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DEGRADATION IN PARALLEL-DISK RHEOMETRY

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ABSTRACT

We analyze quantitatively the oxidative degradation of a sample in a parallel-disk rheometer, as oxygen diffuses inward, radially, from the free boundary. We examine rheometer error mitigation by means of nitrogen blanketing, and also, of parallel-disk partitioning. We arrive at exact analytical expressions for the oxygen concentration, and thus, for the degradation rate. We then integrate this rate over time to get the amount of oxygen reacted as a function of radial position and time in the degrading sample. To illustrate the usefulness of our analytical expressions, we provide two worked examples investigating the effect of nitrogen blanketing and parallel-disk partitioning. We find that, though nitrogen blanketing always produces less degradation, its benefits are limited for short times. Additionally, parallel-disk partitioning provides a simpler solution and allows samples to be run for longer times without degradation compromising measurement, even in samples initially saturated with oxygen. We also consider the effect of antioxidants. We also consider an important special case, without chemical reaction, where the sample dries by evaporation from its free surface. We close by comparing the roles played by polymer degradation in parallel-disk flow *versus* cone-plate flow.

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CONTENTS

I. INTRODUCTION	5
II. STEADY DEGRADATION IN AIR BATH	6
a. Total Oxidation	8
III. UNSTEADY DEGRADATION WITH NITROGEN BLANKETING	8
a. Total Oxidation	12
IV. UNSTEADY DEGRADATION WITHOUT NITROGEN BLANKETING	12
a. Total Oxidation	14
V. UNSTEADY OXIDATION WITH ANTIOXIDANT DOPING	14
VI. WORKED EXAMPLE: NITROGEN BLANKETING	16
VII. WORKED EXAMPLE: PARALLEL-DISK PARTITIONING	17
VIII. WORKED EXAMPLE: EVAPORATION FROM RIM	17
IX. CONCLUSION	19
X. ACKNOWLEDGMENT	19
XI. REFERENCES	38

TABLES

Table I: Dimensional Variables	21
Table II: Dimensionless Variables and Groups	22

FIGURES

Figure 1: Sketch of sample in parallel-disk rheometer without parallel-disk partitioning, defining spherical coordinates and boundaries.....	23
Figure 2: Sketch of sample in parallel-disk rheometer with parallel-disk partitioning.....	24
Figure 3: The effects of degradation on the real and <i>minus</i> the imaginary parts of the complex viscosity of molten polyhydroxy butyrate (PHB) at 190°C in a parallel-disk rheometer [8].	25
Figure 4: Steady state dimensionless concentration profiles from Eq. (30) for $\kappa = 0.1, 1, 10$	26
Figure 5: Dimensionless concentration profiles <i>versus</i> radius, from Eq. (77), for five different times with a dimensionless rate constant of $\kappa = 0.1$	27
Figure 6: Dimensionless concentration profiles <i>versus</i> radius, from Eq. (77), for five different times with a dimensionless rate constant of $\kappa = 1$	28
Figure 7: Dimensionless concentration profiles <i>versus</i> radius, from Eq. (77), for five different times with a dimensionless rate constant of $\kappa = 10$	29
Figure 8: Dimensionless concentration profiles <i>versus</i> radius, from Eq. (94), for five different times with a dimensionless rate constant of $\kappa = 3.93$ and an initial to rim oxygen concentration ratio of $\chi_0 = 1$	30
Figure 9: Normalized concentration profiles <i>versus</i> radius, from Eq. (95), for five different times with a dimensionless rate constant of $\kappa = 3.93$ and an initial to rim oxygen concentration ratio of $\chi_0 = 1.2$	31
Figure 10: Dimensionless concentration profiles <i>versus</i> radius, from Eq. (94), for five different times with a dimensionless rate constant of $\kappa = 3.93$ and an initial to rim oxygen concentration ratio of $\chi_0 = 0.80$	32
Figure 11: Pseudo-steady state dimensionless antioxidant (dashed) [Eq. (104) with Eq. (105)] and doubly-inflecting oxygen (solid) concentration profiles [Eqs. (102) and (103)] and the steady state oxygen concentration profile (dotted) <i>versus</i> radius [Eq. (30)], with $\alpha_l = 0.32$ and dimensionless rate constants of $\kappa = 3.93$ and $\kappa_{AN} = 13.0$, where $\chi_{N0} = 10$	33
Figure 12: Dimensionless concentration profiles <i>versus</i> time, from Eqs. (79) and (96), for three different radii with a dimensionless rate constant of $\kappa = 3.93$ and an initial to rim oxygen concentration ratio of $\chi_0 = 1$, where the solid and dashed curves correspond to the sample exposed to oxygen [Eq. (79)] and the sample blanketed with nitrogen [Eq. (96)].	34
Figure 13: Dimensionless degradate concentration profiles <i>versus</i> radius, from Eqs. (79) and (96), for five different times with a dimensionless rate constant of $\kappa = 3.93$ and an initial to rim oxygen concentration ratio of $\chi_0 = 1$, where the solid and dashed curves correspond to the sample exposed to oxygen and the sample blanketed with nitrogen.	35
Figure 14: Measured error in real part of the complex viscosity of hydroxypropyl cellulose solution, caused by evaporation from rim. Parallel-disk with plate	

partitioning ($R = 25.0\text{mm}$, $\alpha=0.32$, $\eta'(0)=0.875\text{ Pas}$, blue), and without ($R = 8.0\text{mm}$, $\alpha=1$, $\eta'(0)=1\text{ Pas}$, black).	36
Figure 15: Measured error in <i>minus</i> imaginary part of the complex viscosity of hydroxypropyl cellulose solution, caused by evaporation from rim. Parallel-disk with plate partitioning ($R = 25.0\text{mm}$, $\alpha=0.32$, $\eta'(0)=1.69\text{ Pas}$, blue), and without ($R = 8.0\text{mm}$, $\alpha=1$, $\eta'(0)=28.0\text{ Pas}$, black).	37

I. INTRODUCTION

This paper focuses on the particular source of error in parallel-disk rheometry brought about by oxidative degradation of the polymer sample. This problem arises in the characterization of molten plastics, for instance, when the air bath exposes the sample free boundary to atmospheric oxygen. About the latter, Dealy and Wissbrun (Subsection 7.9.4 of [1]) observe “in cone-plate and parallel disk rheometers, the free surface at which degradation and composition changes first occur is at the outside radius where it has the maximum effect on the measured torque and normal force.” Whereas prior work has focused on degradation in the cone-plate fixture [12], we now focus on the parallel-disk geometry, most popular for measuring the complex viscosity. Figure 1 illustrates this rheometer geometry for steady shear flow.

One particular incarnation of the parallel-disk fixture, called *parallel-disk partitioning*, measures the torque over just the middle of the sample [2,3,4,5,6]. By *middle*, we mean the portion of the sample circumscribed by a partitioning gap. Only the material within this gap contributes to the measured torque. We provide a sketch of a partitioned-parallel-disk rheometer geometry performing steady shear flow in Figure 2, where the inner partition has radius, R_p . One unintended advantage of such parallel-disk partitioning is that it suppresses error due to oxidative degradation, by distancing the part of the sample contributing to the measured torque from the free boundary. In this paper, we analyze how well this distancing can suppress error.

When inserting a sample into a rheometer, one can either first remove its dissolved oxygen under vacuum or not. In Section II, we consider a sample that is initially devoid of oxygen, and in Section III, initially saturated. In Section II, we consider the steady state oxygen concentration that develops when the free boundary is exposed to air, and in Section III, to nitrogen.

