12-2023

Development of a User-Friendly Shelf-Life Model to Evaluate the Suitability of Sustainable Materials in Roasted and Ground Coffee Fractional Packs

Matthew Baxley
baxley2@clemson.edu

Recommended Citation

Baxley, Matthew, "Development of a User-Friendly Shelf-Life Model to Evaluate the Suitability of Sustainable Materials in Roasted and Ground Coffee Fractional Packs" (2023). *All Theses*. 4196.
https://tigerprints.clemson.edu/all_theses/4196

DEVELOPMENT OF A USER-FRIENDLY SHELF-LIFE MODEL TO EVALUATE THE SUITABILITY OF SUSTAINABLE MATERIALS IN ROASTED AND GROUND COFFEE FACTIONAL PACKS

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Packaging Science

By
Matthew Baxley
December 2023

Accepted by:
Kay Cooksey Ph.D. Committee Chair
Feng Chen Ph.D.
Patrick Gerard Ph.D.

ABSTRACT

Roasted and ground coffee is a shelf stable product yet quite sensitive to oxidative staling. A consumer acceptance-based shelf-life modeling system was proposed with intent for the rapid determination of suitable coffee packages. This model requires as input the oxygen consumption rate (OCR) of the coffee, barrier values of packages, and the size of the packaging. Within the time period tested, it was shown that this model accurately predicted the oxygen uptake of coffee over time. Four bio-based packaging systems with barrier layers including mPLA, mPE, mcellophane, and paper were compared against a control (mPET). These materials displayed a range of effectiveness in containing moisture and oxygen. It was determined that no materials, including the control, were able deliver a 6-month shelf life of roasted and ground coffee in a non-modified atmosphere at high sensorial rigor. However, the mPET and mcellophane materials could sustain a 6-month shelf life at medium sensorial rigor, and that all materials could sustain a 6-month shelf life at low sensorial rigor. High, medium, and low sensorial rigor were defined as an oxygen uptake of 150, 225, and 300 μg per gram of coffee, respectively. Additional research is needed to measure consumer acceptance more precisely over time with this model.

DEDICATION

To Summer. Without your strength, encouragement, and support I would never have been able to pursue something so interesting and difficult. The early mornings, late nights, and countless weekends you gifted me allowed my curiosity to transform into knowledge I could share with others. Thank you.

To Rowan. May you grow to be someone who sees God’s beauty in our world, who chases down the things which interest you, and who blesses others in every way you discover you can.

ACKNOWLEDGEMENTS

There are many, many people who deserve a hearty ‘thank you’ for their contributions to this thesis. Some of them had a direct impact on the way my research was conducted, data was analyzed, or thoughts were presented. Several more gave their support through encouraging words or practical measures.

To my advisory committee, Dr. Cooksey, Dr. Chen, and Dr. Gerard, thank you for helping me to ask good questions and wrangle solid conclusions from my data. To my classmates, in particular Charles, thank you for all the time you gave to help me make progress when I felt hopelessly stuck. To my family, thank you for encouraging me when things were slower or more difficult than I hoped.

I would also like to thank Methodical Coffee and Printpack Inc. for their contributions of materials and information.

TABLE OF CONTENTS

CHAPTER

Table of Contents (Continued)

Table of Contents (Continued)

VI. CONCLUSIONS

LIST OF TABLES

Table

LIST OF FIGURES

Figure

List of Figures (Continued)

Figure Page

List of Figures (Continued)

Figure

CHAPTER ONE

INTRODUCTION

Although coffee is considered a shelf stable product it experiences definite flavor degradation over time. This duality coupled with wide ranges of consumer expectations due to cultural and other factors can make the task of assigning coffee a shelf life a confusing and frustrating venture. One way coffee merchants can mitigate this problem is by using the techniques of sensory studies and survival analysis (Guerra, 2008). This allows sellers to understand consumer acceptance as a function of time. A drawback of this approach as traditionally applied is the need for repeated sampling and up to several months of waiting while the coffee is allowed to stale (Cardelli, 2001). In this paper, a new technique for the estimation of coffee shelf life as a function of consumer acceptance is proposed. This model is driven by three factors. First, the oxygen consumption rate of a particular coffee (OCR). Second, the oxygen transmission rate (OTR) and water vapor transmission rate (WVTR) of the packaging system. Finally, consumer acceptance behavior at various levels of coffee oxidation- in particular an end of life (EOL) condition must be selected. Each of these variables can be quickly and cheaply assessed in order to estimate the anticipated shelf life. The inclusion of a user-friendly automated tool created in Microsoft Excel allows for users to change parameters such as packaging barrier values, OCR and the level of desired sensory rigor in order to quickly evaluate the anticipated shelf life for new products. This model was validated with bio-based materials as a step towards encouraging the consideration of sustainable materials in industry.

OBJECTIVES

Objective 1: This research will determine whether specialty grade coffee can be effectively packaged in fractional pack style pouches made of bio-based materials.

Objective 2: This research will create a simple to use shelf life modeling tool aimed at helping coffee producers select appropriate packaging materials or shelf life claims.

Objective 3: This research will validate the theoretical shelf life model by characterizing the oxygen consumption characteristics of coffee under various environmental conditions including several bio-based packaging films.

CHAPTER TWO

REVIEW OF LITERATURE

2.1 Flexible Packaging for Coffee

Flexible packaging describes a packaging system which is made of non-rigid materials including polymers, foils, and papers. These materials can be used alone or combined in order to fulfill each relevant purpose of the package; that is to contain, protect, inform and/or advertise, and provide convenience.

Flexible packaging for coffee is typically comprised of at least 3 layers. The innermost layer must be food safe and suitable for sealing. This layer is most commonly 50-90µm polyethylene. The middle layer serves to provide a barrier against oxygen, moisture, and volatile chemical compounds. Common choices for this layer include 6-10µm of aluminum foil or around 12µm of metallized PET. Finally, the outer layer provides a medium for printing graphics and product information, as well as structural support for stand up pouches. Common choices include 20µm of BOPP or 12µm of PET. In addition to these layers, most coffee pouches will include a one way release valve with the purpose of releasing excess CO_2 from the package (Dutta, 2015). For freshly roasted, lightly roasted, and specialty grade coffee these valves are typically considered essential.

Fractional Packs

The packaging used in this experiment is a style of pouch known as fractional packs. This style of packaging varies in a few important ways from typical coffee packaging. Fractional packs are often rectangular fin sealed bags measuring around 3 to 6 inches per side. They contain around 2 ounces of RG coffee and are designed for a single use in commercial coffee machines. Fractional packs tend to be nitrogen flushed and without foil layers. In addition, fractional packs do not have CO_2 release valves- a critical component in other RG flexible package systems. This is due to the relatively small amount of coffee, and therefore carbon dioxide, contained in a fractional pack. Current market fractional packs tend to have a shelf life of 6-18 months.

Polyethylene Terephthalate (PET)

Polyethylene terephthalate (PET) (Figure ?.?.?) is a polyester plastic made by the reaction of terephthalate groups and ethanol. It has good tensile strength, hardness and stiffness (2; Association of plastic). It is resistant to water absorption, has a clear and glassy appearance, and is chemically inert to non-alkaline solutions. PET is the most recycled plastic in the world, due in part to its ability to be recycled completely back to its starting components. These features make PET a great choice for drinks bottling, food packaging, fiber production, and various other operations.

When used in flexible packaging applications, biaxially oriented PET (BOPET) is most commonly used. Biaxial orientation is a process by which the polymeric chains in a film are stretched and made to align with both the machine and transverse directions. This process results in a film with high clarity, improved tensile properties, and decreased moisture and oxygen transmission rates (Drobny, 2014). Additionally, BOPET is suitable for lamination and subsequent printing.

The PET based material used in this study is not recyclable or compostable. This is due to the chemical differences in its barrier layer (mPET) and sealant layer (PE). This reflects industry standards, as the majority of flexible packages are not recyclable or compostable.

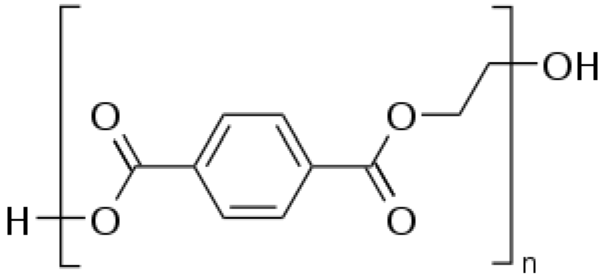


Figure 2.1.1: Molecular structure of a repeating unit of PET

Polylactic acid (PLA)

Polylactic acid (PLA) (figure ?.?.?) is a polymer comprised of lactic acid subunits and one of the most widely used bio-based plastics in the world. Lactic acid is most commonly produced by means of a microbial fermentation and chemical recovery of starchy feedstocks. Although a purely chemical route to lactic acid synthesis exists, it is less cost effective and tends to produce lower quality PLA than a microbial process (Muller, 2017). PLA for use in food packaging is most commonly synthesized via a ring opening polymerization (ROP) reaction (Hu, 2016). The intermediate compound in this ROP is known as lactide. Lactide can exist in three forms- l-lactide, d-lactide and meso-lactide. PLA produced from at least 93% l-conformation lactide will yield a semi-crystalline polymer. Because d and meso-conformation lactides induce twists into the poly-lactic chains, PLA containing less than 93% will be amorphous (Aurus, 2004). PLA is considered to be generally recognized as safe (GRAS) and is commonly used in food packaging applications and direct food contact applications (Mustatea, 2019).

The PLA based package used in this study is industrially compostable. This means that it conforms to the ASTM standards of degradation in a municipal or industrial composting facility (ASTM D6400).

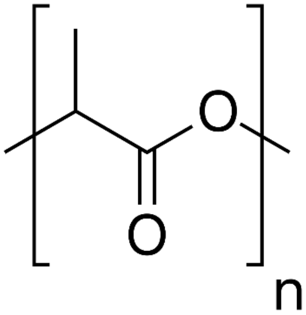


Figure 2.1.2: Molecular structure of a repeating unit of PLA

Polybutylene Succinate (PBS)

Polybutylene succinate (PBS) (Figure ?.?.?) is an aliphatic polyester composed of repeating succinate units. These monomers can be produced through both conventional and bio-based means. PBS boasts good mechanical properties and processability, and is suitable for use in textiles, injection molding, extrusion, and film production (Aliotta, 2022). PBS is a food contact safe material and is seen as a potential replacement for PE and PP in some applications (Platnieks, 2021).

In this study, polybutylene succinate is used as the sealant layer for the cellophane and PLA based packages. It is suitable for both home and industrial composting (ASTM D5488 and ASTM D6400).

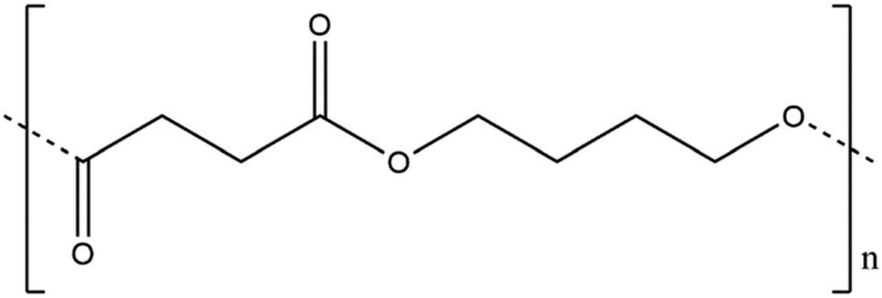


Figure 2.1.3: Molecular structure of a repeating unit of PBS

Cellophane

Cellophane (Figure ?.?.?) is a non-plastic material composed of modified cellulose (Paunonen, 2013). Altering the manufacturing processes can yield a wide range of physical and barrier properties, including some which are suitable for packaging. Cellophane is widely used in food packaging as a clear film with good mechanical and barrier values, although these are susceptible to change in high moisture environments (Tome, 2011).

The cellophane based package used in this study is home compostable. This means that it conforms to the ASTM standards of appropriate environmental degradation (ASTM D5488).

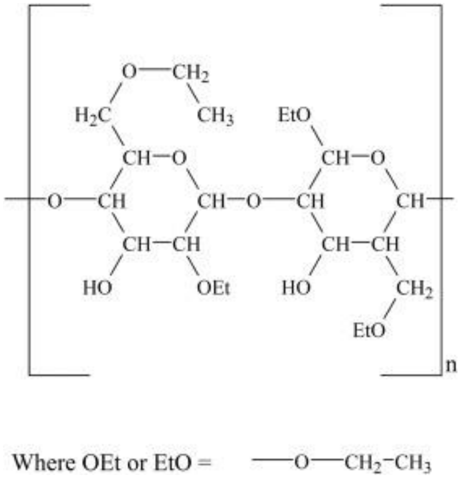


Figure 2.1.4: Molecular structure of a repeating unit of cellophane

Polyethylene (PE)

Polyethylene (PE) (Figure ?.?.?) is a thermoplastic material made of repeated ethylene units. It is very versatile and used in a wide variety of applications, including bottles, films, and structural applications. By controlling the degree of branching within a PE matrix the density and other properties can be adapted to meet specific requirements (Khanam, 2015). In food packaging operations, low density polyethylene (LDPE) films with a moderate oxygen barrier, good vapor barrier and moderate toughness and ductility are commonly used.

The PE based package used in this study is a mono-material comprised of a metallized PE laminated to a non-metalized PE and is eligible for store drop-off recycling. Store drop-off refers to a system of collection, aggregation, and recycling facilitated by grocery stores or other retailers (How2Recycle, 2010). Items such as plastic shopping bags, PE stand up pouches, and other PE film packages can be recycled in this way.

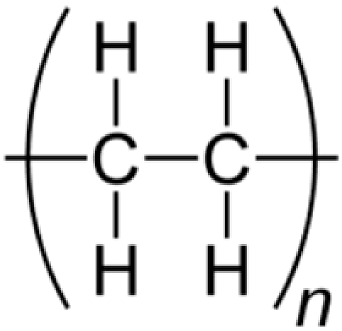


Figure 2.1.5: Molecular structure of a repeating unit of PE

Paper Packaging

The paper used in this experiment is a proprietary laminated multilayer composed of a long fiber layer, short fiber layer, and heat seal layer. The long fibers provide strength and rigidity and the short fibers allow for better printability. The heat seal layer allows for bonding and is not a plastic material. Further details were not disclosed to the researchers in this study. Paper based materials are expected to have minimal barrier properties and are normally not suitable for oxygen sensitive products such as coffee unless they contain a plastic layer. The paper based package used in this study is recyclable through the ordinary paper stream.

Aluminum Foil

Aluminum foil is an important material in the food packaging industry. It is strong, relatively light, offers excellent thermal and corrosive resistance, is recyclable, and provides very strong barriers to oxygen, moisture, aroma compounds, and light (Lamberti, 2007). In food packaging applications, aluminum foil is nearly always used as a laminated composite. Frequently, plastics with a low melting point and other desirable heat sealing and food contact properties are used to separate the foil layer from the food product. Because aluminum foil provides a significant degree of stiffness and rigidity to a system, packages can be classified as rigid, semi-rigid or flexible based on the thickness of the foil layer. Flexible packaging contains foil with a thickness of no more than 50 µm, although frequently foil of 10 µm or less is used.

Metallization

Metallization is a process by which a thin layer of metal - typically aluminum- is deposited onto another surface such as a polymer film (Bayus, 2016). This layer is extremely thin at around 0.5 µm thick and does not have a large effect on mechanical properties such as tear strength or sealability. However, metallization can provide pronounced improvements in barrier properties. To our current knowledge, metallization does not have a negative effect on recyclability or compostability.

Adhesive Lamination

Adhesive lamination is the process by which adhesive is applied to one web and then combined with another web (Food packaging & Principles, pg 130). The two films involved in this process can afterwards be thought of as a single material containing a novel set of physical and barrier properties. Adhesive lamination can be performed in a dry, or solventless, style and in a wet, or solvent-based, style. Solventless adhesive laminations can make use of materials which require curing, such as epoxies, polyurethanes, urea-formaldehydes, and urethaneisocyanates. They can also be performed with materials which do not require curing, such as vinyl acetate, vinyl chloride, rubber, nitrocellulose, and polyesters (Robertson, 98). Broadly speaking, the solvents and adhesives used in creating laminated materials may have negative impacts on recycling and composting streams and must be carefully considered even with the use of bio-based materials (Kim, 98).

