp_0} \equiv \nu \quad (3)$$

Due to the simplicity and confirmed usefulness of the BAS derived oxidation rate function (1) [2], it is used in the present work for predicting the diffusionally induced oxygen profiles and subsequent oxidative degradation within polymers in various circumstances and geometries. Should a newly derived oxygen consumption rate with a different O_2 pressure dependence be confirmed, most of the equations and qualitative conclusions in this work will subsist by replacing the new function in place of (1) in all subsequent derivations. It should be acknowledged that some variance concerning the mechanistic oxidation scheme has been suggested [8–11], but, as of now, experimental confirmation of a concise oxidation rate function and non-conformity with the previously established BAS [2,7] derived rate from such mechanisms are outstanding.

From a practical perspective, being able to predict and understand DLO profile development during accelerated aging of polymers or material assemblies is important to avoid the complications introduced by DLO (i.e. for properties that relate to bulk behavior) that will result in bias for actual material performance data and could inadvertently affect material lifetime predictions [15,20–22]. As an example, for better performance predictions based on accelerated aging of small seal samples, a cylindrical model of DLO was used to predict when DLO degradation profiles could be ruled out and oxidative damage was expected to occur nearly uniformly throughout the test specimen [15]. This resulted in better lifetime predictions for these seals in air environments as the damage evolution under accelerated conditions matched those encountered during the application. A similar concern about the interference of DLO has been raised for the performance prediction of nuclear power plant cables under thermal-radiative environments for which it is strongly recommended to eliminate the occurrence of DLO during accelerated aging [23–26].

The prediction of DLO based on equation (1) during material aging has mostly utilized the numerical technique proposed by Cunliffe and Davis [1], which provides a spatial profile of oxygen useful for predicting oxidation in one-dimensional (1D) circumstances. For instance, Wise and Gillen have used modulus profiling data along with oxidation rate measurements to find the correlation of the spatial variance of oxidative degradation due to DLO [19]. Similar studies were also conducted under oxidative-radiative conditions [19,23,27,28] or applied to other polymers including cross-correlations between degradation chemistry using spatially resolved FTIR analysis and modulus trends under DLO conditions for nitrile, neoprene or HTPB based elastomers

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