Sometimes, polymer degradation is unavoidable during rheological characterization. For small-amplitude oscillatory shear flow measurements, a method has been devised for correcting for polymer degradation (see Subsection 19.2.3.2 of [1]).

Throughout this work we treat samples subject to oxidative degradation following a reaction that is first order in the concentration of oxygen, c_A . Both the initiation and propagation steps of oxidative polymer degradation, for instance, are typically first order in c_A [7]:

In this work we focus on the amount of oxygen consumed by the degradation process, and not on the rich diversity of reactions that can happen next (see **Oxidative Degradation, Chemistries** in [7]).

The total amount of polymer degradative oxidation is given by:

$$d = -\int_0^t R_A dt \quad (3)$$

where $d[=]$ mol L^{-3} and where:

$$R_A = -k'''c_A \quad (4)$$

so that:

$$\begin{aligned}
d &= - \int_0^t -k''' c_A dt \\
&= k''' \int_0^t c_A dt
\end{aligned} \tag{5}$$

Figure 3 illustrates the effects of degradation on the real and *minus* the imaginary parts of the complex viscosity as a function of time in a parallel-disk rheometer (see Fig. 3. of [8]). We see that for polyhydroxy butyrate (PHB), the effects of degradation at the rim, dictated by Eq. (3), arise immediately.

We complete our analysis with three worked examples in Sections VI through VIII to determine when it is best to nitrogen blanket, to investigate the benefits of parallel-disk partitioning, and to explore the special case of sample damage by evaporation from the rim.

II. STEADY DEGRADATION IN AIR BATH

In this section, we solve for the steady state concentration profile that develops in the nearly isothermal degrading sample in an air bath. The sample is subject to oxidative degradation following a reaction that is irreversible and first order in the concentration of oxygen, c_A , with the atmospheric boundary:

$$c_A(R, \theta, z) = c_{AR} \tag{6}$$

centerline symmetry:

$$\frac{\partial c_A(0, \theta, z)}{\partial r} = 0 \tag{7}$$

and impermeable walls:

$$\frac{\partial c_A(r, \theta, \pm \frac{1}{2}h)}{\partial z} = 0 \tag{8}$$

We first consider the steady state, supposing that:

$$c_A = c_A(r) \tag{9}$$

We simplify our equation of continuity (Eq. (B.4-3) of [9]), as follows:

$$\begin{aligned}
c \left(\frac{\partial x_A}{\partial t} + v_r \frac{\partial x_A}{\partial r} + \frac{v_\theta}{r} \frac{\partial x_A}{\partial \theta} + v_z \frac{\partial x_A}{\partial z} \right) \\
= - \left[\frac{1}{r} \frac{\partial}{\partial r} (r J_{Ar}^*) + \frac{1}{r} \frac{\partial J_{A\theta}^*}{\partial \theta} + \frac{\partial J_{Az}^*}{\partial z} \right] + x_B R_A - x_A R_B
\end{aligned} \tag{10}$$

$$0 = - \frac{1}{r} \frac{\partial}{\partial r} (r J_{Ar}^*) + R_A \tag{11}$$

using the standard substitutions for the mole-based equation found at the end of Section B.10 in [9], where $R_A [=] \text{mol} / L^3 / t$. We assume that the concentration of oxygen remains small relative to the polymer allowing for simplification of the reaction term in Eq. (10). For first order oxidative degradation:

$$0 = - \frac{1}{r} \frac{\partial}{\partial r} (r J_{Ar}^*) - k''' c_A \tag{12}$$

where $c_A [=] \text{mol} / L^3$ and where $k''' [=] t^{-1}$.

We next eliminate the radial flux in terms of the molar concentration using Fick's law (Eq. (B.3-4) of [9]):

$$J_{Ar}^* = -c \mathcal{D}_{AB} \frac{\partial x_A}{\partial r} = -\mathcal{D}_{AB} \frac{\partial c_A}{\partial r} \quad (13)$$

where:

$$cx_A \equiv c_A \quad (14)$$

to get:

$$0 = \mathcal{D}_{AB} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_A}{\partial r} \right) \right] - k''' c_A \quad (15)$$

Since all derivatives are with respect to r :

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{dc_A}{dr} \right) - \frac{k'''}{\mathcal{D}_{AB}} c_A = 0 \quad (16)$$

or:

$$\frac{1}{\alpha} \frac{d}{d\alpha} \left(\alpha \frac{d(c_A/c_{AR})}{d\alpha} \right) - \kappa^2 \left(\frac{c_A}{c_{AR}} \right) \equiv 0 \quad (17)$$

where:

$$\kappa^2 \equiv \frac{k''' R^2}{\mathcal{D}_{AB}} \quad (18)$$

is the second Damköhler number, $Da_{II} = \kappa^2$, and where:

$$\alpha \equiv \frac{r}{R} \quad (19)$$

Eq. (17) has the form of the Emden-Fowler equation [10,11]:

$$\frac{d^2 y}{dx^2} + \frac{1}{x} \frac{dy}{dx} - a^2 y = 0 \quad (20)$$

which has general solution:

$$y = C_1 J_0(iax) + C_2 Y_0(-iax) \quad (21)$$

so that:

$$\chi \equiv \frac{c_A}{c_{AR}} = C_1 J_0(i\kappa\alpha) + C_2 Y_0(-i\kappa\alpha) \quad (22)$$

which is subject to Eqs. (6) and (7). In Eq. (22), J_0 is zeroth order Bessel function of the first kind, and Y_0 , of the second kind. Differentiating Eq. (22), we find:

$$\frac{d\chi}{d\alpha} = i\kappa C_2 Y_1(-i\kappa\alpha) - i\kappa C_1 J_1(i\kappa\alpha) \quad (23)$$

Subjecting Eq. (23) to Eq. (7) gives:

$$0 = C_2 Y_1(0) - C_1 J_1(0) \quad (24)$$

$$0 = C_2(\infty) - C_1(0) \quad (25)$$

and thus:

¹ $\alpha\kappa\tau\iota\nu\alpha$ is Greek for radius.

$$C_2 = 0 \quad (26)$$

so that:

$$\chi = C_1 J_0(ik\alpha) \quad (27)$$

which when subjected to Eq. (6):

$$1 = C_1 J_0(i\kappa) \quad (28)$$

gives:

$$C_1 = \frac{1}{J_0(i\kappa)} \quad (29)$$

so that:

$$\chi = \frac{J_0(ik\alpha)}{J_0(i\kappa)} = \frac{I_0(\kappa\alpha)}{I_0(\kappa)} \quad (30)$$

where I_0 is the zeroth order modified Bessel function of the first kind. Eq. (30) gives the dimensionless steady state concentration profile of oxygen in the sample. Figure 4 illustrates the steady state concentration profiles for low, medium and high reaction rates, κ . As we expect, lower reaction rates ($\kappa = 0.1$) allow oxygen diffusion from the rim to dominate causing the sample to be fully saturated, whereas large reaction rates ($\kappa = 10$) deplete the sample interior of oxygen.

Comparing Eq. (30) with Eq. (29) of [12], both at $\alpha = 1$, we discover that the rim oxygen concentration in the parallel-disk and cone-plate fixtures match.

a. Total Oxidation

Evaluating Eq. (5) at steady state, gives:

$$d = c_A k''' t \quad (31)$$

and substituting Eq. (30) into Eq. (31) gives the total amount of degradative polymer oxidation at any position r in the sample:

$$\frac{d}{c_{AR}} = \frac{J_0(ik\alpha)}{J_0(i\kappa)} \kappa \tau \quad (32)$$

which rely on a steady state solution, Eq. (30), and thus neglects the initial condition and all transient behavior. Comparing Eq. (32) with Eq. (32) of [12], both at $\alpha = 1$, we discover that total amount of rim degrade in the parallel-disk and cone-plate fixtures match.