2.2 Shelf-Life of Coffee

2.1.1 Microbiology

Roasted and ground coffee possess a naturally low moisture content and water activity, generally being around 1-3 percent moisture (dry basis) and having a water activity of 0.100 - .250 (Wang 2012, Pittia, 2007). In addition, the roasting process acts as a thermal kill-step for all kinds of microorganisms. Thus, roasted and ground coffee poses very little threat of contamination or spoilage by microorganisms. This can be highlighted by the work of Agustini and Yusya in which roasted and ground coffee was found to decrease in bacterial load from 1.2 x 10^3 to 1.7 x 10^2 CFU/g (Agustini, 2020). For these reasons, coffee is generally regarded as a shelf stable product (Nicoli, 2009). However, although coffee may be indefinitely safe to consume, it does experience quality loss, especially related to flavor. In this study, as throughout much of the literature, the term shelf life is used to refer to a loss of acceptability among at least 50% of consumers (Anese, 2006; Cardelli, 2001).

2.1.2 Acceptability Limit

The shelf life of coffee is greatly affected by many factors, both intrinsic and extrinsic. Intrinsic factors include the grind size, roast level, water activity, glass transition and terroir of the coffee. Extrinsic factors include the packaging materials, residual oxygen, pressure differential, relative humidity, and storage temperature. Together, these variables can create coffee with a threshold of acceptability ranging from less than 1 day to several years (Manzocco, 2016*)* . Although these intrinsic factors may be defined or unchangeable for a particular product, the extrinsic factors can be manipulated in order to generate a desirable shelf life.

It is important to note that although coffee is a nearly globally enjoyed beverage and has been studied for decades, there is no specific, agreed upon shelf life to derive from the literature. This stems from the fact that each coffee is different- there may be differences in country of origin, roast level, grind size, moisture content and that consumers from different demographics have different preferences. In the words of Guerra et al. “there is not a univocal method suitable for the determination of sensory shelf life of microbiologically stable products…we can conclude that the shelf life concept for [coffee] is more company or researcher driven than product or consumer dependent” (Guerra 2008). It is for this reason that performing a survival analysis in order to generate an end of life (EOL) condition for each product can be valuable for coffee producers. The tool generated during this study allows for easy analysis of shelf life when the end of life condition is set to different levels of rigor; for example 150 or 300 µg of oxygen consumed per gram of coffee as EOL.

This being said, previous literature suggests the generally accepted range for coffee shelf life approximates to 20 - 30 weeks when packed under vacuum or with inert gasses, and 2 - 12 weeks when packed under normal atmospheric conditions. A summary of shelf life estimates found in previous literature is shown below in Table 2.1.

Packaging Style	**Shelf Life**	**Reference**
Non-Modified Atmosphere	2 - 3 weeks	Anese 2006
	4 - 12 weeks	Nicoli 2005 *(Manzocco 2016)*
	2- 6 weeks	Guerra 2008
	5 weeks	Nicoli 2009
MAP (>5% O_2)	22.5 weeks	Cardelli 2001
	30+ weeks	Labuza 1997
	28 - 40 weeks	Kreuml 2014, Nicoli 2005 *(Manzocco 2016)*
	24 - 52 weeks	Moon 1999
	10 - 20 weeks	Nicoli 2009

Table 2.1 Estimates of Coffee Shelf Life

2.1.3 Flavor Loss- Mechanisms

The loss of freshness and perceived quality of coffee is a chemically highly complex process, yet it may be understood as primarily occurring through three processes (Yeretzian, 2017). First, the loss of volatile compounds from the coffee bean into the headspace and ultimately outside atmosphere. This can be mediated very effectively with the use of packaging which can be impermeable to aroma molecules, most of which are relatively large. Secondly, the oxidation of aroma compounds and lipids. This too can be slowed with the use of low OTR packaging. However, oxygen proves harder to control than large aroma compounds and will likely not be completely controlled. Third, intra-package reactions between volatile organic compounds (VOC) can generate undesirable products or simply destroy desirable ones. This mechanism is the most complicated of the three due to the high number of VOCs inherent to coffee and the unpredictability of their subsequent chemistry.

2.1.4 Flavor Loss- End of Life Measures

Due to the complex nature of coffee flavor loss, it can be measured and estimated in a variety of ways. These include measuring total oxygen uptake (Witik, 2019), measuring total volatile compounds and hexanol levels in the headspace (Anese, 2006), DMDS / MeSH ratio (Ross, 2006), consumer hedonics or acceptance (Cardelli, 2001), and other techniques (Sunarharum, 2014). Although a multi-pronged approach using two or more of these techniques is likely to yield the most exact results, this is not practical among the majority of coffee producers and sellers. Because oxygen uptake is well-studied, reasonably sensitive, highly correlated with shelf life, and simple and cheap to determine, it has been chosen as the metric to determine end of shelf life in this study.

2.1.5 Shelf Life- Previous Work

Cardelli and Labuza’s 2001 paper determined the most important factors in preserving the shelf life of roasted and ground coffee (Cardelli, 2001). To do this, several samples of roasted and ground coffee were held at various combinations of constant oxygen partial pressures, water activities, and temperatures. Untrained sensory panels and a Weibull hazard analysis were used to derive the impact of each of these variables. Oxygen concentration was found to be the most important, with a 2000% increase in shelf life when oxygen concentration was reduced from atmospheric levels to 0.05%. Water activity was the next most important factor, increasing shelf life by about 60% for each increase of 0.1 aw. It is important to note that in real world scenarios, residual oxygen will have an immediate impact on packaged coffee while increases in the water activity will happen more slowly in tandem with allowed moisture ingress. Finally temperature was found to have a relatively moderate impact of 20% shelf life reduction for each 10° C increase. This study found that coffee became unacceptable to 50% of consumers after it had consumed 150-300 µg of oxygen per gram of coffee.

As discussed above, moisture has an important effect on the oxidation rates of coffee products. A 2019 paper by Wyzer and Witik (Witik, 2019) illuminates the interactions between moisture and oxygen in an instant coffee product in flexible packaging. The authors developed a model which considers both moisture and oxygen changes over time in order to more precisely characterize changes and predict shelf life. This model was created based on empirical values derived from measuring the oxygen consumption rate of coffee held at various moisture contents. In conjunction with a moisture sorption isotherm, these values were used to predict the total oxygen consumption of coffee over time. Because it was shown that moisture significantly increases oxidation rates within the general parameters of the Wyzer and Witik study, the present study will also use this model in order to consider both moisture and oxygen flux.

In summary, two previous studies have conducted similar examinations to the present study regarding the OCR of coffee. Oxygen consumption rate (OCR) can be defined as the amount of oxygen which is taken from a surrounding atmosphere in order to fuel other reactions. As discussed, Witik et al monitored the oxygen consumption rate of roasted and ground coffee in hermetically sealed containers (Witik, 2019). This was followed up with testing done in permeable pouches. In addition, Cardelli measured the OCR of coffee in a hermetically sealed environment and in a permeable package (Cardelli, 1997). The defined oxygen consumption rates across these studies fell between 2.13 x 10-7 and 3.7 x 10-7 gO2/gcoffee/day/mbar. These numbers fit well with the OCR generated during this study, 9.80 x 10-7 gO2/gcoffee/day/mbar. Although this number is higher than the other two values, it is within one order of magnitude and reflects a fresh and lightly roasted specialty grade coffee.

2.3 Coffee Chemistry

2.3.1 Carbon Dioxide

During the roasting process, a considerable amount of carbon dioxide is produced, in large part due to pyrolysis and Strecker degradation reactions (Hodge, 1953). Although different coffees roasted to different levels will release various amounts of CO_2, most types of coffee can be expected to release approximately 2 -5 mL of CO_2 per gram (Shimoni, 2007). For this reason, freshly roasted and immediately packed coffee can deform or burst it’s packaging after a period of a few days. Therefore, coffee is often left to degas for a period of several hours before packing. Additionally, many coffee packages make use of degassing valves- one way pressure release valves aimed at allowing CO_2 to exit without introducing extraneous oxygen to the system. Grinding coffee before packing also goes a long way towards solving this problem.

Within 5 minutes of grinding, about half of the trapped CO_2 will leave the system (Heiss, 1977). Thus, in the present study, each gram of coffee was expected to generate 0.5 - 2.5 mL of CO_2.

2.4 Moisture Sorption Isotherm

A moisture sorption isotherm describes the relationship between the water activity and subsequent moisture content of a product. Water activity is defined as the "ratio of vapor pressure of water (p) at equilibrium with [the coffee] to the vapor pressure of pure water (p_o) at the same temperature" (Cardellli-Freire, 2004). Moisture content (dry basis) is defined as the mass of water in grams in 100 grams of dry matter.

Equations for water activity and moisture content are shown below. As the moisture content of a product increases the water activity will also go up, though this relationship is not necessarily linear. Previous work on the moisture sorption isotherms of coffee demonstrates a predictable exponential relationship between a_w and MC within the normal boundaries of shipping and storage conditions (Witik 2019, Labuzza 2001).

Equation 2.1

$$\text{Water activity} = \frac{P}{P_0}$$

Where:

P = vapor pressure in coffee

P_0 = vapor pressure of pure water

Equation 2.2

$$\text{Moisture Content (dry basis)} = \frac{W_W}{W_d} \times 100$$

Where:

W_w = weight of the water in a sample

W_d = weight of the dry matter in a sample

CHAPTER THREE

METHODS AND PROCEDURES

3.1 General Flow of Procedures

This study consisted of three distinct experiments. First, a Q_{10} study was performed in order to generate the oxygen consumption rate (OCR) for the RG coffee under various environmental conditions. A moisture sorption isotherm was also generated. From a theoretical perspective, this information is sufficient to calculate the expected shelf life of the coffee in each packaging system. In the second phase a mathematical model for shelf-life prediction was created. The third phase validated this model by measuring the oxygen consumption of coffee over time of several bio-based and non-bio-based sample sets.

3.2 Ground Coffee Preparation

The coffee used in this experiment was a 50/50 blend of naturally processed Yellow Catuai coffee varietal and a honey processed Mondo Novo coffee varietal roasted to a medium level by Methodical Coffee Roasters in Greenville, SC. The coffee was packed in foil lined non-valved pouches immediately after roasting, and within 24 hours was stored in a commercial freezer at -25^{o} F until needed. All samples were ground to a medium-fine level immediately before packing for use in the shelf-life study with an Ambex commercial coffee grinder, Model Arg-1.

3.3 Characterizing Oxygen Consumption Rate (OCR)

3.3.1 Q_{10} Study

As discussed in the literature review a Q_{10} study was conducted both to generate a baseline OCR for the product and to quantify the impact that environmental factors have during an accelerated shelf life study. The full study consisted of six separate combinations of temperature and relative humidity, as shown in Table 3.1

Label	Temperature (C)	Relative Humidity
21C	21	53
31C	31	53
35C	35	53
49R	31	48
72R	31	72
84R	31	84

Table 3.1 Temperature and Humidity Conditions of Q_{10} Ground Coffee Sample Groups

For each of the 6 groups, 10 glass jars with a volume of 126.5 mL were filled with 15.0 g of R&G coffee. Three of the sample sets had salt sachets placed inside the glass jars in order to set the humidity to a specified amount. The sachets used to control relative humidity were about 1 inch by 2 inch rectangles filled with desiccant, and were purchased from Boveda (Minnetonka, MN). Jars which did not contain a sachet were packed at an ambient RH of 53%. After packing, all samples were held at a constant temperature until ready to be measured. An example of this setup is shown below in figure 3.1.

Figure 3.1 Glass jars used in the Q_{10} study

All samples were allowed to equilibrate to 21C before analysis. An Illinois instruments (Johnsburg, IL) 6600 headspace analyzer was used to measure the percent of oxygen in the headspace, and the total micrograms of oxygen was calculated from this value, using equation 3.1.

Equation 3.1

$$\text{Total µg of } O_2 \text{ in Headspace} = V_{HS} \times O_2 \times P_{O2} \times 1^{06}$$

Where:

V_{HS} = Volume of the headspace (mL)

O_2% = Percent O_2 in the headspace

ρ_{O2} = Density of O_2 gas (g / mL)

Measurements were taken immediately after packing, and at 21 hours, 47 hours, and 94 hours after packing. All sampling was done in triplicate, and coffee samples were discarded after analysis.

3.3.2 Oxygen Consumption Rate Determination

After measuring the oxygen consumption over time in a particular set of environmental conditions, the collected data was analyzed in order to generate an OCR with respect to the partial pressure of oxygen (P_{O2}). When plotted, this data was shown to resemble an exponential decay function and thus a line of best fit was created to match the following equation, as per Witik 2019:

Equation 3.2

$$P_{O2(t)} = P_{O2,initial}{}^{-OCR \times m \times \frac{P_{atm}}{V_{HS}} \times t}$$

Where:

$P_{O2}(t)$ = partial pressure of oxygen at time t

$P_{O2,\ initial}$ = partial pressure of oxygen at time t = 0

m = mass of coffee

P_{atm} = pressure inside of the test chamber

V_{HS} = volume of headspace inside of the test chamber

t = number of days after t = 0.

The value $P_{O2}(t)$ was calculated by multiplying the V_{HS} by the atmospheric partial pressure of oxygen, that is 20.9%. The values of m, P_{atm} and V_{HS} were known and taken as constants throughout the experiment. Establishing a line of best fit was accomplished by means of using the Excel solver function to minimize the sum of squares between the actual *[y]* and predicted values of $P_{O2}(t)$ *[$y_{calculated}$]* given time *[x]* when OCR was being optimized and all other values where constrained. A generalized reduced gradient nonlinear solver algorithm was used.

3.4 Other Mathematical Procedures

An Excel spreadsheet was created with which to model the cumulative oxygen uptake of the coffee over time. This model is based on some known initial and environmental values, an experimentally derived OCR_{MC}, and a moisture sorption isotherm. The required initial values consist of the moisture content of the coffee immediately after packaging ($MC_{db,initial}$), the water activity of the coffee immediately after packaging (aw_{coffee}), the volume of the headspace immediately after packaging ($V_{headspace}$), storage RH ($RH_{storage}$), and the mass of the coffee in each package (g_{coffee}). The methods used to determine OCR_{MC} and an MSI curve are described below.

The sheet has predefined models which will calculate the water vapor pressure outside the package based on user selected relative humidity and temperature values during storage. Many of these calculations are taken from Witik et als 2019 paper and are marked as such below. From this the WVTR value and subsequent water uptake (WU) can be calculated. Based on the calculated WU over a given time period, the new $MC_{db(t)}$ of the coffee can be calculated. The curve generated during the Q_{10} study illuminating the effect of MC on OCR allows the OCR at any MC ($OCR_{MC(t)}$) to be calculated. When $OCR_{MC(t)}$ is expressed as g_{O2} / g_{coffee} / day / mbar, we can determine the amount of oxygen removed from the bags headspace each day ($O_{2,consumed(t)}$). Furthermore, based on the oxygen partial pressure differential across the barrier and the OTR value the oxygen ingress ($OI_{(t)}$) or amount of oxygen which enters the package each day is known. The net value of $O_{2,consumed(t)}$ and $OI_{(t)}$ into the headspace gives a new partial pressure of the headspace ($P_{O2,(t)}$) each day.

In addition, the model used in this study included a factor used to correct for the non-linear nature of OCR at decreasing oxygen concentration. This factor was determined empirically by plotting values of a coffee's OCR against its oxygen concentration and fitting a least squares regression to these values, as shown in figure 4.25. This was found to significantly improve the accuracy of the model. The equation is shown below in equation 3.3:

Equation 3.3

$$\text{OCR} = 6.34976^{-07} \times \ln\left(P_{O2(t)}\right) - 2.4579^{-06}$$

The equations used to calculate each value in the model are given below.