III. UNSTEADY DEGRADATION WITH NITROGEN BLANKETING

In this section, we treat the nearly isothermal sample initially saturated with air (with an oxygen concentration of c_{A0}) and blanketed in nitrogen upon loading into the viscometer. The sample is subject to oxidative degradation following a reaction that is irreversible and first order in the oxygen concentration, c_A . We solve for the unsteady oxygen concentration profile in the nearly isothermal degrading sample.

Here we improve upon Eq. (9) of Section II by supposing that:

$$c_A(r, t) \quad (33)$$

We further use the atmospheric boundary condition:

$$c_A(R, t) = 0 \quad (34)$$

for the nitrogen blanketing, with the initial condition:

$$c_A(r, 0) = c_{A0} \quad (35)$$

for the initial oxygen saturation, and with centerline symmetry:

$$\frac{\partial c_A(0, t)}{\partial r} = 0 \quad (36)$$

Our equation of continuity (Eq. (B.4-3) of [9]) simplifies as follows:

$$\begin{aligned} c \left(\frac{\partial x_A}{\partial t} + v_r \frac{\partial x_A}{\partial r} + \frac{v_\theta}{r} \frac{\partial x_A}{\partial \theta} + v_z \frac{\partial x_A}{\partial z} \right) \\ = - \left[\frac{1}{r} \frac{\partial}{\partial r} (r J_{Ar}^*) + \frac{1}{r} \frac{\partial J_{A\theta}^*}{\partial \theta} + \frac{\partial J_{Az}^*}{\partial z} \right] + x_B R_A - x_A R_B \end{aligned} \quad (37)$$

so that:

$$c \frac{\partial x_A}{\partial t} = \frac{-1}{r} \frac{\partial}{\partial r} (r J_{Ar}^*) + R_A \quad (38)$$

where $R_A [=] \text{mol} / L^3 / t$ and where:

$$c x_A \equiv c_A \quad (39)$$

For first order oxidative degradation:

$$\frac{\partial c_A}{\partial t} = \frac{-1}{r} \frac{\partial}{\partial r} (r J_{Ar}^*) - k''' c_A \quad (40)$$

where $c_A [=] \text{mol} / L^3$ and where $k''' [=] t^{-1}$. Eliminating the fluxes using Eq. (13), we get:

$$\frac{\partial c_A}{\partial t} = \mathcal{D}_{AB} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_A}{\partial r} \right) \right] - k''' c_A \quad (41)$$

We proceed by non-dimensionalizing with Eq. (19) and with:

$$X \equiv \frac{c_A}{c_{A0}} \quad (42)$$

we get:

$$\frac{\partial X}{\partial t} = \frac{\mathcal{D}_{AB}}{R^2} \left[\frac{1}{\alpha} \frac{\partial}{\partial \alpha} \left(\alpha \frac{\partial X}{\partial \alpha} \right) \right] - k''' X \quad (43)$$

Introducing:

$$\tau \equiv \frac{t \mathcal{D}_{AB}}{R^2} \quad (44)$$

and:

$$\kappa^2 \equiv \frac{k''' R^2}{\mathcal{D}_{AB}} [=] 1 \quad (45)$$

we get:

$$\frac{\partial X}{\partial \tau} = \frac{1}{\alpha} \frac{\partial}{\partial \alpha} \left(\alpha \frac{\partial X}{\partial \alpha} \right) - \kappa^2 X \quad (46)$$

where $\chi(\alpha, \tau)$. Non-dimensionalizing Eqs. (34) through (36):

$$X(1, \tau) = 0 \quad (47)$$

$$X(\alpha, 0) = 1 \quad (48)$$

$$\frac{\partial X(0, \tau)}{\partial \alpha} = 0 \quad (49)$$

Eq. (46) is thus subject to the initial condition, Eq. (47), and to boundary conditions Eqs. (48) and (49). In Eq. (45), $R^2/\mathcal{D}_{AB}$ is uncovered as the characteristic time for the diffusion.

Supposing that:

$$X(\alpha, \tau) \equiv f(\tau)g(\alpha) \quad (50)$$

so that from Eq. (47):

$$f(\tau)g(1) = 0 \quad (51)$$

and thus, we have the rim condition:

$$g(1) = 0 \quad (52)$$

and from Eq. (49):

$$\frac{\partial}{\partial \alpha} [f(\tau)g(0)] = 0 \quad (53)$$

$$\left. \frac{\partial g}{\partial \alpha} \right|_{\alpha=0} = 0 \quad (54)$$

Substituting Eq. (50) into Eq. (46):

$$\frac{1}{f} \frac{\partial f}{\partial \tau} = \frac{1}{g\alpha} \frac{\partial}{\partial \alpha} \left(\alpha \frac{\partial g}{\partial \alpha} \right) - \kappa^2 \quad (55)$$

$$\frac{1}{f} \frac{\partial f}{\partial \tau} = C = \frac{1}{g\alpha} \frac{\partial}{\partial \alpha} \left(\alpha \frac{\partial g}{\partial \alpha} \right) - \kappa^2 \quad (56)$$

$$\frac{1}{f} \frac{df}{d\tau} = C \quad (57)$$

which has general solution:

$$f = C_1 e^{C\tau} \quad (58)$$

and:

$$\frac{d^2 g}{d\alpha^2} + \frac{1}{\alpha} \frac{dg}{d\alpha} - D^2 g = 0 \quad (59)$$

in which:

$$D^2 \equiv C + \kappa^2 \quad (60)$$

Eq. (59) has the form of Eq. (20), so that:

$$g = C_3 J_0(iD\alpha) + C_4 Y_0(-iD\alpha) \quad (61)$$

Subjecting Eq. (61) to the rim condition, Eq. (52) yields:

$$0 = C_3 J_0(iD) + C_4 Y_0(-iD) \quad (62)$$

Differentiating Eq. (61):

$$\frac{dg}{d\alpha} = i\kappa C_4 Y_1(-i\kappa\alpha) - i\kappa C_3 J_1(i\kappa\alpha) \quad (63)$$

and subjecting this to Eq. (54):

$$0 = C_4 \quad (64)$$

and thus:

$$g = C_3 J_0(iD\alpha) \quad (65)$$

and our rim condition, Eq. (52), gives:

$$0 = C_3 J_0(iD) \quad (66)$$

so that:

$$D_n = \pm i j_{0,n}; n \geq 1 \quad (67)$$

where $j_{0,n}$ is the n th zero of J_0 , so that:

$$C_n = -j_{0,n}^2 - \kappa^2 \quad (68)$$

Substituting Eq. (67) into Eq. (65):

$$g_n = C_{3,n} J_0(i j_{0,n} \alpha) \quad (69)$$

Substituting Eqs. (58), (68) and (69) into Eq. (50) yields:

$$X(\alpha, \tau) = \sum_{n=1}^{\infty} A_n e^{-(j_{0,n}^2 + \kappa^2)\tau} J_0(-j_{0,n} \alpha) \quad (70)$$