Moisture Content Calculation

The total water uptake of the coffee was redefined at each time period based on the following equation, taken from Witik et al, 2019:

Equation 3.4

$$MC_{tn} = MC_{tn-1} + WU_{tn}$$

Where:

MC_{tn} = Moisture content of the coffee at time t_n

WU = Water uptake of coffee at time t_n (grams)

Water Uptake Calculation

The total water uptake of the coffee was redefined at each time period based on the following equation, taken from Witik et al, 2019:

Equation 3.5

$$WU_{tn} = WVTR \times A \times \frac{P_{H2O,atm} - P_{H2O,sat} \times Aw_{tn-1}}{P_{H20,test}} \times \Delta t$$

$WU_{(tn)}$ = WVTR * A (($P_{H2O,atm}$ - ($P_{H2O,sat\ *\ aw(tn-1)}$)) / $P_{H2O,test}$) * **Δ**t

Where:

A = permeable surface area of package (cm^2)

$P_{H2O,atm}$ = water vapor pressure at storage RH% (mbar)

$P_{H2O,sat}$ = water vapor pressure in saturated air at storage temperature (mbar)

$P_{H20,\ test}$ = water vapor pressure differential during WVTR test (mbar)

t= time (days)

Oxygen Consumption Calculation

The total oxygen consumption of the coffee was redefined at each time period based on the following equation, taken from Witik et al, 2019:

Equation 3.6

$$O2_{cons(tn)} = O2_{cons(tn-1)} + OCR_{MC(tn-1)} \times PO_{2(tn-1)} \times m \times \Delta t$$

Where:

$O_{2,consumed}V_{O2(tn)}$ = Volume of O_2 in the headspace at time t_n (mL) = Oxygen consumed at time t_n (g_{O2})

$OCR_{MC(tn)}$ = Oxygen consumption rate at MC(t_n) (g_{O2} / g_{coffee} / day / mbar)

$P_{O2(tn)}$ = Partial pressure of oxygen in the headspace (mbar)

m = mass of coffee

Oxygen Ingress Calculation

The oxygen ingress of the package at time t_n was redefined at each time period based on the following equation, taken from Witik et al, 2019:

Equation 3.7

$$OI_{tn} = A \times OTR \times \left(PO_{atm} - PO_{2(tn-1)}\right) \times \Delta t$$

Where:

A = area of the package (m^2)

OTR = Oxygen transmission rate ($mL/m^2/day/mbar$)

PO_{atm} = Partial pressure of atmospheric oxygen

$PO_{2(tn)}$ = Partial pressure of oxygen inside package

Oxygen Partial Pressure Calculation

The oxygen partial pressure of the package at time t_n was redefined at each time period based on the following equation, taken from Witik et al, 2019:

Equation 3.8

$$PO_{2(tn)} = PO_{2(tn-1)} + OI_{(tn-1)} - O_{2,cons(tn-1)} \times \frac{P_{atm}}{V_{HS}} \times \Delta t$$

Where:

P_{atm} = Pressure of the atmosphere (1013 mbar)

V_{HS} = Volume of the headspace

Volume of Headspace Calculation

The volume of the headspace at time t_n was redefined at each time period based on the following experimentally derived equation:

Equation 3.9

$$V_{HS} = log_{4.6}(t_n) * 9.5$$

This equation was derived by plotting the amount of CO_2 released by each sample over time, as shown in figure 4.23.

Initial Headspace Calculation

Initial headspace of the packages was calculated for each package after their sampling. By multiplying the measured values of percent O_2 and percent CO_2 by the total volume of the headspace, the volume of each gas V_{O2} and V_{CO} could be determined. Subtracting these two values from the total headspace volume V_{HS} gives the volume of all other gasses in the headspace, here called V_N. V_N is assumed to be unchanged over time and therefore can be used as the initial headspace volume. Because the initial concentrations of O_2 (20.9%) and CO_2 (~0%) are known, the sum of V_N and $V_{O2, initial}$ is equivalent to the initial headspace volume. This is shown below in equation 3.10:

Equation 3.10

$$V_N = V_{HS(tn)} + V_{O2(tn)} + V_{CO2(tn)}$$

Where V_N = Volume of non-O_2 and non-CO_2 gasses in the headspace (mL)

$V_{HS(tn)}$ = total volume of the headspace at time t_n (mL)

$V_{O2(tn)}$ = Volume of O_2 in the headspace at time t_n (mL)

$V_{CO2(tn)}$ = Volume of CO_2 in the headspace at time t_n (mL)

During model validation, the V_N of each pouch was determined and the average V_N for each set of materials was calculated. This value was used as the V_N for the iterative model.

Q_{10} Testing

Q_{10} testing is a tool used to help estimate the actual shelf life of a product in conjunction with accelerated shelf life testing. The Q_{10} value serves as an estimate of the impact which an increase in temperature, relative humidity, or other environmental conditions will have on the shelf life of a product. It is represented by the equation 3.11.

Equation 3.11

$$Q_{10} = \left(\frac{R_2}{R_1}\right)^{\left(\frac{10}{T_2 - T_1}\right)}$$

In which R is the time required to reach a designated spoilage value and T is the temperature (relative humidity, etc.) at which testing is performed. In the present study, two separate Q10 tests were performed. The first characterized the effect of temperature on the oxygen consumption rate and the second characterized the effect of moisture content.

Although Q10 tests are generally associated with accelerated shelf life testing, one is used here for a slightly different purpose. By correlating the OCR of this coffee with its water activity the OCR at any point in time based on the known water activity can be predicted. This leads to a much more accurate estimation of the total oxygen consumed over time.

In addition, performing the Q_{10} study prior allowed the OCR_{MC} to be defined for this study. This was accomplished by means of equation 3.11, as discussed in section 3.10

3.5 Packaging Materials

3.5.1 Barrier Testing

The packaging materials used in this study were obtained from commercial sources (Printpack, Atlanta, GA). The general construction and corresponding OTR and WVTR values of each pouch was as follows, shown in table 3.2.

Material	**Form**	**OTR** (cc/100 in^2/day)	**WVTR** (gm/100 in^2/day)
Met-cellophane	90 Ga mcellophane / adh / 125 GA Bio-PBS	0.013	0.255
Met-PLA	80 Ga mPLA / adh / 125 GA Bio-PBS	0.176	0.158
Met-PE	96 GA mPE / adh / 150 GA PE	0.163	0.084
Met-PET Foil Replacement	UHB mPET / adh / 300 GA Peelable PE	0.018	0.006
Two Layer Bleached Paper Bag	Long Fiber / adh / Short Fiber	0.06	17.06

Table 3.2 Construction and Barrier Values of Packaging Materials

In table 3.2 PLA stand for Polylactic acid, PE stand for polyethylene, PET stands for polyethylene terephthalate, PBS stand for polybutylsuccinate, and UHB stand for ultra-high barrier.

All materials were laminated and allowed to fully cure for 1 week before barrier testing and use in this study. Barrier testing was performed by Printpack (Atlanta, GA) and carried out according to ASTM F129 (23^o C, 0% RH) and ASTM D3985 (37.8^o C, 90% RH) standards. Additionally, TAPPI T448 (23^o C, 50% RH) was used in order to generate a secondary WVTR value for the paper product. The TAPPI value for the paper product was 1.09 gm$_{H20}$/100 in^2/day.

3.5.2 Pouch Construction

Pouches were made by hand in the following manner. First, blanks were folded along the longer side. Then, one short side and one long side were sealed using an impulse heat sealer using pre-selected time, temperature, and pressure settings (see appendix A for further detail). The fractional packs used in this study measured 9.25 by 5.75 inches and contained 30 grams of RG coffee. After packing with product, the pouches were immediately sealed with an impulse heat sealer (Model 9MS #1091, Toyo Jidoki CO., LTD, Tokyo, Japan). One set of pouches was placed in a Koch UV 250 (Wichita KS, USA) vacuum packer and nitrogen flushed to approximately 0.010% residual oxygen. This machine automatically sealed each pouch after nitrogen flushing. Another set of pouches was sealed with no modification to the headspace.

3.4.3 Nitrogen Flushed Bags

The samples which were nitrogen flushed before sealing were checked each week for seal integrity by means of headspace analysis. This ensured that CO_2 was not leaking from seals over time, and that RG coffee still consumes oxygen at very low levels. During packing, nitrogen flushed samples were checked immediately after sealing with an Illinois Instruments 6600 headspace analyzer (Johnsburg, IL). Because the nitrogen flush and seal machine had less control over sealing parameters than did the impulse sealer previously used (Model 9MS #1091, Toyo Jidoki CO., LTD, Tokyo, Japan), only the mPET, mcellophane, and mPE materials could be effectively flushed and sealed.

3.4.4 Pouch testing

In order to ensure adequate and consistent sealing of pouches, ten pouches from each type of materials were randomly selected for seal testing. This was carried out by means of using a negative pressure burst tester to ASTM standard F1140-2013. When pressurized until failure, pouches tore before seals could fail. Additionally, pouches were put under vacuum by means of a Visual Check Machine (Bubble test) and visually inspected for presence of bubbles indicating a leak. Paper pouches were excluded from this quality check. No bubbles were observed. Both of these tests indicated successful sealing.

During packing, one out of every 10 bags was randomly selected for analysis to determine the amount of residual oxygen in the headspace. This was done by means of a Illinois Instruments 6600 headspace analyzer (Johnsburg, IL) with a degree of accuracy of +/- 0.005%. The bags showed an average of 0.010% oxygen in the headspace.

3.5 Moisture Sorption Isotherm

In order to generate a moisture sorption isotherm (MSI) for the present study, samples were conditioned to various water activities with the use of commercially available saturated salt solutions. These salt solutions were stored in air tight jars for 24 hours in order to condition them to the appropriate level of humidity. Three jars were prepared at each of the seven humidity levels for a total of 21 jars. Approximately 0.01 grams of ground coffee was weighed on a mass balance with a degree of accuracy of +/- 0.0001 grams and subsequently dosed into each jar. The moisture content of the coffee used in this MSI was determined using a halogen moisture analyzer (Mettler Toledo HE53) (Columbus, OH). The salt solutions and their corresponding water activities are found below in Table 3.3

Water Acttivity	**Salt Substance**
0.010	Drierite
0.225	Potassium Acetate ($KC_2H_3O_2$)
0.428	Potassium Carbonate (K_2CO_3)
0.54	Magnesium Nitrate ($Mg[NO_3]_2\ 4H_2O$)
0.75	Sodium Chloride (NaCl)
0.85	Potassium Chloride (KCl)
0.92	Potassium Nitrate (KNO_3)

Table 3.3 Water Activity Values of Salt Solutions

3.6 Shelf-Life Validation of Ground Coffee

3.6.1 Sample Preparation

In order to validate the calculated results, a 9-week shelf life test was performed. For each of the 5 bag structures, 80 identical pouches were made. These pouches were made from blanks measuring 9.25 by 11.5 inches. Each blank was folded in half along the longer side to create a 3-seal pouch shape approximately 9.25 by 5.75 inches in length. Prior to packing, two sides were sealed. Each pouch was packed with 30 grams of freshly ground coffee, ground to the same specifications as what was used in the Q_{10} study. Immediately after packing, pouches were sealed with an impulse heat sealer (Model 9MS #1091, Toyo Jidoki CO., LTD, Tokyo, Japan). Half of the pouches were nitrogen flushed to ~0.01% residual oxygen using a Koch tabletop vacuum packer and immediately sealed. Headspace samples were taken with a Illinois Instruments 6600 headspace analyzer (Johnsburg, IL) every 10th bag to ensure consistent nitrogen flushing. The other half of the samples were packed under atmospheric conditions. All samples were stored at approximately 21 C for 9 weeks, with triplicate samples taken once per week from each sample set.

3.6.2 Headspace Analysis

During sampling, an Illinois instruments 6600 headspace analyzer (Illinois instruments (Johnsburg, IL) was used to measure the percent of oxygen in the headspace of each pouch. The volume was calculated by means of water displacement, adapted from Hughes 2005. In short, a 2 L container was filled with 1 L water and placed onto an electronic scale. A plunger was secured directly above the container. This plunger was set to descend to the same depth each time it extended. After securing a coffee pouch to the plunger, it was pushed into the container and allowed to settle. Archimedes' principle states that “any body completely or partially submerged in a fluid at rest is acted upon by an upward, or buoyant, force, the magnitude of which is equal to the weight of the fluid displaced by the body. The volume of displaced fluid is equivalent to the volume of an object fully immersed in a fluid.” (Encyclopedia Brittanica). In other words, the change in water volume in the graduated cylinder is equivalent to the volume of the package. Additionally, because the weight-pouch is at rest, we know its net forces are zero.

In other words, “the immersed object is equivalent to a virtual volume of water of exactly the same size and shape.” (Hughes, 2005). Therefore the increase in volume of the water can also be expressed as the weight of the submerged pouch divided by the density of water.

Equation 3.12:

$$Volume_{Pouch} = \frac{Weight_{pouch}}{Density_{water}}$$

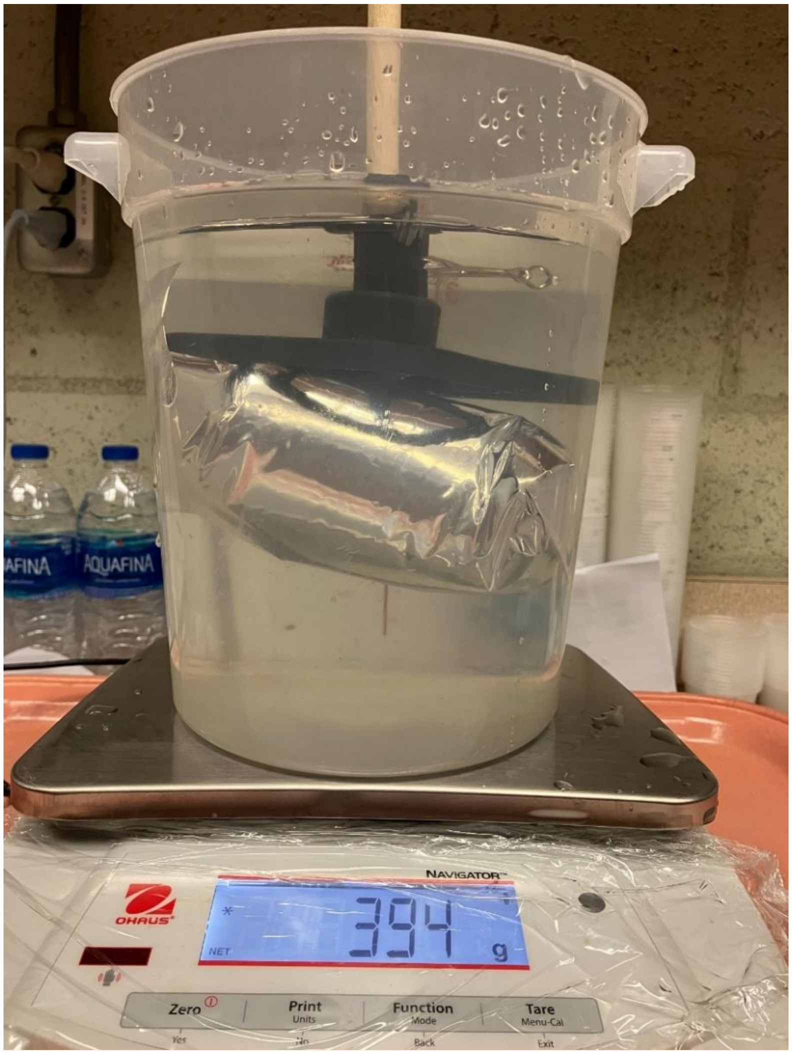


Figure 3.6 Instrument for Determination of Volume

3.7 Real World Modeling

In order to determine the effectiveness of each packaging material for small scale coffee producers, the iterative model was set up to estimate shelf life at the following conditions. Thirty grams of coffee stored in a package with 48.38 in^2 non-sealed surface area and 20 mL of headspace. This simulates a standard size fractional pack and dose of coffee in which most of the residual air is squeezed out before sealing, but no gas flushing is performed. End of life conditions were set to 150, 225, and 300 µg O_2 consumed per gram of coffee in order to represent a high, medium, and low level of shelf life rigor (Cardelli, 2001; Yeretzian 2017).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Q_{10} Analysis Results

The measured oxygen consumption rate from each sample set is shown in table 4.1

Label	Temperature (C)	Relative Humidity	OCR
21C	21	53	9.80E-07
31C	31	53	1.15E-06
35C	35	53	1.19E-06
49R	31	48	1.17E-06
72R	31	72	1.59E-06
84R	31	84	2.01E-06

Table 4.1 Oxygen Consumption Rates and Environmental Conditions of Q_{10} Ground Coffee

When equation 3.11 is used to calculate the Q_{10} values for 10 degrees Celsius and 0.1 water activity, the values in tables 4.2 and 4.3 were generated.

Label	Q10 Value
21C - 31C	1.173
21 C - 35C	1.149
Average Temperature Q10	1.161

Table 4.2 Temperature Q_{10} Effect Values for Ground Coffee

Label	Q10 Value
49R - 72R	1.496
49R - 84R	1.442
Average Humidity Q10	1.469

Table 4.3 Humidity Q_{10} Effect Values for Ground Coffee

In order to generate the humidity based Q_{10} values, the a_w values were converted to their corresponding MC_{db} values, as determined by an MSI. These values were substituted into equation 3.11 and calculations were performed. These values show that for every 10^{o}C increase in temperature, the OCR increases by approximately 16.1% and for every 0.1 increase in a_w, the OCR increases by 46.9%. These values align with previous studies, namely with Cardelli and Labuza's 2001 study in which it was determined that a 10^{o}C increase in temperature decreased shelf life by approximately 20% and an increase of a_w by 0.1 decreased shelf life by approximately 60% (Cardelli, 2001).

4.2 Moisture Sorption Isotherm Results

Table 4.4 and figure 4.1 describe the results from the MSI procedure carried out in section 3.5.

Water Activity	**Moisture Content (% dry basis)**
0.01	1.66
0.23	3.33
0.43	4.09
0.54	6.49
0.75	12.04
0.85	18.40
0.92	32.94

Table 4.4 Water Activity and Moisture Content of Roasted and Ground Coffee

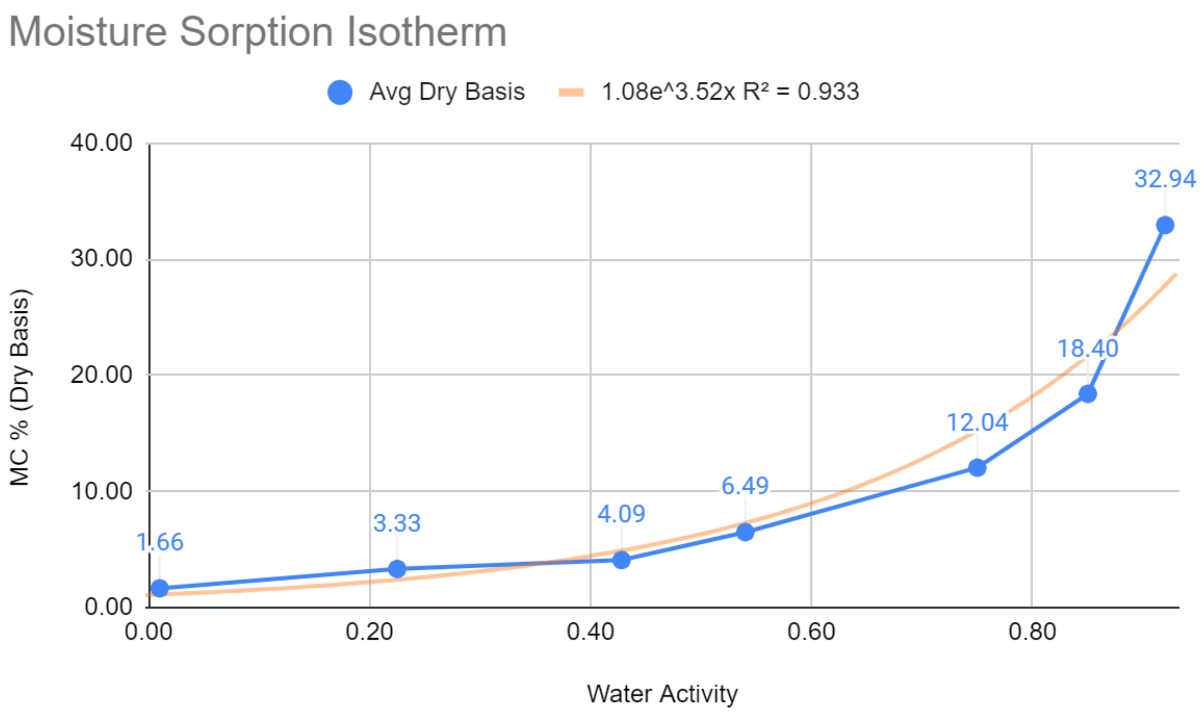


Figure 4.1 Moisture Sorption Isotherm of Roasted and Ground Coffee

As shown in figure 4.1, the moisture sorption isotherm generated by the present data demonstrates a BET type III curve. This is consistent with MSI data already in the literature, namely that of Anese et. Al 2006, Baptestini et Al. 2014, and Escobar et Al. 2022 (Anese, 2006; Baptestini, 2014, Escobar, 2022). Moreover these papers show similar moisture and water activity values to the present study.

When the data is fitted to an exponential curve, the line of best fit takes the form y = 1.08e^3.52(x). This equation was used in order to model the water activity of the coffee based on the calculated MC value.

4.3 Nitrogen Flushed Bags

The nitrogen flushed bags generated for this experiment were monitored for CO_2 release and seal failure over time. After 50 days, the mPET nitrogen flushed bags released 1.80 mL of CO_2 per gram of coffee, the mcellophane nitrogen flushed bags released 1.57 mL CO_2 per gram of coffee, and the mPE nitrogen flushed bags released 1.25 mL CO_2 per gram of coffee. These values are within the upper and lower bounds of the non-nitrogen-flushed bags and do not reflect any seal failures.

Every nitrogen flushed bag which was sampled, across all materials and time periods, contained so little oxygen that it was below the detectable level (+/- 0.005%) of the headspace analyzer, (Illinois Instruments, Johnsburg, IL). This suggests that coffee will continue to consume oxygen even at very low (<0.5%) levels.

4.4 Shelf-Life Results

4.4.1 mPET Shelf-Life Results

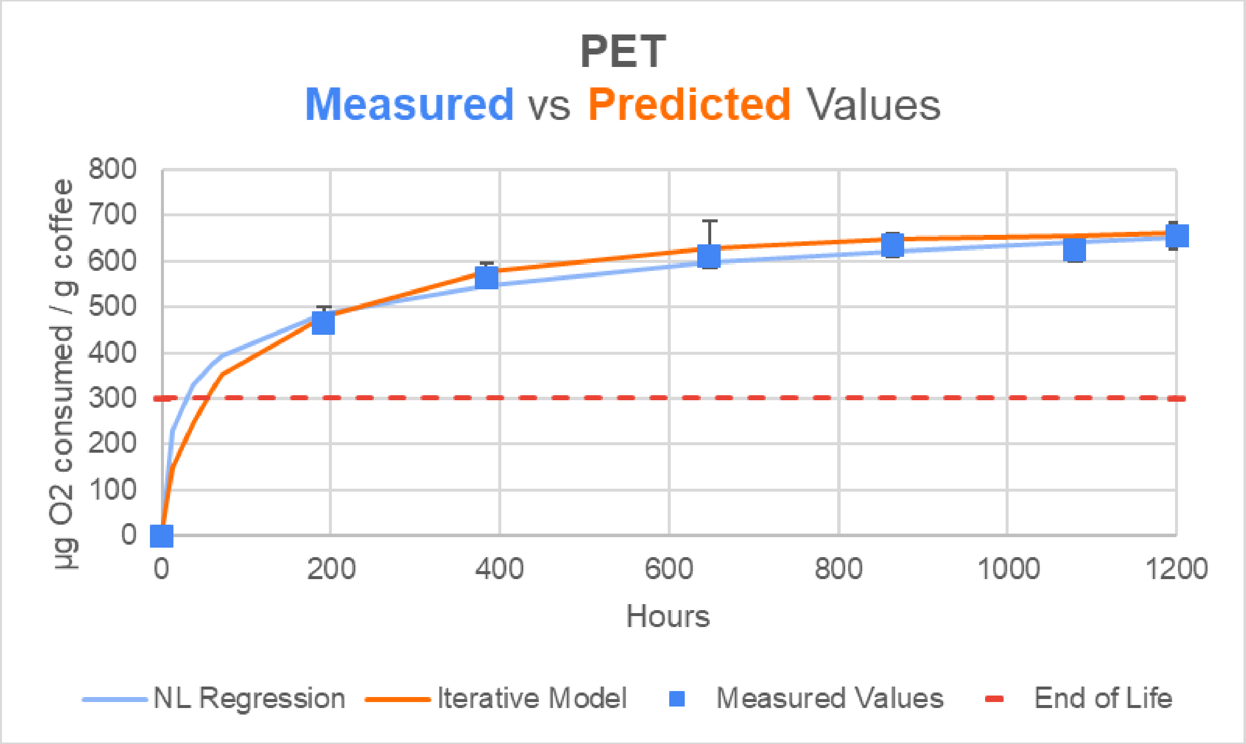


Figure 4.3: Measured and Predicted Oxygen Consumption of Roasted Ground Coffee in mPET

Figure 4.3 shows the predictive model vs measured values generated for the roasted and ground coffee in the mPET pouches. The predictive model reaches the EoL value of 300 µg of oxygen per g of coffee at 53 hours. A non-linear regression fitted to the measured values shows that at 53 hours, each sample had consumed 366 µg of oxygen per g of coffee . This amounts to a difference of 66 micrograms, or 18.03% of the total shelf life. The relative standard error between the measured and predicted values is 1.195E-3. The maximum and minimum measured values are represented by error bars at each data point. Some error bars are obscured by data points.

In order to determine the effectiveness of the mPET packaging for small scale coffee producers, the iterative model was set up to estimate shelf life as described in section 3.7. According to these calculations, this packaging material and method of packaging is capable of a shelf life of 69 days at high rigor, 283 days at medium rigor, and 497 days at low rigor for roasted and ground coffee. This means that a coffee producer could claim a 6 month shelf life if they deemed a low or medium rigor acceptable, but not if they required high rigor.

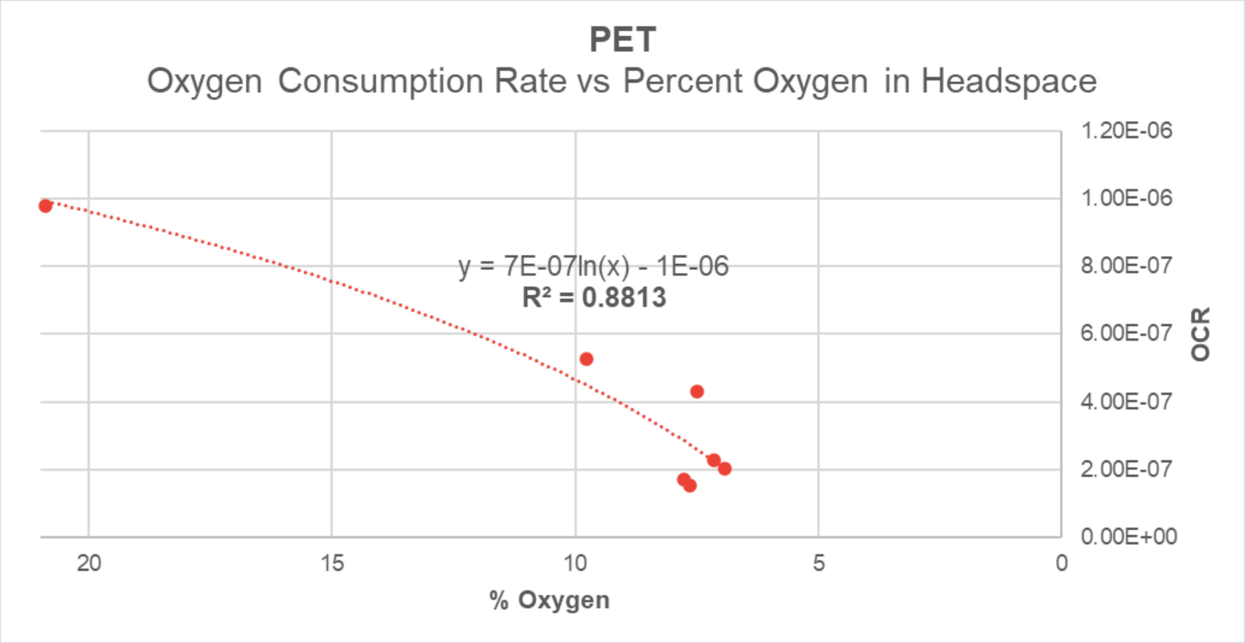


Figure 4.4: mPET Oxygen Consumption rate and Percent Oxygen in Headspace

As shown in figure 4.4, the coffee packed in mPET pouches begins with an OCR of 9.80E-07 µg$_{O2}$ / coffee / day / mbar and decreases to a minimum value 1.54E-07. When the OCR is plotted against the oxygen concentration of the headspace, oxygen consumption is shown to be a first order reaction fitting well to the logarithmic function Y = 7.1507E-07 ln(x) - 1.1802E-06 (R^2 = 0.8813).