Applying Eq. (48) to Eq. (70):

$$\begin{aligned} X(\alpha, 0) &= 1 = \sum_{n=1}^{\infty} A_n J_0(-j_{0,n} \alpha) \\ &= \sum_{n=1}^{\infty} A_n J_0(j_{0,n} \alpha) \end{aligned} \quad (71)$$

since $J_0(-j_{0,n} \alpha) = J_0(j_{0,n} \alpha)$. For such infinitely summed series, we multiply through by $\alpha J_0(j_{0,m} \alpha)$, and then integrate over the entire range of α to get:

$$\int_0^1 \alpha J_0(j_{0,m} \alpha) d\alpha = \sum_{n=1}^{\infty} A_n \int_0^1 \alpha J_0(j_{0,n} \alpha) J_0(j_{0,m} \alpha) d\alpha \quad (72)$$

Mindful of the following orthogonal properties (Eqs. (5.16) and (5.17) of [13]):

$$\int_0^1 \alpha J_0(j_{0,n} \alpha) J_0(j_{0,m} \alpha) d\alpha = \begin{cases} 0; & m \neq n \\ \frac{1}{2} J_1^2(j_{0,n}); & m = n \end{cases} \quad (73)$$

Eq. (72) then becomes:

$$\int_0^1 \alpha J_0(j_{0,m} \alpha) d\alpha = A_m \frac{1}{2} J_1^2(j_{0,m}) \quad (74)$$

Reversing m back to n gives::

$$\int_0^1 \alpha J_0(j_{0,n} \alpha) d\alpha = A_n \frac{1}{2} J_1^2(j_{0,n}) \quad (75)$$

so that:

$$A_n = \frac{2 \int_0^1 \alpha J_0(j_{0,n} \alpha) d\alpha}{J_1^2(j_{0,n})} = \frac{2 J_1(j_{0,n})}{j_{0,n} J_1^2(j_{0,n})} = \frac{2}{j_{0,n} J_1(j_{0,n})} \quad (76)$$

Substituting this into Eq. (70) gives:

$$X(\alpha, \tau) = 2 \sum_{n=1}^{\infty} \frac{J_0(j_{0,n} \alpha)}{j_{0,n} J_1(j_{0,n})} e^{-(j_{0,n}^2 + \kappa^2) \tau} \quad (77)$$

which is the dimensionless concentration profile for time-dependent diffusion with first order reaction, and is illustrated in Figure 5 through Figure 7 for low, medium and high reaction rates, respectively. Comparing Eq. (77) with Eq. (86) of [12], both at $\alpha = 1$, we discover that the rim oxygen concentration in the parallel-disk and cone-plate fixtures match.

a. Total Oxidation

Substituting Eq. (77) into Eq. (5) yields:

$$\frac{d}{c_{A0}} = \frac{2k'''R^2}{\mathcal{D}_{AB}} \int_0^\tau \sum_{n=1}^{\infty} \frac{J_0(j_{0,n} \alpha)}{j_{0,n} J_1(j_{0,n})} e^{-(j_{0,n}^2 + \kappa^2) \tau} d\tau \quad (78)$$

so that:

$$\frac{d}{c_{A0}} = 2\kappa^2 \sum_{n=1}^{\infty} \frac{J_0(j_{0,n} \alpha)}{j_{0,n} J_1(j_{0,n})} \frac{1 - e^{-(j_{0,n}^2 + \kappa^2) \tau}}{j_{0,n}^2 + \kappa^2} \quad (79)$$

which is the total amount of degradate when the sample is blanketed with nitrogen. By *degradate*, we mean the amount of oxygen consumed by the polymer oxidation. Comparing Eq. (79) with Eq. (90) of [12], both at $\alpha = 1$, we discover that total amount of rim degradate in the parallel-disk and cone-plate fixtures match.

IV. UNSTEADY DEGRADATION WITHOUT NITROGEN BLANKETING

Now suppose that the rim concentration of oxygen was not zero, so that:

$$c_A(R, t) = c_{AR} \quad (80)$$

for which the steady state solution is given by Eqs. (30). We need to combine the transient part of the nitrogen blanketing problem, Eq. (77), with the steady state part of the air bath problem, Eq. (30), as follows:

$$\chi(\alpha, \tau) \equiv \frac{c_A(\alpha, \tau)}{c_{AR}} = \chi_s(\alpha) + \chi_t(\alpha, \tau) \quad (81)$$

To get the transient part, we revise the atmospheric boundary condition, Eq. (34), to:

$$c_A(R, t) = c_{AR} \quad (82)$$

so that Eq. (47) becomes:

$$\chi(1, \tau) = \chi_s(1) + \chi_t(1, \tau) = 1 \quad (83)$$

and from Eq. (30):

$$\chi_s(1) = 1 \quad (84)$$

we rearrange Eq. (83) to:

$$\chi_t(1, \tau) = 0 \quad (85)$$

The initial condition must also be revised to:

$$\chi(\alpha, 0) = \chi_s(\alpha) + \chi_t(\alpha, 0) = \frac{c_{A0}}{c_{AR}} \equiv \chi_0 \quad (86)$$

so that:

$$\chi_t(\alpha, 0) = \chi_0 - \frac{J_0(i\kappa\alpha)}{J_0(i\kappa)} \quad (87)$$

Because the initial condition is the only difference from the nitrogen blanket, we can start by following Eq. (70):

$$\chi_t = \sum_{n=1}^{\infty} B_n e^{-(j_{0,n}^2 + \kappa^2)\tau} J_0(-j_{0,n}\alpha) \quad (88)$$

which we subject to Eq. (87) to get:

$$\chi_0 - \frac{J_0(i\kappa\alpha)}{J_0(i\kappa)} = \sum_{n=1}^{\infty} B_n J_0(j_{0,n}\alpha) \quad (89)$$

Following Eq. (75):

$$\chi_0 \int_0^1 \alpha J_0(j_{0,m}\alpha) d\alpha - \int_0^1 \frac{J_0(i\kappa\alpha)}{J_0(i\kappa)} \alpha J_0(j_{0,m}\alpha) d\alpha = \int_0^1 \sum_{n=1}^{\infty} B_n \alpha J_0(j_{0,n}\alpha) J_0(j_{0,m}\alpha) d\alpha \quad (90)$$

which is only nonzero when $m = n$:

$$\chi_0 \frac{J_1(j_{0,n})}{j_{0,n}} - \frac{\kappa J_0(j_{0,n}) I_1(\kappa) + j_{0,n} J_1(j_{0,n}) I_0(\kappa)}{J_0(i\kappa)(j_{0,n}^2 + \kappa^2)} = B_n \frac{1}{2} J_1^2(j_{0,n}) \quad (91)$$

Solving for B_n , we get:

$$B_n = \frac{2}{J_1(j_{0,n})} \left[\frac{\chi_0}{j_{0,n}} - \frac{j_{0,n}}{j_{0,n}^2 + \kappa^2} \right] \quad (92)$$

Substituting this into Eq. (88) gives us the transient part:

$$\chi_t = 2 \sum_{n=1}^{\infty} \frac{1}{J_1(j_{0,n})} \left[\frac{\chi_0}{j_{0,n}} - \frac{j_{0,n}}{j_{0,n}^2 + \kappa^2} \right] e^{-(j_{0,n}^2 + \kappa^2)\tau} J_0(j_{0,n}\alpha) \quad (93)$$

Substituting this and Eq. (30) into Eq. (81) gives finally, the unsteady dimensionless concentration profile of oxygen in the degrading sample without nitrogen blanketing:

$$\chi(\alpha, \tau) \equiv \frac{c_A(\alpha, \tau)}{c_{AR}} = \frac{I_0(\kappa\alpha)}{I_0(\kappa)} + 2 \sum_{n=1}^{\infty} \frac{1}{J_1(j_{0,n})} \left[\frac{\chi_0}{j_{0,n}} - \frac{j_{0,n}}{j_{0,n}^2 + \kappa^2} \right] e^{-(j_{0,n}^2 + \kappa^2)\tau} J_0(j_{0,n}\alpha) \quad (94)$$

where the reactivity to diffusivity ratio, κ , and the initial to rim oxygen concentration ratio, χ_0 , are the only adjustable parameters. Figure 8 illustrates the concentration profile of oxygen when the initial and rim concentrations match, $\chi_0 = 1$.