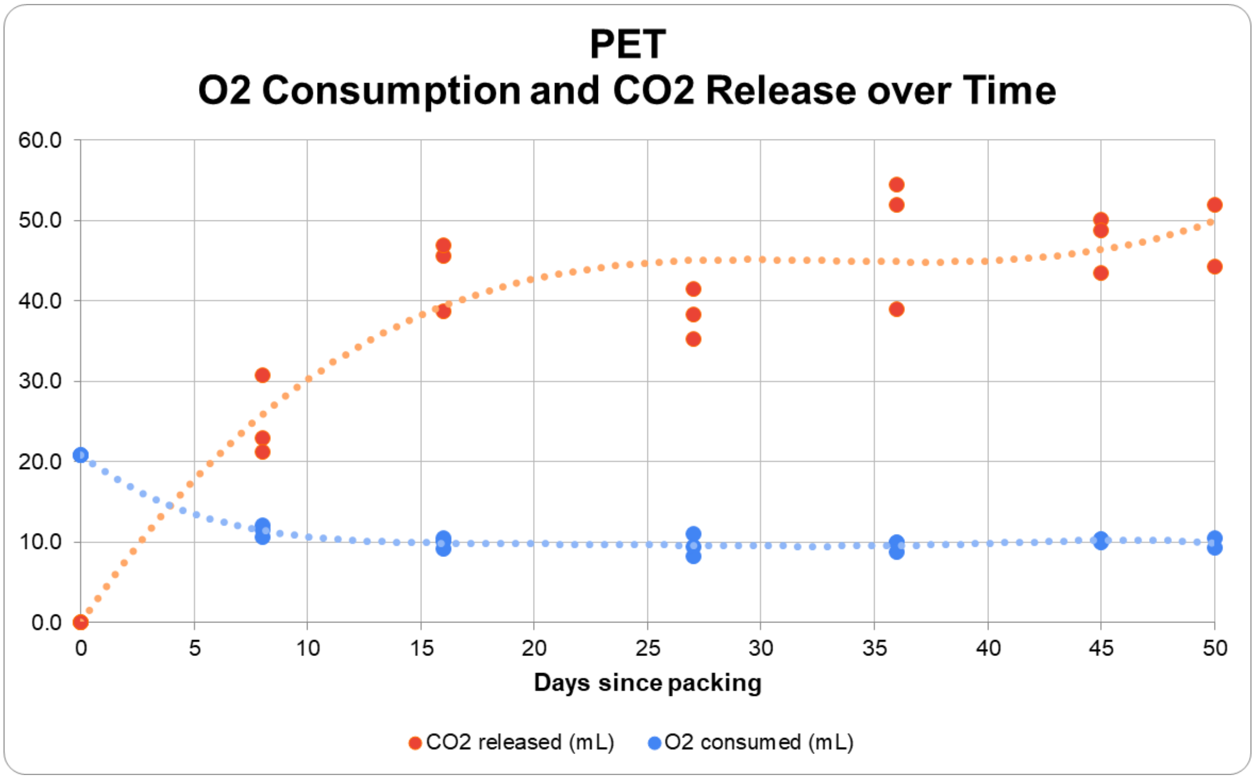


Figure 4.5: PET O_2 Consumption and CO_2 Release over Time

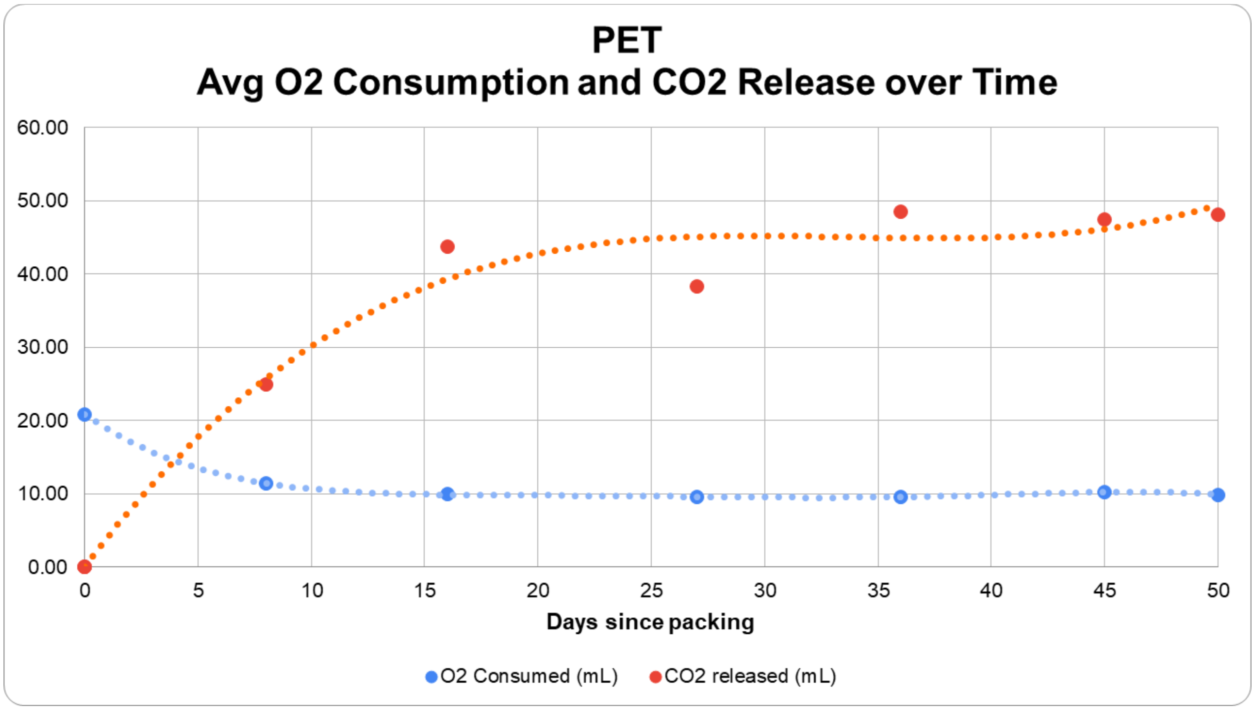


Figure 4.6: mPET Average O_2 Consumption and CO_2 Release over Time

The PET pouches used in this experiment had an average headspace of 99.8 mL. Oxygen falls from an atmospheric level of 20.9 mL (20.9%) per pouch down to 9.92 mL (7.8%) levels by 15 days. At this stage oxygen consumption is limited to the amount of ingress allowed by the package's barrier values. The coffee releases 48 mL of CO_2 within 15 days, and then stabilizes. No significant change was observed after this time. This amounts to each gram of coffee releasing 1.6 mL of CO_2, which accords with the expected value (Shimoni, 2007).

4.4.2 mcellophane Shelf-Life Results

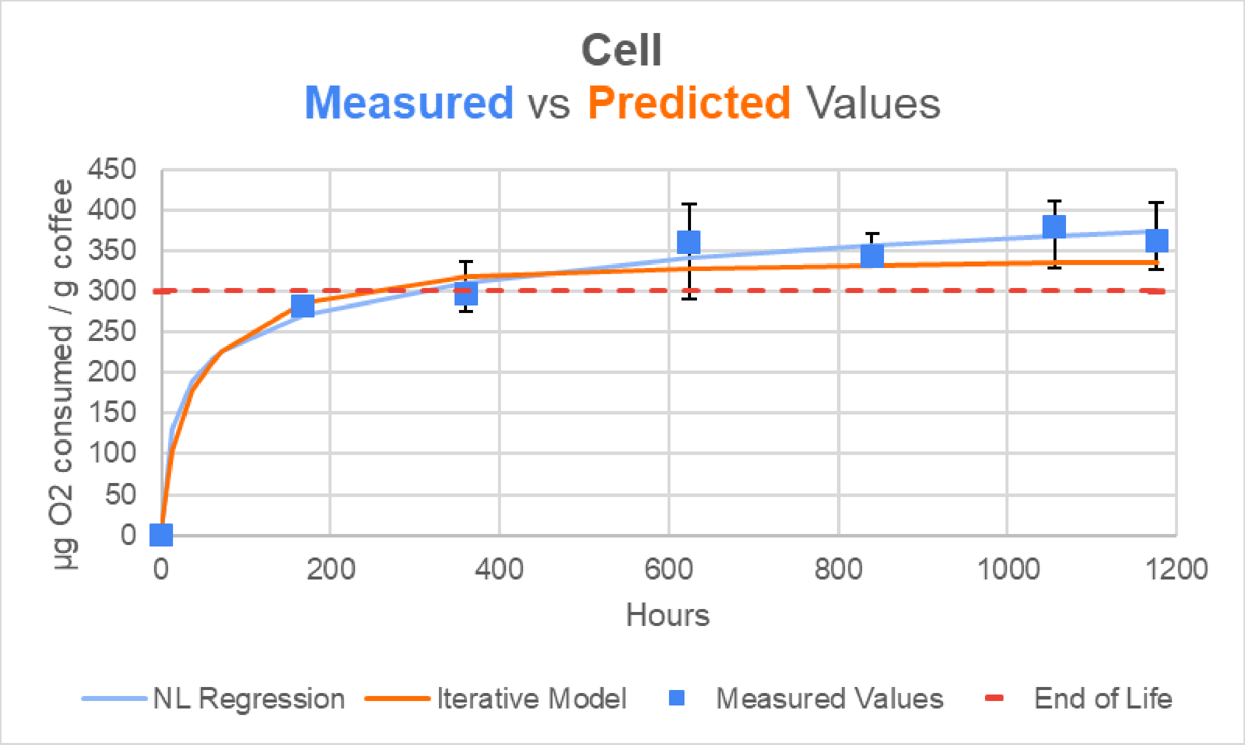


Figure 4.7: mcellophane Measured and Predicted Oxygen Consumption

Figure 4.7 shows the predictive model vs measured values generated for the mcellophane pouches. The predictive model reaches the EoL value of 300 µg of oxygen per g of coffee at 218 hours. A non-linear regression fitted to the measured values shows that at 218 hours, each sample had consumed 285 µg of oxygen per g of coffee This amounts to a difference of 15 micrograms, or 5.26% of the total shelf life. The relative standard error between the measured and predicted values is 1.299E-03. The maximum and minimum measured values are represented by error bars at each data point. Some error bars are obscured by data points.

In order to determine the effectiveness of the mcellophane packaging for small scale coffee producers, the iterative model was set up to estimate shelf life as described in section 3.7. According to these calculations, this packaging material and packaging method is capable of a shelf life of 72 days at high rigor, 309 days at medium rigor, and 545 days at low rigor. This means that a coffee producer could claim a 6 month shelf life if they deemed a low or medium rigor acceptable, but not if they required high rigor.

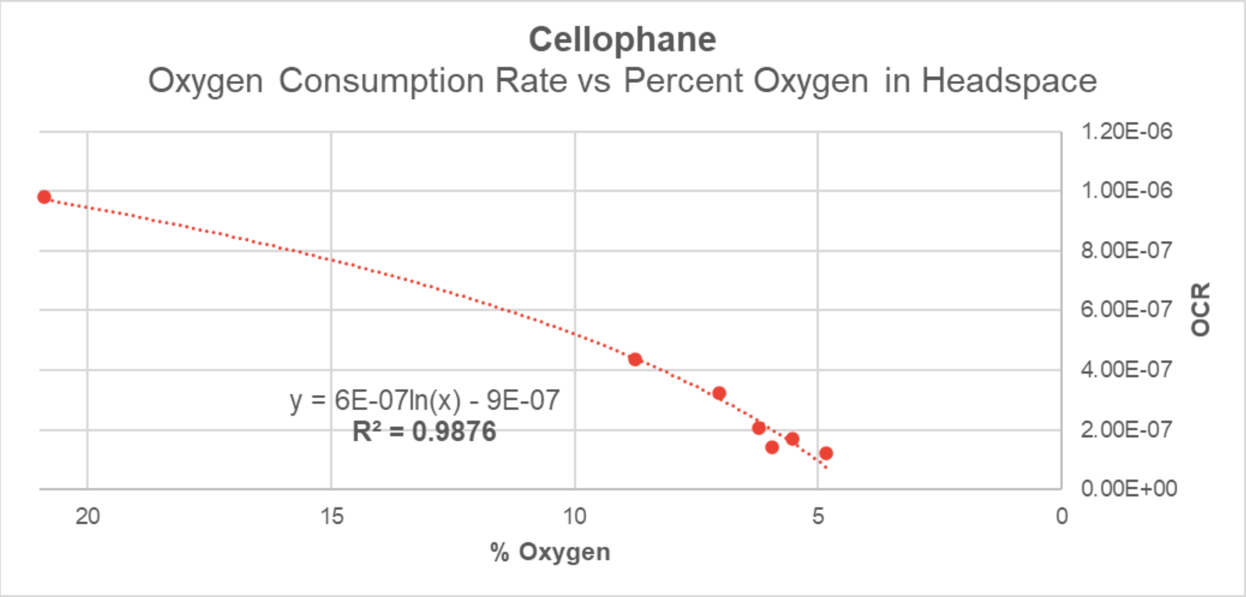


Figure 4.8: mcellophane Oxygen Consumption rate and Percent Oxygen in Headspace

As shown in figure 4.8, the coffee packed in mcellophane pouches begins with an OCR of 9.80E-07 μg_{O2} / coffee / day / mbar and decreases to a minimum value of 1.22E-07. When the OCR is plotted against the oxygen concentration of the headspace, oxygen consumption is shown to be first order reaction fitting well to the logarithmic function Y = 6.1301E-07 ln(X) - 8.9073E-07 (R^2 = 0.9876).

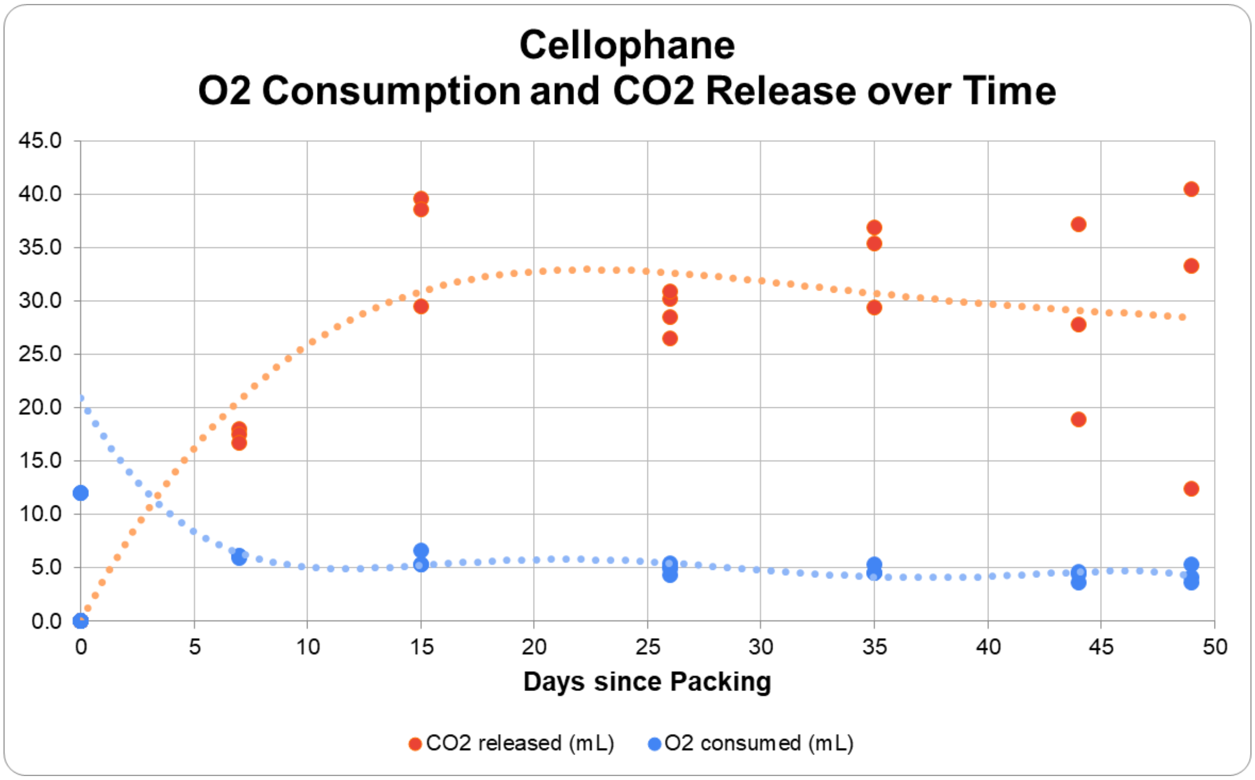


Figure 4.9: mcellophane O_2 Consumption and CO_2 Release over Time

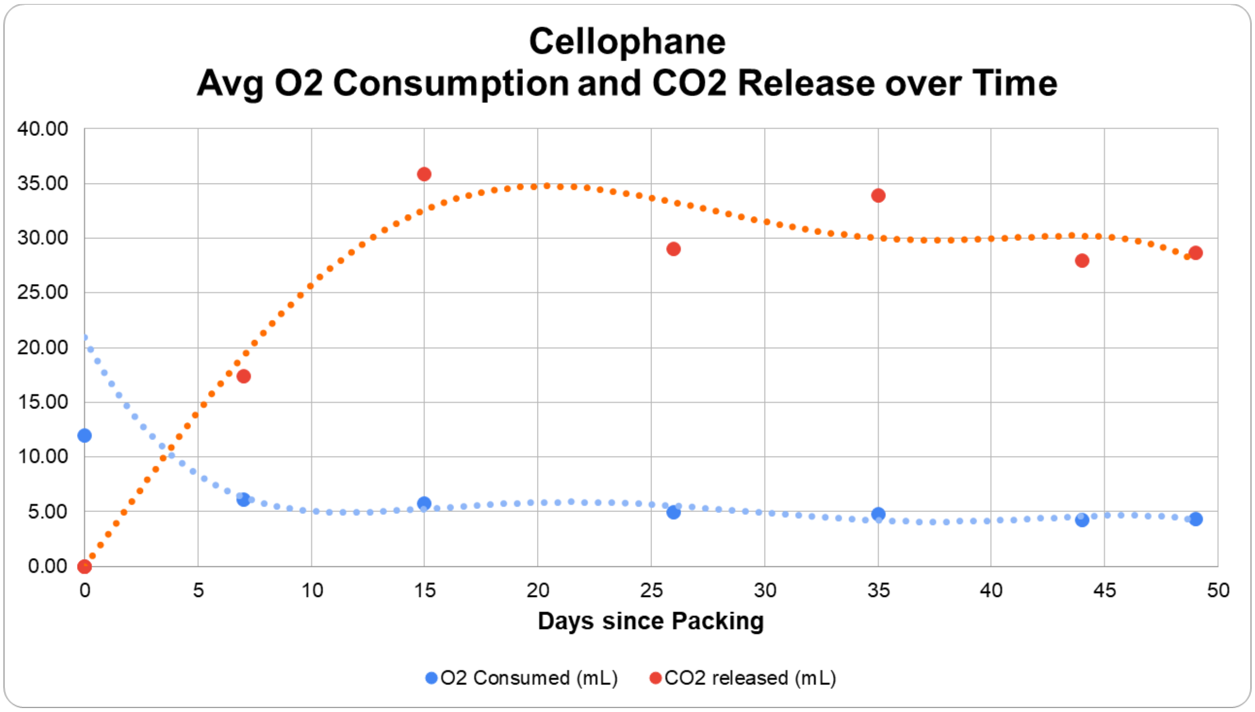


Figure 4.10: mcellophane Average O_2 Consumption and CO_2 Release over Time

The cellophane pouches used in this experiment had an average headspace of 58 mL. Oxygen falls from an atmospheric level of 12.1 mL (20.9%) per pouch down to 4.95 mL (4.9%) levels by 26 days. At this stage oxygen consumption is limited to the amount of ingress allowed by the package's barrier values. The coffee releases 31.1 mL of CO_2 within 21 days, and then stabilizes. No significant change was observed after this time. This amounts to each gram of coffee releasing 1.04 mL of CO_2, which accords with the expected value (Shimoni, 2007).

4.4.3 mPLA Shelf-Life Results

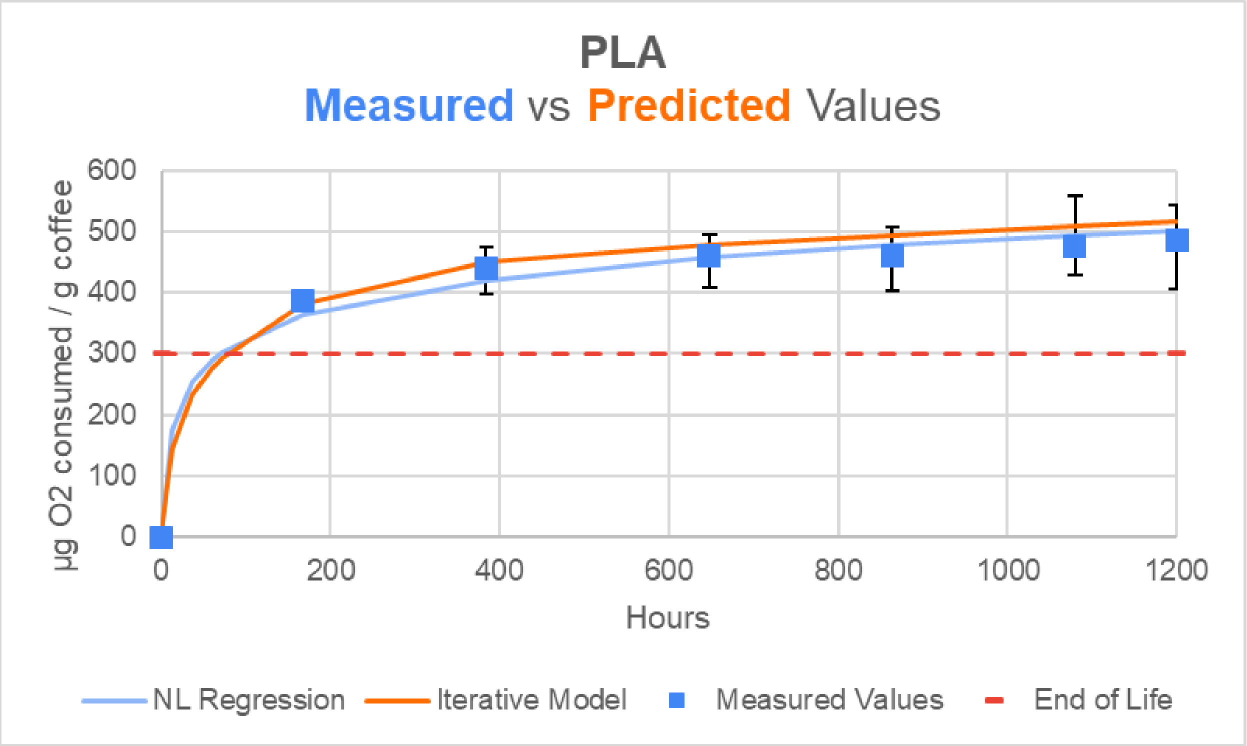


Figure 4.11: mPLA Measured and Predicted Oxygen Consumption

Figure 4.11 shows the predictive model vs measured values generated for the mPLA pouches. The predictive model reaches the EoL value of 300 µg of oxygen per g of coffee at 72 hours. A non-linear regression fitted to the measured values shows that at 72 hours, each sample had consumed 308 µg of oxygen per g of coffee . This amounts to a difference of 8 micrograms, or 2.60% of the total shelf life. The relative standard error of the measured and predicted values is 1.203E-3. The maximum and minimum measured values are represented by error bars at each data point. Some error bars are obscured by data points.

In order to determine the effectiveness of the mPLA packaging for small scale coffee producers, the iterative model was set up to estimate shelf life as described in section 3.7. According to these calculations, this packaging material and packaging method is capable of a shelf life of 37 days at high rigor, 126 days at medium rigor, and 208 days at low rigor. This means that a coffee producer could claim a 6 month shelf life if they deemed a low rigor acceptable, but not if they required a medium or high rigor.

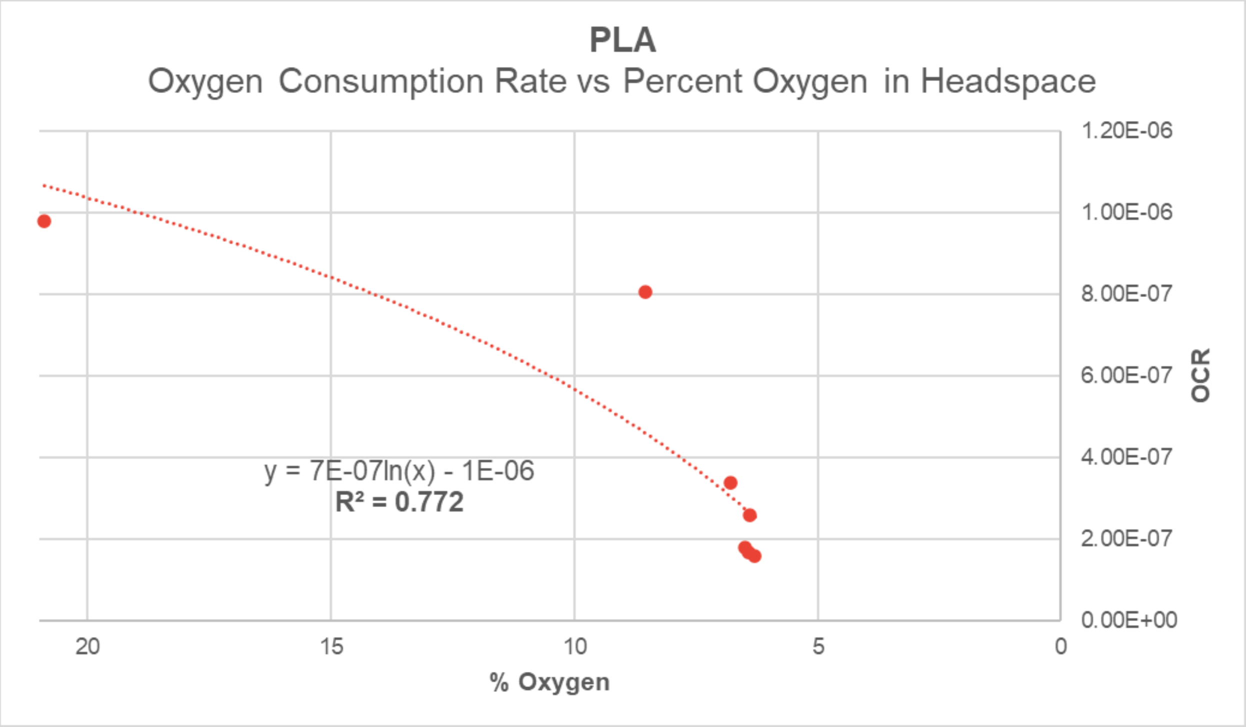


Figure 4.12: PLA Oxygen Consumption rate and Percent Oxygen in Headspace

As shown in figure 4.12, the coffee packed in mPLA pouches begins with an OCR of 9.80E-07 µg$_{O2}$ / coffee / day / mbar and decreases to a minimum value of 1.59E-07. When the OCR is plotted against the oxygen concentration of the headspace, oxygen consumption is shown to be a first order reaction fitting well to the logarithmic function Y = 7.7772E-07 ln(X) - 9.9393E-07 (R^2 = 0.772). When the outlier at 8% oxygen is removed, the R^2 value is improved to 0.969.

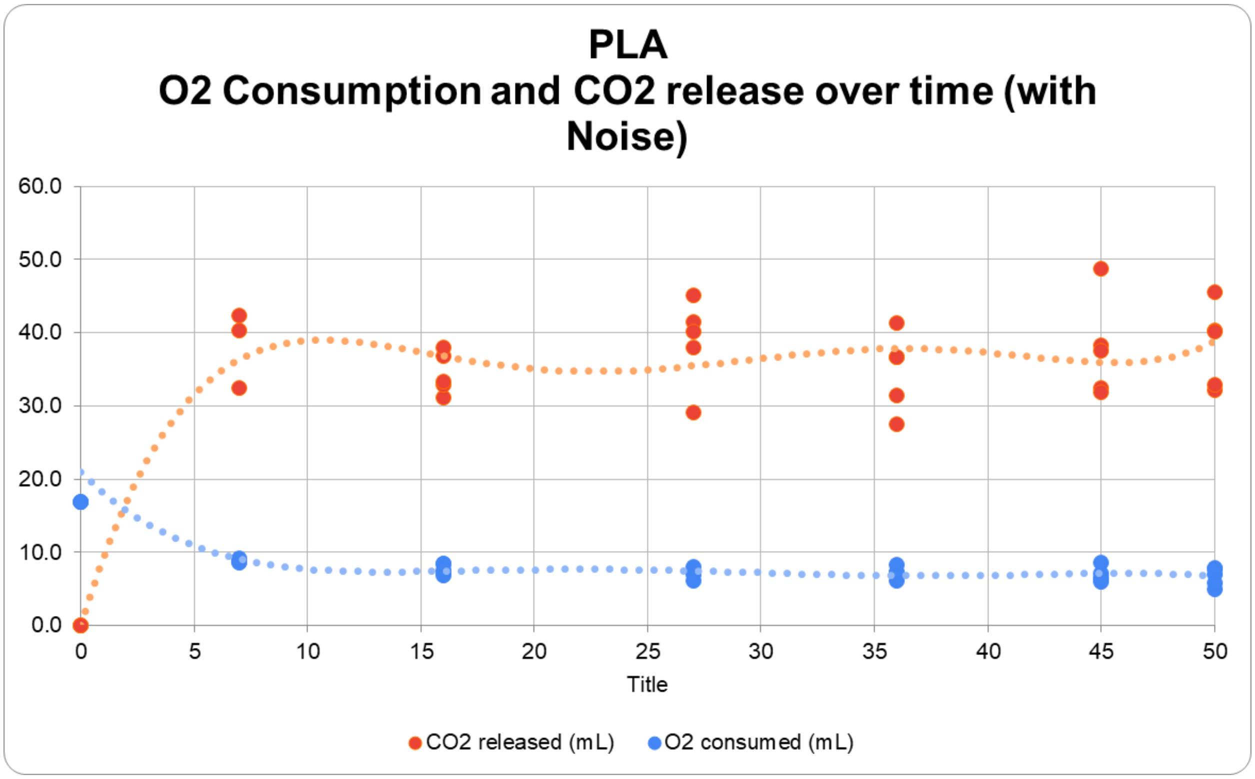


Figure 4.13: PLA O_2 Consumption and CO_2 Release over Time

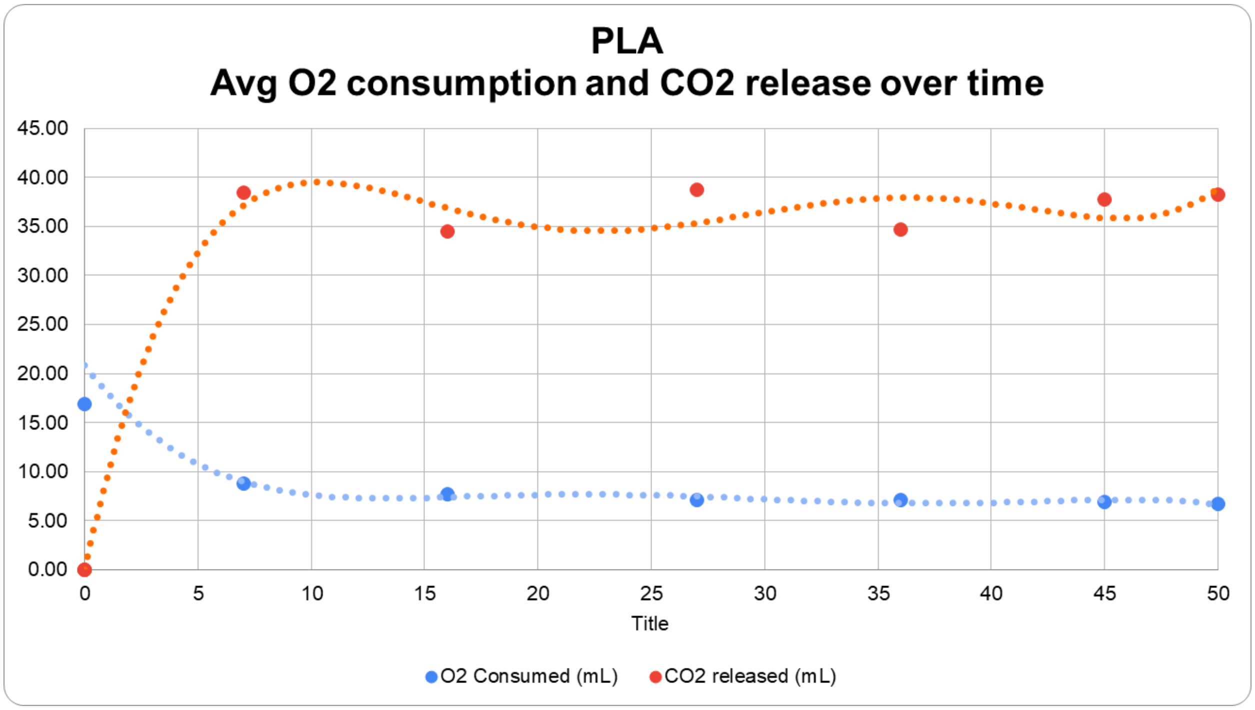


Figure 4.14: PLA Average O_2 Consumption and CO_2 Release over Time

The PLA pouches used in this experiment had an average headspace of 78.73 mL. Oxygen falls from an atmospheric level of 16.45 mL (20.9%) per pouch down to 6.72 mL (6.41%) levels by 16 days. At this stage oxygen consumption is limited to the amount of ingress allowed by the package's barrier values. The coffee releases 38.4 mL of CO_2 within 7 days, and then stabilizes. No significant change was observed after this time. This amounts to each gram of coffee releasing 1.28 mL of CO_2, which accords with the expected value (Shimoni, 2007).