Eq. (94) can be normalized using χ_0 to find:

$$X(\alpha, \tau) \equiv \frac{\chi(\alpha, \tau)}{\chi_0} = \frac{1}{\chi_0} \left[\frac{I_0(\kappa\alpha)}{I_0(\kappa)} + 2 \sum_{n=1}^{\infty} \frac{1}{J_1(j_{0,n})} \left[\frac{\chi_0}{j_{0,n}} - \frac{j_{0,n}}{j_{0,n}^2 + \kappa^2} \right] e^{-(j_{0,n}^2 + \kappa^2)\tau} J_0(j_{0,n}\alpha) \right] \quad (95)$$

For the special case initially devoid of oxygen, $\chi_0 = 0$, we must use Eq. (94). By contrast, if a sample equilibrates at room temperature, and is then inserted into the hot parallel-disk fixture for study at elevated temperature, $c_{A0} > c_{AR}$, then Eq. (95) is called for (see Figure 9). If the sample is degassed before testing, so that its initial concentration of oxygen falls below the rim concentration, $c_{A0} < c_{AR}$, then Eq. (94) is appropriate (see Figure 10). In normal laboratory practice, we see $c_{A0} > c_{AR}$ more often than $c_{A0} < c_{AR}$.

Comparing Eq. (94) with Eq. (104) of [12], both at $\alpha = 1$, or by comparing Eq. (95) with Eq. (105) of [12], also both at $\alpha = 1$, we discover that the rim oxygen concentration in the parallel-disk and cone-plate fixtures match.

a. Total Oxidation

Substituting Eq. (94) into Eq. (5) gives:

$$\frac{d}{c_{AR}} = \kappa^2 \left[\frac{I_0(\kappa\alpha)}{I_0(\kappa)} \tau + 2 \sum_{n=1}^{\infty} \frac{J_0(j_{0,n}\alpha)}{J_1(j_{0,n})} \left[\frac{\chi_0}{j_{0,n}} - \frac{j_{0,n}}{j_{0,n}^2 + \kappa^2} \right] \frac{1 - e^{-(j_{0,n}^2 + \kappa^2)\tau}}{j_{0,n}^2 + \kappa^2} \right] \quad (96)$$

which is the total amount of degradate when the sample edge is exposed to oxygen. Comparing Eq. (96) with Eq. (108) of [12], both at $\alpha = 1$, we discover that total amount of rim degradate in the parallel-disk and cone-plate fixtures match.

V. UNSTEADY OXIDATION WITH ANTIOXIDANT DOPING

To avoid sample oxidation, the polymer is commonly doped with antioxidant. The uninitiated may expect antioxidant doping to suppress all polymer degradation. In this section, we test this expectation and investigate the nature of the polymer degradation induction time arising from adding antioxidant. Antioxidant consumption follows a reaction that is zeroth order in antioxidant concentration [14], c_N , and thus:

$$R_N = -k_N''' c_A \quad (97)$$

where we use first order dependence on oxygen concentration as the simplest relevant case.

To incorporate the effects of antioxidants, we modify the reaction term in Eq. (38) to include both Eq. (4) and Eq. (97) to get:

$$c \frac{\partial x_A}{\partial t} = \frac{-1}{r} \frac{\partial}{\partial r} (r J_{Ar}^*) - (k''' + k_N''') c_A \quad (98)$$

which in turn modifies only the dimensionless rate constant from Eq. (18) to (see EXAMPLE 18.3-1 of [9]; [15]):

$$\text{Da}_{II} = \kappa_{NA}^2 \equiv \frac{(k''' + k_N''') R^2}{\mathcal{D}_{AB}} \quad (99)$$

Eqs. (98) and (38) share the same form, and if κ is replaced with κ_{NA} , any solution to Eq. (38) can be taken over for antioxidant doping. Thus, so long as the antioxidant has

not yet been exhausted at the edge, Eq. (77) (with nitrogen blanketing), or Eqs. (94) and (95) (without nitrogen blanketing) can be taken over for antioxidant doping.

Focusing on the latter, an antioxidant-doped sample without nitrogen blanketing, we can determine a new degradation profile as well as an antioxidant concentration profile. We begin with the latter using the definition:

$$c_N \equiv c_{N0} + \int_0^t R_N dt' = c_{N0} - k_N''' \int_0^t c_A dt' \quad (100)$$

where we use the subscripted N to represent antioxidant. Inserting Eq. (94) into Eq. (100), and mindful of Eq. (44), we find:

$$X_N \equiv \frac{c_N}{c_{N0}} = 1 - \frac{\kappa_N^2}{\chi_{N0}} \left[\frac{I_0(\kappa\alpha)}{I_0(\kappa)} \tau + 2 \sum_{n=1}^{\infty} \frac{J_0(j_{0,n}\alpha)}{J_1(j_{0,n})} \left[\frac{\chi_0}{j_{0,n}} - \frac{j_{0,n}}{j_{0,n}^2 + \kappa^2} \right] \frac{1 - e^{-(j_{0,n}^2 + \kappa^2)\tau}}{j_{0,n}^2 + \kappa^2} \right] \quad (101)$$

where $\kappa_N^2 \equiv k_N''' R^2 / \mathcal{D}_{AB}$ and $\chi_{N0} \equiv c_{N0} / c_{AR}$.

From Eq. (101), we can get the induction time at the edge ($\alpha = 1$), that is, the time required for the antioxidant to vanish ($X(1, \tau) = 0$). When $\chi_{N0} = 10$ and $k_N''' = 10k'''$, we find that the antioxidant vanishes at the edge in 1.64 hours, and that the degradate concentration exceeds 5% of the oxygen concentration at the sample edge in 49.4 minutes. Increasing χ_{N0} extends the induction time proportionally. This also shows that the presence of antioxidant does not prevent degradation at the rim. However, antioxidants do decelerate degradation by inducing the 49.4 minute induction.