4.4.4 mPE Shelf-Life Results

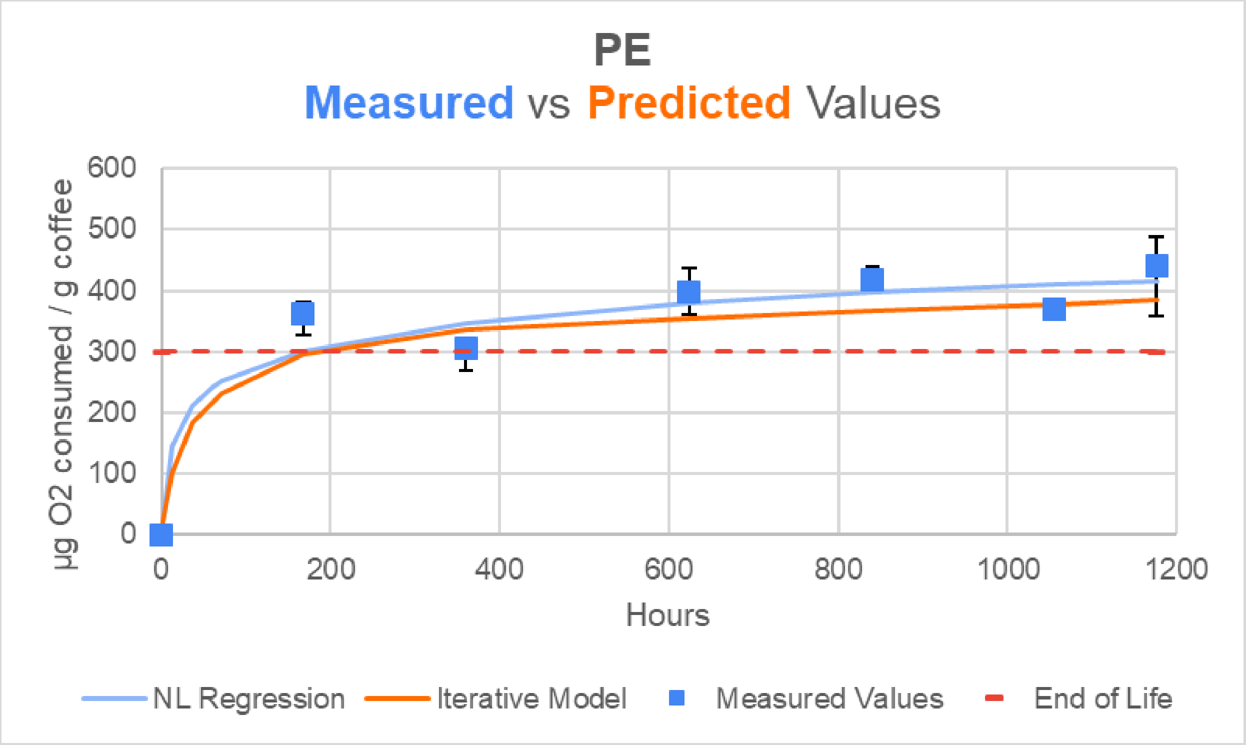


Figure 4.15: PE Measured and Predicted Oxygen Consumption

Figure 4.15 shows the predictive model vs measured values generated for the mPE pouches. The predictive model reaches the EoL value of 300 µg of oxygen per g of coffee at 180 hours. A non-linear regression fitted to the measured values shows that at 180 hours, each sample had consumed 306 µg of oxygen per g of coffee . This amounts to a difference of 6 micrograms, or 1.96% of the total shelf life. The relative standard error between the measured and predicted values is 8.116E-03. The maximum and minimum measured values are represented by error bars at each data point. Some error bars are obscured by data points.

In order to determine the effectiveness of the mPE packaging for small scale coffee producers, the iterative model was set up to estimate shelf life as described in section 3.7. According to these calculations, this packaging material and packaging method is capable of a shelf life of 38 days at high rigor, 130 days at medium rigor, and 221 days at low rigor. This means that a coffee producer could claim a 6 month shelf life if they deemed a low rigor acceptable, but not if they required a medium or high rigor.

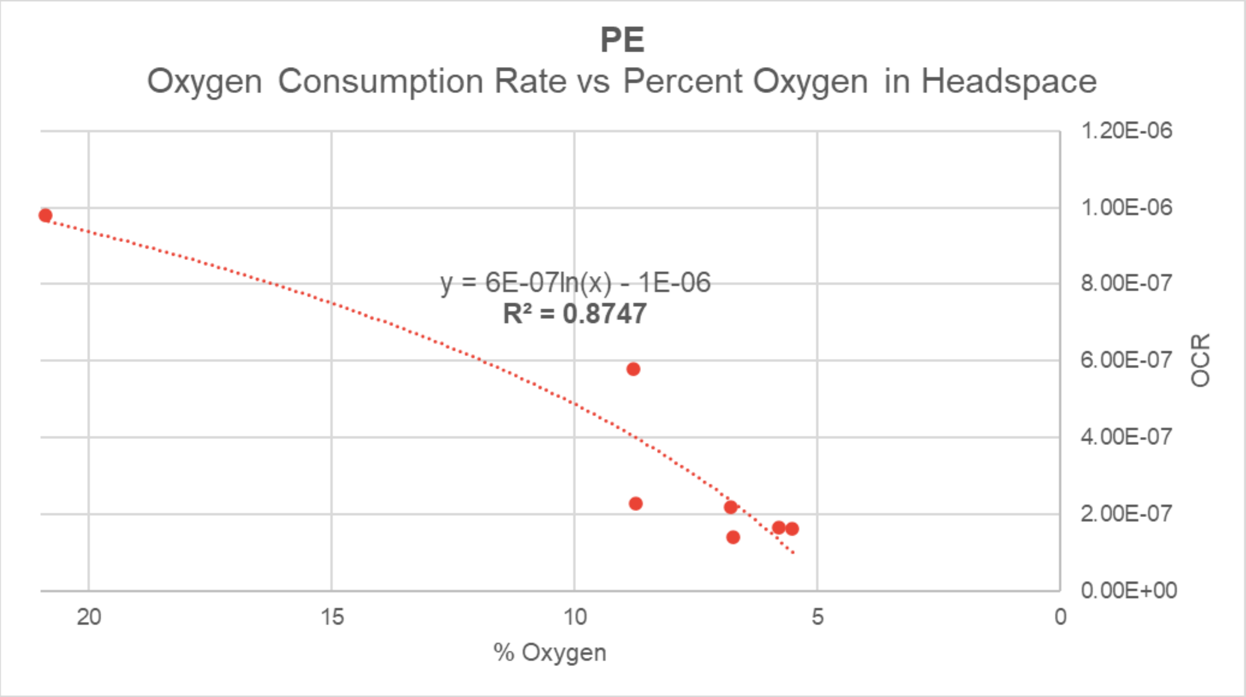


Figure 4.16: PE Oxygen Consumption rate and Percent Oxygen in Headspace

As shown in figure 4.16, the coffee packed in mPE pouches begins with an OCR of 9.80E-07 μg_{O2} / coffee / day / mbar and decreases to a minimum value of 1.39E-07 When the OCR is plotted against the oxygen concentration of the headspace, oxygen consumption is shown to be a first order reaction fitting well to the logarithmic function Y = 6.4987E-07 ln(X) - 1.0094E-06 (R^2 = 0.8747).

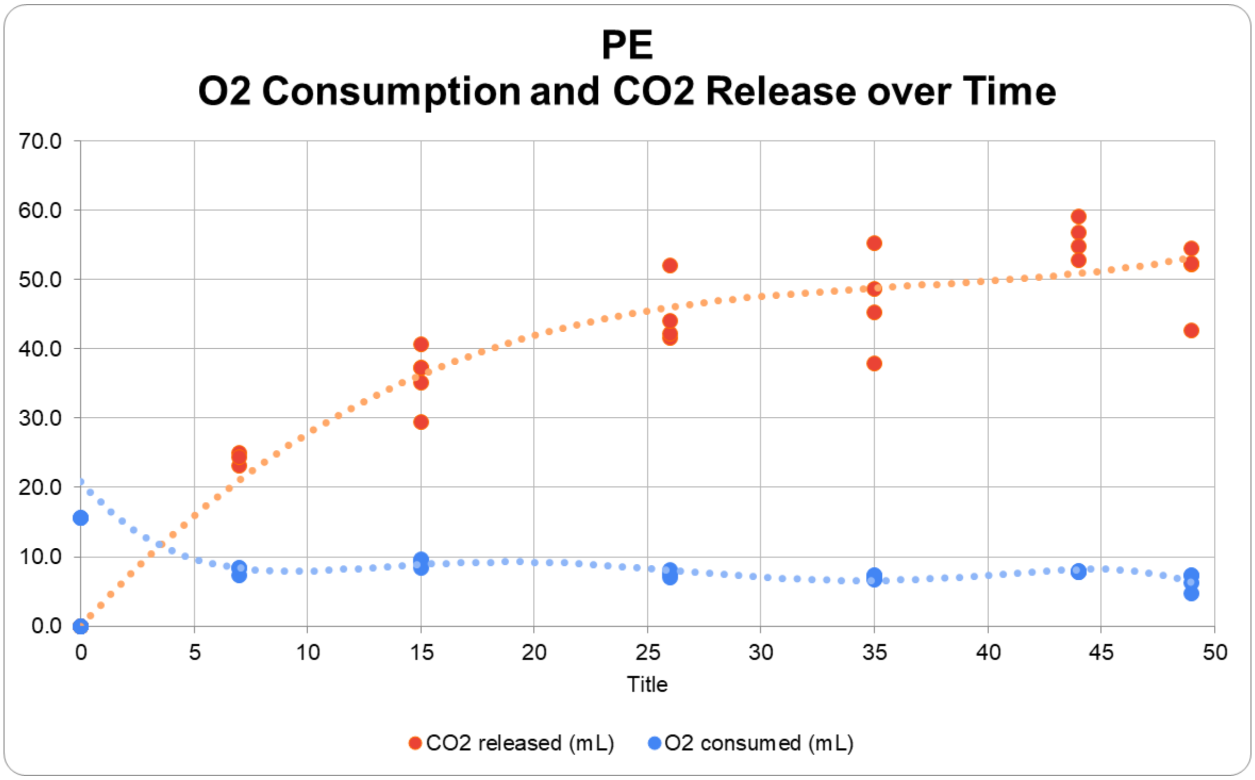


Figure 4.17: PE O_2 Consumption and CO_2 Release over Time

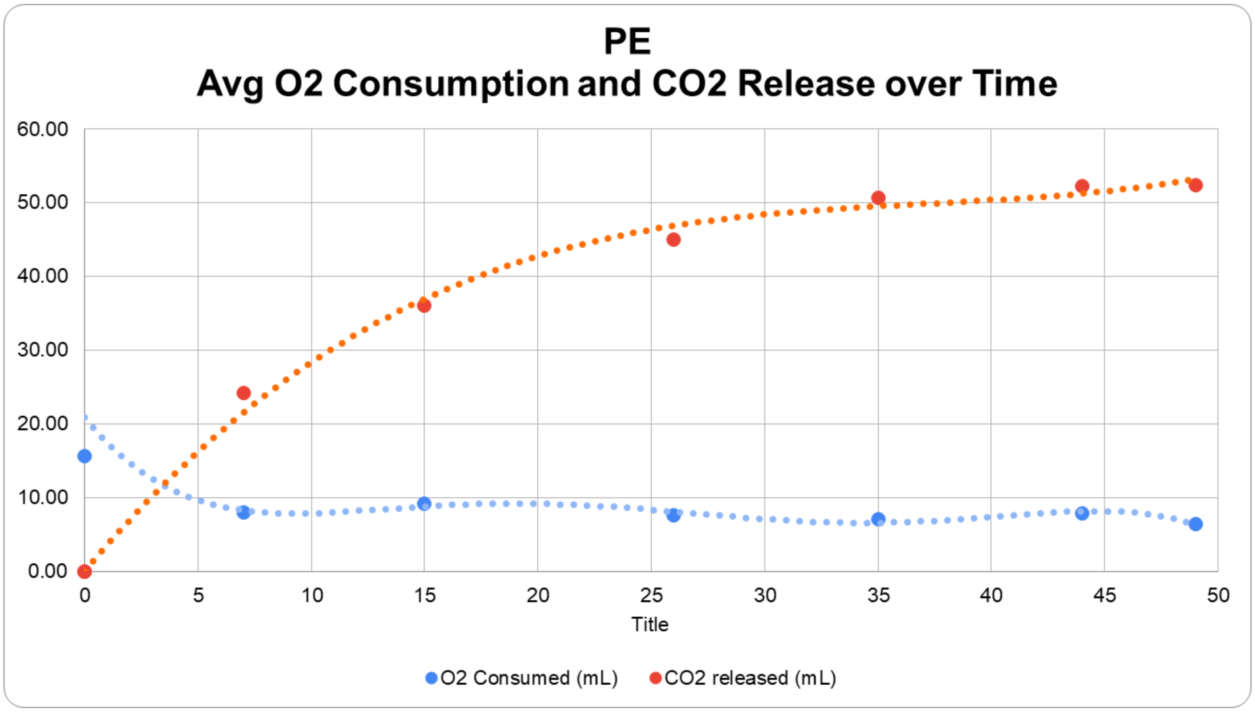


Figure 4.18: PE Average O_2 Consumption and CO_2 Release over Time

The PE pouches used in this experiment had an average headspace of 73.41 mL. Oxygen falls from an atmospheric level of 15.63 mL (20.9%) per pouch down to 8.03 mL (8.79%) levels by 7 days. At this stage oxygen consumption is limited to the amount of ingress allowed by the package's barrier values. The coffee releases 55.89 mL of CO_2 within 44 days, and then stabilizes. No significant change was observed after this time. This amounts to each gram of coffee releasing 1.86 mL of CO_2, which accords with the expected value (Shimoni, 2007).