Though Eq. (101) is useful for short times, to study the longer term benefit of antioxidants, we must replace Eq. (95) with a pair of equations. By *short times*, we mean before the antioxidant is consumed completely at the rim. Specifically, we must account for the absence of antioxidant once it is consumed entirely, at each polymer layer. For simplicity, we use a pseudo-steady state approach for determining the radius of the receding antioxidant front. First, from Eq. (17), we find the steady state solutions for the regions without:

$$\chi = \frac{\kappa \left[I_1(\kappa\alpha_I) K_0(\kappa\alpha_I) + K_1(\kappa\alpha_I) I_0(\kappa\alpha_I) \right] I_0(\kappa_{AN}\alpha)}{\left(\kappa \left[K_0(\kappa) I_1(\kappa\alpha_I) + I_0(\kappa) K_1(\kappa\alpha_I) \right] I_0(\kappa_{AN}\alpha) \right.} \quad (102)$$

$$\left. + \kappa_{AN} \left[I_0(\kappa) K_0(\kappa\alpha_I) - K_0(\kappa) I_0(\kappa\alpha_I) \right] I_1(\kappa_{AN}\alpha_I) \right); 0 \leq \alpha < \alpha_I$$

and with antioxidant:

$$\chi = \frac{\left(\kappa_{AN} \left[K_0(\kappa\alpha_I) I_0(\kappa\alpha) - I_0(\kappa\alpha_I) K_0(\kappa\alpha) \right] I_1(\kappa_{AN}\alpha_I) \right.} \quad (103)$$

$$\left. + \kappa \left[I_1(\kappa\alpha) K_0(\kappa\alpha) + K_1(\kappa\alpha_I) I_0(\kappa\alpha) \right] I_0(\kappa_{AN}\alpha_I) \right) \left(\kappa \left[K_0(\kappa) I_1(\kappa\alpha_I) + I_0(\kappa) K_1(\kappa\alpha_I) \right] I_0(\kappa_{AN}\alpha_I) \right. \right.$$

$$\left. + \kappa_{AN} \left[I_0(\kappa) K_0(\kappa\alpha_I) - K_0(\kappa) I_0(\kappa\alpha_I) \right] I_1(\kappa_{AN}\alpha_I) \right)$$

where $\kappa_{AN}^2 \equiv \kappa^2 + \kappa_N^2$, α_I is the radius of the receding antioxidant front, and K_n is the n th order modified Bessel function of the second kind.

To determine the time-dependence of α_I , we insert Eq. (103) into Eq. (100) to get:

$$X_N \equiv \frac{c_N}{c_{N0}} = 1 - \frac{\kappa_N^2}{\chi_{N0}} \frac{\kappa \left[I_1(\kappa \alpha_I) K_0(\kappa \alpha_I) + K_1(\kappa \alpha_I) I_0(\kappa \alpha_I) \right] I_0(\kappa_{AN} \alpha)}{\left(\kappa \left[K_0(\kappa) I_1(\kappa \alpha_I) + I_0(\kappa) K_1(\kappa \alpha_I) \right] I_0(\kappa_{AN} \alpha) + \kappa_{AN} \left[I_0(\kappa) K_0(\kappa \alpha_I) - K_0(\kappa) I_0(\kappa \alpha_I) \right] I_1(\kappa_{AN} \alpha_I) \right)} \tau \quad (104)$$

Since $\alpha = \alpha_I$ when $X_N = 0$:

$$\tau = \frac{\chi_{N0}}{\kappa \kappa_N^2} \frac{\left(\kappa \left[K_0(\kappa) I_1(\kappa \alpha_I) + I_0(\kappa) K_1(\kappa \alpha_I) \right] I_0(\kappa_{AN} \alpha_I) + \kappa_{AN} \left[I_0(\kappa) K_0(\kappa \alpha_I) - K_0(\kappa) I_0(\kappa \alpha_I) \right] I_1(\kappa_{AN} \alpha_I) \right)}{\left[K_0(\kappa \alpha_I) I_1(\kappa \alpha_I) + K_1(\kappa \alpha_I) I_0(\kappa \alpha_I) \right] I_0(\kappa_{AN} \alpha_I)} \quad (105)$$

which is the time required for antioxidant to retreat to a particular radius, α_I .

We find that the antioxidant is completely consumed at the sample edge in 1.63 hours, and that the degradate concentration exceeds 5% of the oxygen saturation concentration in 4.93 seconds, when $\chi_{N0} = 10$ and $k_N''' = 10 k'''$. As expected, the pseudo-steady state approximation underestimates the induction time at the rim as a worst case, since it assumes that the oxygen concentration peaks immediately. If we consider the inner plate radius of a typical cone-partitioned-plate geometry, $\alpha_p = 0.35$, we find that it takes 16.3 hours for the antioxidant front to retreat to the plate partition. Additionally, the degradate concentration will compromise cone-partitioned-plate measurement after 49.0 minutes. This falls below, and thus underestimates, the time for degradate to impact measurement using an unsteady solution without antioxidant (of 1.39 hours, see above). Because this pseudo-steady state approximation provides a worst-case underestimation, an engineer could expect to have more than 1.39 hours to run a sample using a cone-partitioned-plate. We illustrate the antioxidant and doubly-inflected oxygen concentration profiles for this worked example in Figure 11 when $\alpha_I = 0.35$.

VI. WORKED EXAMPLE: NITROGEN BLANKETING

A rheologist wants to know if she needs to use a nitrogen blanket when measuring the viscoelastic properties of her polymer melt undergoing steady shear in a parallel-disk rheometer. Specifically, she needs to know what the critical dimensionless time, τ_c , at which the degradation in a sample exposed to air greatly exceeds that of a sample subjected to a nitrogen blanket. At the temperature of her experiment, she knows the diffusivity of oxygen in her polymer is $\mathcal{D}_{AB} = 1.10 \times 10^{-9} \text{ m}^2/\text{s}$. She also knows that the rate of oxidative degradation is first order in polymer concentration with a rate coefficient of $k''' = 1.70 \times 10^{-4} \text{ s}^{-1}$. The parallel-disk radii are $R = 1.0 \text{ cm}$.

Because she is interested in the total degradation, she compares Eqs. (79) and (96) by plotting the degradate concentration profiles *versus* dimensionless time in Figure 12. From this figure, the engineer sees that degradate concentration for a sample exposed to oxygen immediately diverges from that of the sample blanketed in nitrogen at $\tau = 0$. However, near the centerline the amount of degradation with and without nitrogen blanketing is similar for short times. Subtracting Eq. (96) from Eq. (79) and dividing by Eq. (79) yields the percent difference in degradate concentration

from the nitrogen blanketed case. If the engineer can tolerate a 5% increase in degradate concentration for her sample exposed to oxygen, she finds that the critical runtime for her measurements at $\alpha = [1, 0.5, 0.001]$ are $\tau_c = [0, 0.051, 0.12]$, which corresponds to $t = [0, 4600, 11000]$ s. Thus, she can run her sample for an hour before the degradation exceeds her tolerance at the point halfway between the cone tip and the outer edge. Since the material at the sample edge has the largest impact on her measurements, she finds that using a nitrogen blanket always reduces degradation and improves her measurement accuracy. She next explores the ability of parallel-disk partitioning (without nitrogen blanketing) to reduce the effect of degradation on her measurements.

VII. WORKED EXAMPLE: PARALLEL-DISK PARTITIONING

The polymer engineer is still studying the polymer in section VI. She wants to know if using a cone-partitioned-plate will increase the amount of time she can run her experiment without a nitrogen blanket. She can still only tolerate a 5% increase in degradate concentration for her sample exposed to oxygen. She begins by plotting, in Figure 13, degradate concentration *versus* radius for exposure to air and to nitrogen. From Figure 13, she notices that for short times the degradation profiles only differ near the sample edge and that the maximum degradation occurs near the center for nitrogen-blanketed samples and near the edge for samples exposed to air. Using a similar method to the previous section, the engineer determines the critical radii at which the degradation in her sample exposed to oxygen exceeds 5% of the degradation in the nitrogen-blanketed sample. She finds that for $\tau = [0, 0.01, 0.05, 0.1, 0.5]$, or $t = [0, 0.25, 1.26, 2.53, 12.6]$ h, the critical radii are $\alpha_c = [1, 0.77, 0.44, 0, 0]$, which translate to $r_c = [10, 7.7, 4.4, 0, 0]$ mm for a cone having radius $R = 10$ mm. Thus, she can operate without a nitrogen blanket for 1.26 hours using a partitioned-plate have inner partition radius of $R_p = 4.4$ mm.

Commercial parallel-disk partitioned rheometers typically employ an inner radius of $\frac{1}{4} \leq \alpha_p \leq \frac{1}{2}$, [6,16]. If she uses $\alpha_p = 0.32$, she can run her measurement for 1.39 hours without degradation impacting her measurements. This is a distinct improvement over the partitionless parallel-disk of the previous example, where without a nitrogen blanket, degradation impacts measurement immediately. Thus, nitrogen blanketing is called for in a parallel-disk when the polymer degrades readily. However, cone-partitioned-plates can be the better solution to degradation if the measurement duration does not exceed the critical time for the inner partition radius.

Comparing this worked example, with that in Section V above, we learn of the advantage over doping of parallel-disk partitioning for delaying or suppressing oxidative degradation in parallel-disk flow.

VIII. WORKED EXAMPLE: EVAPORATION FROM RIM

Rheological experiments were performed using a parallel-disk rheometer (MCR702 TwinDrive, Anton Paar, Physica, Graz, Austria) with a gap of 1.0mm. Hydroxypropyl cellulose (20% by weight) was dissolved in water-glycerol-ethanol (67-28-5% by

weight). Small-amplitude oscillatory shear flow as a time-sweep was performed in the linear régime with an angular velocity of 1 rad/s, at a shear strain amplitude of 10%, at room temperature (24.4°C). The complex viscosity was sampled every 5 seconds. Figure 14 reports the evolving measured real parts of the complex viscosity, $\eta'(t)$, normalized with its initial values, $\eta'(0) \equiv 60 \text{ Pa}\cdot\text{s}$, *versus* time. Figure 14 compares parallel-disk geometries, with and without disk-partitioning. Whereas, the disk-partitioned sample yields a constant $\eta'(t)$, evaporation damages the sample without partitioning after just a few minutes.

For wet samples, susceptible to evaporation from the rim [17,18], we can identify sample damage by evaporation from the rim as the special case of Eq. (95) without chemical reaction, with $\kappa = 0$, so that:

$$X(\alpha, \tau) \equiv \frac{c_A}{c_{A0}} \equiv \frac{\chi(\alpha, \tau)}{\chi_0} = \frac{1}{\chi_0} \left[1 + 2[\chi_0 - 1] \sum_{n=1}^{\infty} \frac{J_0(j_{0,n}\alpha)}{j_{0,n}J_1(j_{0,n})} e^{-j_{0,n}^2\tau} \right] \quad (106)$$

and where, for the wet sample, $\chi_0 \equiv c_{A0}/c_{AR} > 1$, and where A now represents the diffusing evaporant rather than oxygen. Eq. (106) is thus relevant to samples such as wet food, or polymers dissolved in volatile solvents, or surfactant solutions.

Differentiating Eq. (106):

$$\frac{dc_A}{dr} = \frac{2[1 - \chi_0]c_{A0}}{\chi_0 R} \sum_{n=1}^{\infty} \frac{J_1(j_{0,n}\alpha)}{J_1(j_{0,n})} e^{-j_{0,n}^2\tau} \quad (107)$$

and substituting this into Eq. (B.3-4) of §B.3 of [9] gives the molar flux of water:

$$J_{Ar}^* = \frac{2[\chi_0 - 1]\mathcal{D}_{AB}c_{A0}}{\chi_0 R} \sum_{n=1}^{\infty} \frac{J_1(j_{0,n}\alpha)}{J_1(j_{0,n})} e^{-j_{0,n}^2\tau} \quad (108)$$

Evaluating this at the rim gives:

$$J_{Ar}^* = \frac{2[\chi_0 - 1]\mathcal{D}_{AB}c_{A0}}{\chi_0 R} \sum_{n=1}^{\infty} e^{-j_{0,n}^2\tau} \quad (109)$$

Multiplying this by the area of the sample rim, gives the molar flux of evaporate:

$$N_{AR} = \frac{4\pi h[\chi_0 - 1]\mathcal{D}_{AB}c_{A0}}{\chi_0} \sum_{n=1}^{\infty} e^{-j_{0,n}^2\tau} \quad (110)$$

which can be used to arrive at the average concentration of solute in the damaged sample.

Eqs. (106) through (110) are for constant rim evaporate concentration, c_{AR} . One can, of course, attack the drying problem by immersing the loaded sample in either (1) an immiscible fluid, such as mercury or silicone oil, or (2) gas saturated with the evaporate, such as air at its dew point. However, if the sample is not initially saturated, so that $c_{AR} < c_{A0}$, then dilution will damage the sample by inward diffusion. We leave the detailed analysis of dilution by inward diffusion, Item (2), for another day [which would begin with Eq. (94), setting $\kappa = 0$]. This is why we prefer plate-partitioning to sample immersion for protecting measurements from drying error (see [blue](#) circles in Figure 14).

IX. CONCLUSION

We analyze quantitatively the oxidative degradation of a sample in a parallel-disk rheometer, as oxygen diffuses inward, radially, from the free boundary. We examine rheometer error mitigation by means of nitrogen blanketing, and also, of parallel-disk partitioning (by comparing worked examples). We arrive at exact analytical expressions for the oxygen concentration (Eq. (77) with nitrogen blanketing, and Eqs. (94)-(95), without), and thus, for the degradation rate. We then integrate these rates over time to get the amount of oxygen reacted as a function of radial position and time in the degrading sample (Eq. (79) with nitrogen blanketing, and Eq. (96), without). To illustrate the usefulness of our analytical expressions, we provide two worked examples investigating the effect of nitrogen blanketing and parallel-disk partitioning (Sections VI and VII). We find that, though nitrogen blanketing always produces less degradation, its benefits are limited for short times. Comparing these worked examples, we deepen our understanding of the advantage of parallel-disk partitioning for delaying or suppressing oxidative degradation in parallel-disk flow.

Additionally, parallel-disk partitioning provides a simpler solution than nitrogen blanketing, and allows samples to be run for longer times without degradation compromising measurement, even in samples initially saturated with oxygen. We also examine the effect of antioxidants. We arrive at expressions for the induction time at the edge [Eq. (101)], for the receding antioxidant front [Eq. (105)], for the associated concentration profiles [Eqs. (102) through (104)], and thus, degradation rates.

Comparing our results for parallel-disk with those known for the cone-plate fixture [19], we discover that the rim oxygen concentration and the total amount of rim degradate in the parallel-disk and cone-plate fixtures match.

We close with a worked example on sample damage caused by evaporation from the rim (Section VIII). We identify this as the special case of our results for polymer degradation without chemical reaction, with the evaporant replacing oxygen. We measure the effects of evaporative sample damage to both parts of the complex viscosity for the illustrative example, dissolved hydroxypropyl cellulose. When so damaged by evaporation, while the sample concentrates, the sample radius will decrease. Since we find that both parts of the complex viscosity of an evaporating sample grow (Figure 14 and Figure 15), over the shrinking radius, evaporative concentration dominates measurement error. We thus leave the corresponding Arnold problem in cylindrical coordinates for another day (see EXAMPLE 20.1-1 of [9]). We also find that partitioning the parallel-disk fixture suppresses evaporative error, yielding rock steady parts of the measured complex viscosity for our hydroxypropyl cellulose solution. In other words, partitioning the parallel-disk fixture obviates the need for sample immersion.

In this paper, we have not linked the change in rheological properties with the calculated changes in concentrations of either the oxygen, or the evaporate. For these complications, one might begin with the Martin equation, Eq. (3.6-15) of [20].

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Table I: Dimensional Variables

Name	Symbol	Dimensions	Range
Molar flux evaporate	N_{AR}	$\text{mol}t^{-1}$	$\mathbb{R}$
Axial cylindrical coordinate	z	L	≥ 0
Concentration	c	$\text{mol}L^{-3}$	≥ 0
Concentration, antioxidant	c_N	$\text{mol}L^{-3}$	≥ 0
Concentration, initial antioxidant	c_{N0}	$\text{mol}L^{-3}$	≥ 0
Concentration, initial oxygen	c_{A0}	$\text{mol}L^{-3}$	≥ 0
Concentration, oxygen	c_A	$\text{mol}L^{-3}$	≥ 0
Concentration, rim oxygen	c_{AR}	$\text{mol}L^{-3}$	≥ 0
Diffusivity of oxygen through sample	$\mathcal{D}_{AB}$	L^2t^{-1}	≥ 0
First order rate constant, antioxidant	k_N'''	t^{-1}	≥ 0
First order rate constant, degradate	k'''	t^{-1}	≥ 0
Gap between disks	h	L	≥ 0
Mass average velocity, i th component	v_i	Lt^{-1}	$\mathbb{R}$
Molar flux of oxygen, i th component	J_{Ai}^*	$\text{mol}L^{-2}t^{-1}$	$\mathbb{R}$
Radial cylindrical coordinate	r	L	≥ 0
Radial cylindrical coordinate, critical	r_c	L	≥ 0
Radius, plate	R	L	≥ 0
Radius, plate partition	R_p	L	≥ 0
Reaction rate, antioxidant	R_N	$\text{mol}L^{-3}t^{-1}$	≤ 0
Reaction rate, oxygen	R_A	$\text{mol}L^{-3}t^{-1}$	≤ 0
Time	t	t	≥ 0
Total oxidative degradation	d	$\text{mol}L^{-3}$	≥ 0

Legend: $M \equiv$ mass; $L \equiv$ length; $t \equiv$ time; $T \equiv$ temperature

Table II: Dimensionless Variables and Groups

Name	Symbol	Range
Modified Eigenvalue, defined in Eq. (60)	D	≥ 0
Concentration, oxygen	$\chi \equiv c_A / c_{AR}$	≥ 0
Concentration, oxygen, steady part	χ_s	≥ 0
Concentration, oxygen, transient part	χ_t	≥ 0
Mole fraction, oxygen	x_A	$(0,1)$
Mole fraction, sample	x_B	$(0,1)$
Normalized concentration, oxygen	$X \equiv c_A / c_{A0}$	≥ 0
Radial coordinate	$\alpha \equiv r / R$	$(0,1)$
Radius, antioxidant interface	α_I	$(0,1)$
Radius, critical	α_c	$(0,1)$
Radius, partition	α_p	$(0,1)$
Ratio of initial antioxidant to rim oxygen concentration	$\chi_{N0} \equiv c_{N0} / c_{AR}$	≥ 0
Reaction rate constant, antioxidant	$\kappa_N \equiv R \sqrt{k_N''' / \mathcal{D}_{AB}}$	≥ 0
Reaction rate constant, degradate	$\kappa \equiv R \sqrt{k''' / \mathcal{D}_{AB}}$	≥ 0
Second Damköhler number, antioxidant	$Da_{II} \equiv (k''' + k_N''') R^2 / \mathcal{D}_{AB}$	≥ 0
Second Damköhler number, degradate	$Da_{II} = \kappa^2$	≥ 0
Separated function of τ and α	$f(\tau), g(\alpha)$	≥ 0
Time	$\tau \equiv t \mathcal{D}_{AB} / R^2$	≥ 0
Time, critical	τ_c	> 0

Legend: $\mathbb{R} \equiv$ real numbers

Figure 1: Sketch of sample in parallel-disk rheometer without parallel-disk partitioning, defining spherical coordinates and boundaries.

Figure 2: Sketch of sample in parallel-disk rheometer with parallel-disk partitioning.

Figure 3: The effects of degradation on the real and *minus* the imaginary parts of the complex viscosity of molten polyhydroxy butyrate (PHB) at 190°C in a parallel-disk rheometer [8].

Figure 4: Steady state dimensionless concentration profiles from Eq. (30) for $\kappa = 0.1, 1, 10$.

Figure 5: Dimensionless concentration profiles *versus* radius, from Eq. (77), for five different times with a dimensionless rate constant of $\kappa = 0.1$.

Figure 6: Dimensionless concentration profiles *versus* radius, from Eq. (77), for five different times with a dimensionless rate constant of $\kappa = 1$.

Figure 7: Dimensionless concentration profiles *versus* radius, from Eq. (77), for five different times with a dimensionless rate constant of $\kappa = 10$.

Figure 8: Dimensionless concentration profiles *versus* radius, from Eq. (94), for five different times with a dimensionless rate constant of $\kappa = 3.93$ and an initial to rim oxygen concentration ratio of $\chi_0 = 1$.

Figure 9: Normalized concentration profiles *versus* radius, from Eq. (95), for five different times with a dimensionless rate constant of $\kappa = 3.93$ and an initial to rim oxygen concentration ratio of $\chi_0 = 1.2$.

Figure 10: Dimensionless concentration profiles *versus* radius, from Eq. (94), for five different times with a dimensionless rate constant of $\kappa = 3.93$ and an initial to rim oxygen concentration ratio of $\chi_0 = 0.80$.

Figure 11: Pseudo-steady state dimensionless antioxidant (**dashed**) [Eq. (104) with Eq. (105)] and doubly-inflecting oxygen (**solid**) concentration profiles [Eqs. (102) and (103)] and the steady state oxygen concentration profile (**dotted**) *versus* radius [Eq. (30)], with $\alpha_l = 0.32$ and dimensionless rate constants of $\kappa = 3.93$ and $\kappa_{AN} = 13.0$, where $\chi_{N0} = 10$.

Figure 12: Dimensionless concentration profiles *versus* time, from Eqs. (79) and (96), for three different radii with a dimensionless rate constant of $\kappa = 3.93$ and an initial to rim oxygen concentration ratio of $\chi_0 = 1$, where the solid and dashed curves correspond to the sample exposed to oxygen [Eq. (79)] and the sample blanketed with nitrogen [Eq. (96)].

Figure 13: Dimensionless degradate concentration profiles *versus* radius, from Eqs. (79) and (96), for five different times with a dimensionless rate constant of $\kappa = 3.93$ and an initial to rim oxygen concentration ratio of $\chi_0 = 1$, where the solid and dashed curves correspond to the sample exposed to oxygen and the sample blanketed with nitrogen.

Figure 14: Measured error in real part of the complex viscosity of hydroxypropyl cellulose solution, caused by evaporation from rim. Parallel-disk with plate partitioning ($R = 25.0\text{mm}$, $\alpha=0.32$, $\eta'(0)=0.875 \text{ Pas}$, **blue**), and without ($R = 8.0\text{mm}$, $\alpha=1$, $\eta'(0)=1 \text{ Pas}$, **black**).

Figure 15: Measured error in *minus* imaginary part of the complex viscosity of hydroxypropyl cellulose solution, caused by evaporation from rim. Parallel-disk with plate partitioning ($R = 25.0\text{mm}$, $\alpha=0.32$, $\eta'(0)=1.69 \text{ Pas}$, **blue**), and without ($R = 8.0\text{mm}$, $\alpha=1$, $\eta'(0)=28.0 \text{ Pas}$, **black**).

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