4.4.5 Paper Shelf-Life Results

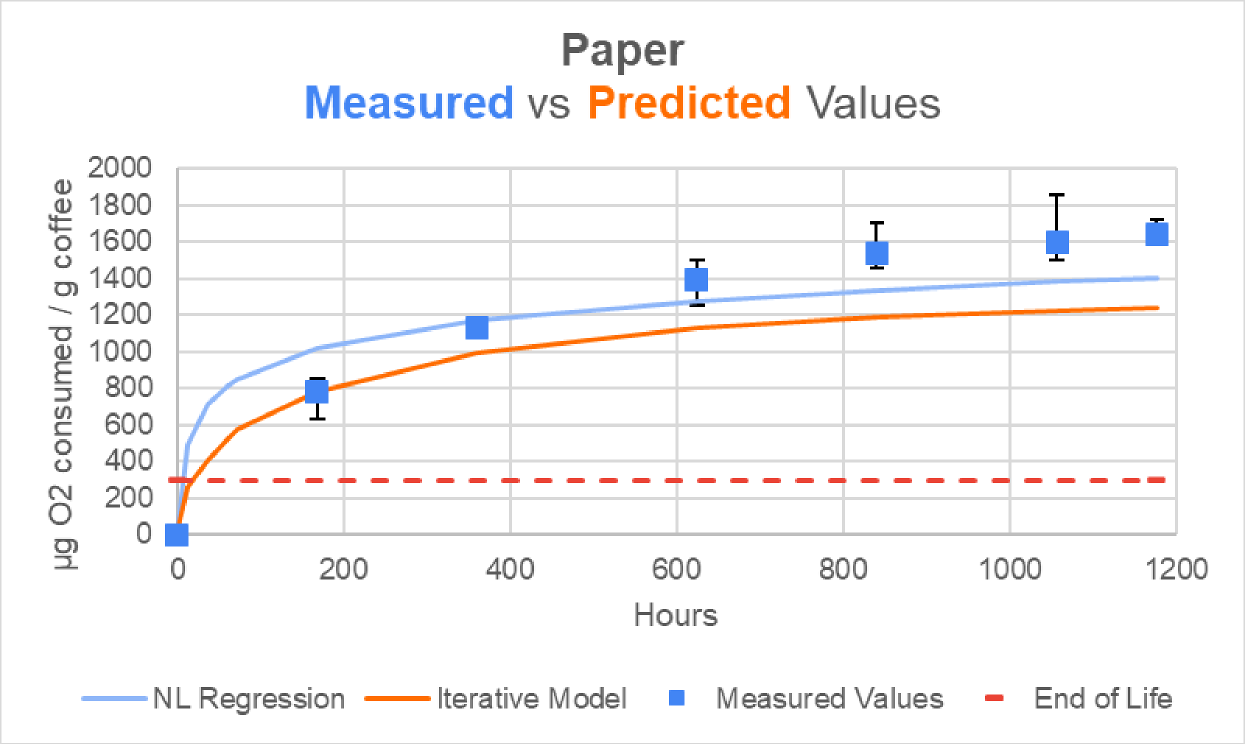


Figure 4.19: Paper Measured and Predicted Oxygen Consumption

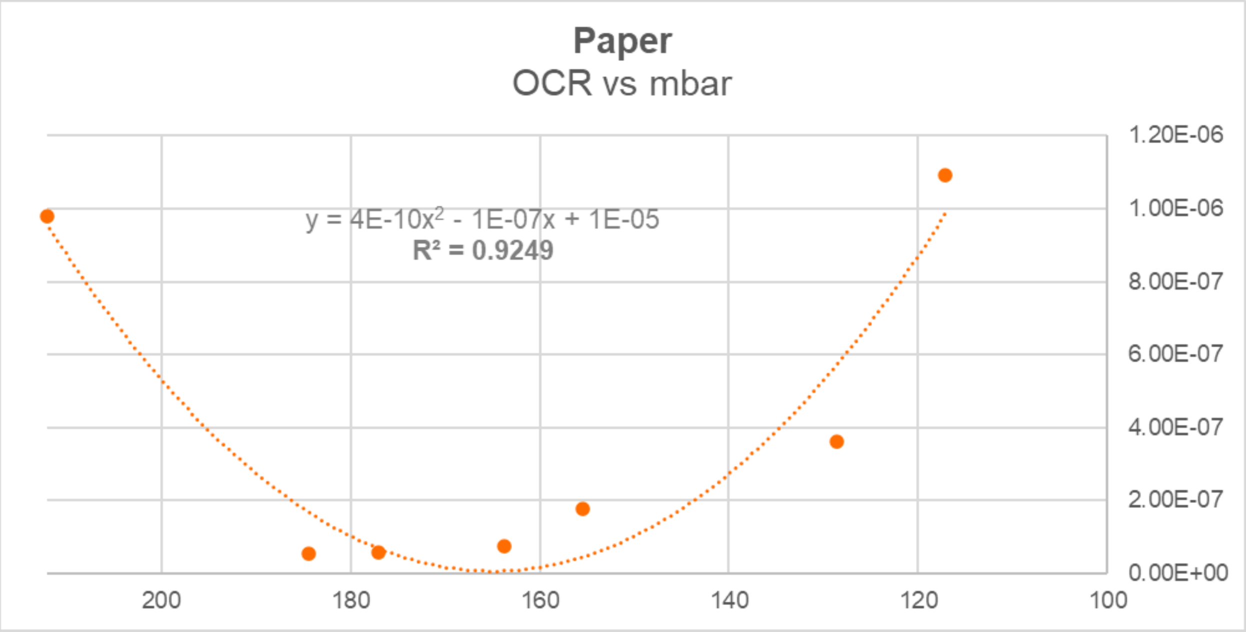


Figure 4.20: Paper Oxygen Consumption rate and Percent Oxygen in Headspace

As shown in figure 4.20, the coffee packed in paper pouches begins with an OCR of 9.80E-07 μg_{O2} / coffee / day / mbar and decreases to a minimum value of 5.33E-08 before trending back up to near the initial OCR. When the OCR is plotted against the oxygen concentration of the headspace, oxygen consumption fits best to a second order reaction. This may be due to moisture ingress into the package and its subsequent increase in OCR, failing seals, or water absorption in the packaging medium causing an increase in OTR. Because the WVTR of the paper system is very high compared to the plastic materials, moisture is allowed to both absorb into the paper pouches and migrate through it much more quickly than the other sample sets.

In order to determine the effectiveness of the paper packaging for small scale coffee producers, the iterative model was set up to estimate shelf life as described in section 3.7.

According to these calculations, this packaging material and packaging method is capable of a shelf life of 51 days at high rigor, 192 days at medium rigor, and 332 days at low rigor. This means that a coffee producer could claim a 6-month shelf life if they deemed a low or medium rigor acceptable, but not if they required a high rigor. Because the paper packages were found to not model as accurately as other systems, these predictions must be held with a lower confidence.

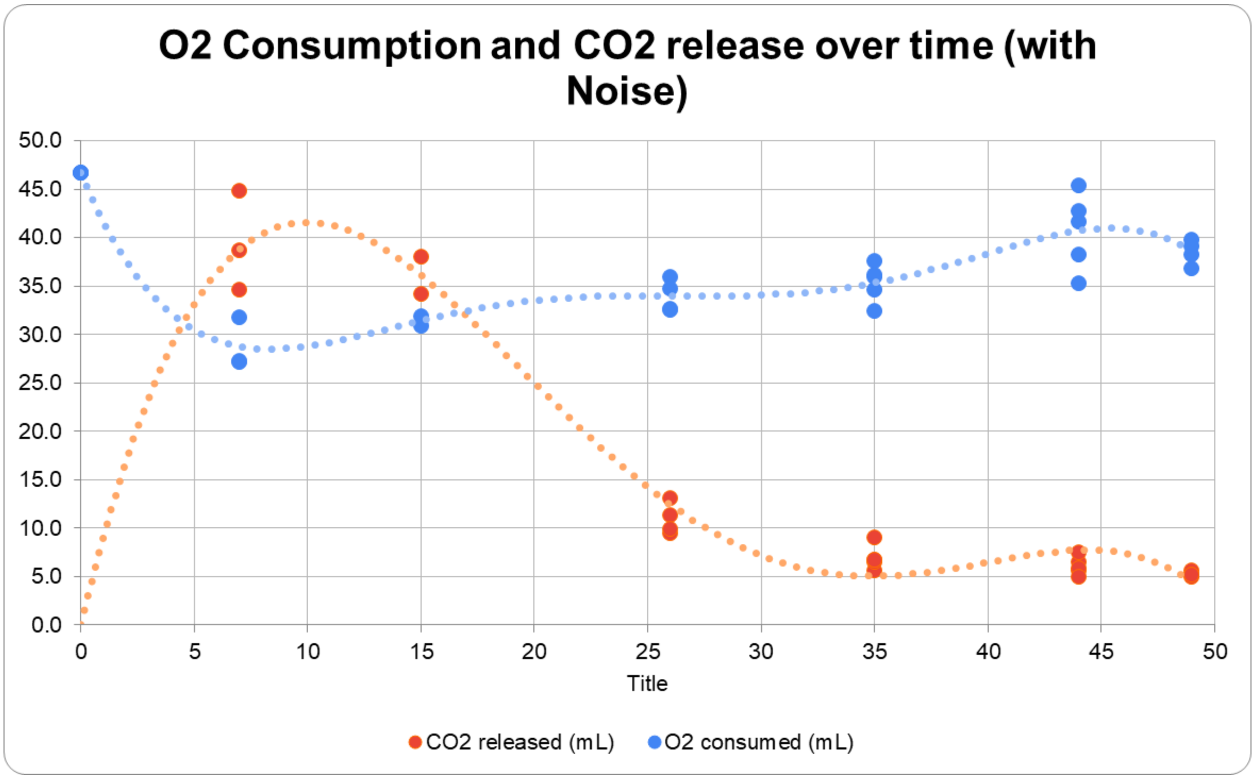


Figure 4.21: O_2 consumption and CO_2 release over time in Paper Pouches

The paper pouches used in this experiment had an average headspace of 223.65 mL. Oxygen fell from an atmospheric level of 46.40 mL (20.9% O_2) per pouch down to 26.21 mL

(11.56%) levels by 7 days. After this point, the measured mL of oxygen in the pouch increases back to nearly atmospheric levels (39.59 milliliters at 17.48% O_2). This is probably due to failing seals or water absorption by the paper significantly increasing its OTR. The coffee releases 39.42 mL of CO_2 within 7 days, and then stabilizes until around day 15. No significant change was observed after this time. This amounts to each gram of coffee releasing 1.31 mL of CO_2, which accords with the expected value (Shimoni, 2007). However, after this time, CO_2 levels drop until they are down to nearly atmospheric levels. This suggests a failure of seals and could also be caused by moisture adsorption of the package greatly increasing the CO_2 transmission rate.

Because the results gathered from the paper system did not fit well to the model and were divergent from the other packaging systems, their data was broadly excluded from the subsequent calculations which combined data across sample sets.

4.4.6 Summary of Shelf-Life Results

Table 4.5 shows the amount of CO_2 released by each gram of coffee throughout the 50 day shelf life study.

Material	**mPET**	**mcellophane**	**mPLA**	**mPE**	**Paper**	**Average**
mL CO_2 per g Coffee	1.6	1.04	1.28	1.86	1.31	1.42

Table 4.5 Milliliters of CO_2 Released after 50 days per Gram of Coffee in Each Material

Figures 4.22 and 4.23 below show the CO_2 release characteristics of each packaging system over time (paper omitted).

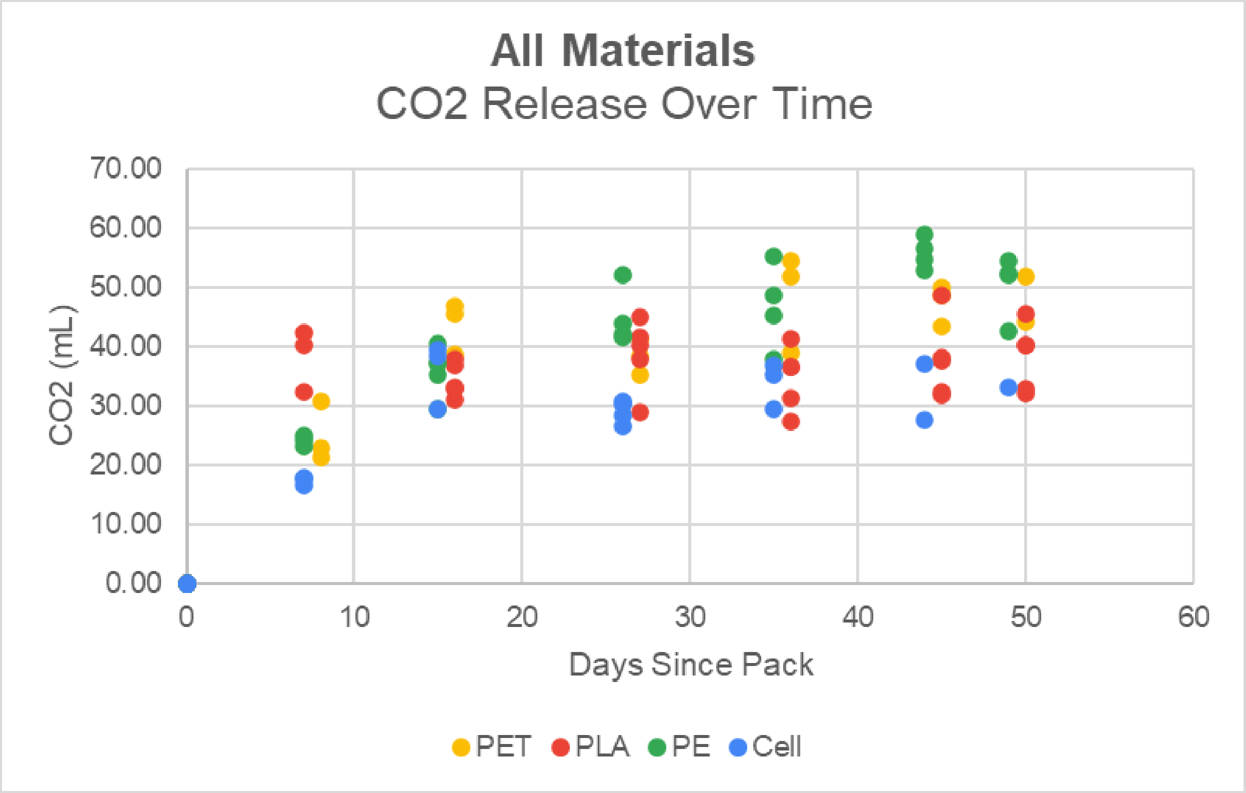


Figure 4.22: CO_2 Release Over Time of All Materials

Figure 4.22 was used to generate equation 3.9, which was used to predict the volume of the headspace of each package over time. An exponential decay function was selected for curve fitting using Excel's solver tool.

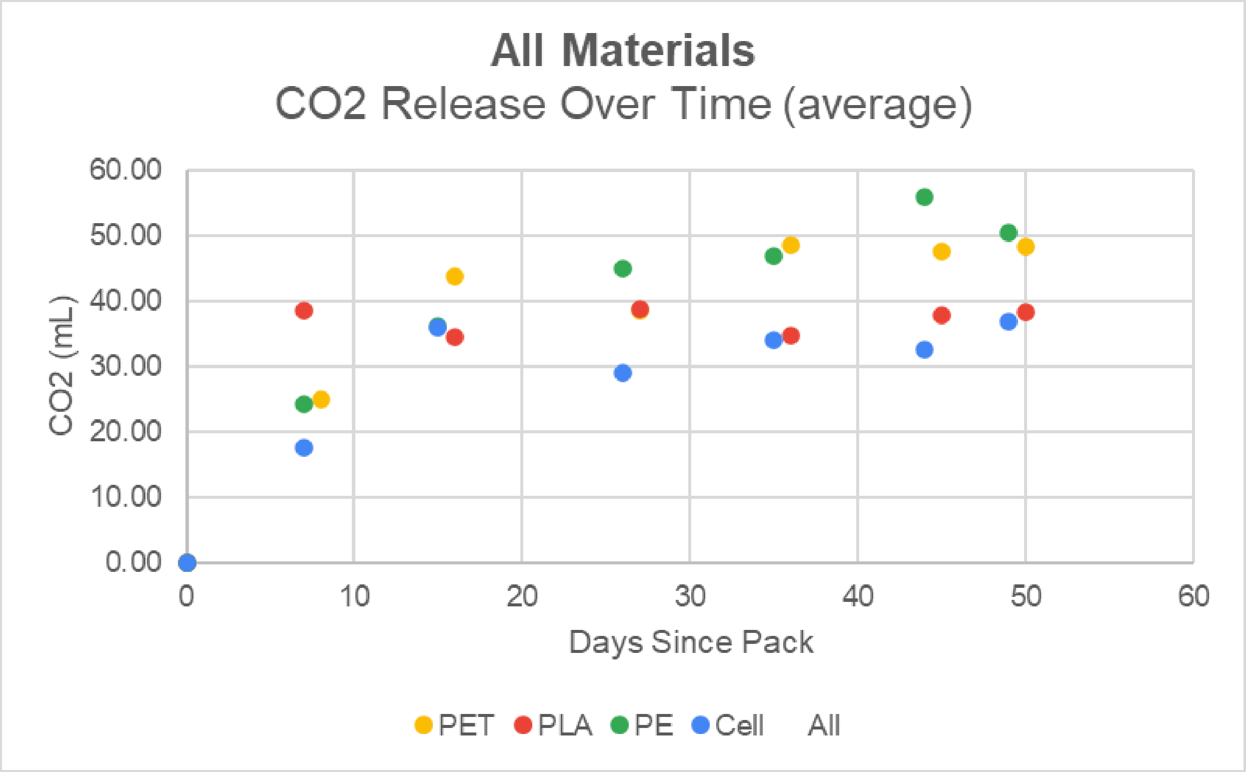


Figure 4.23 CO_2 Release Over Time of All Materials, Average Values

A repeated measures ANOVA was performed on the mean values of CO_2 within each sample set at each sampling date (paper excluded). These data points are shown in figure 4.23 This analysis revealed that there was a statistically significant effect of the package type on the values of CO_2 in a package at a given sample date F(3, 18) = 4.75, p = 0.013. This result is unexpected given that the same coffee was used across all sample sets. Reasons for this result are discussed in section 5.1.

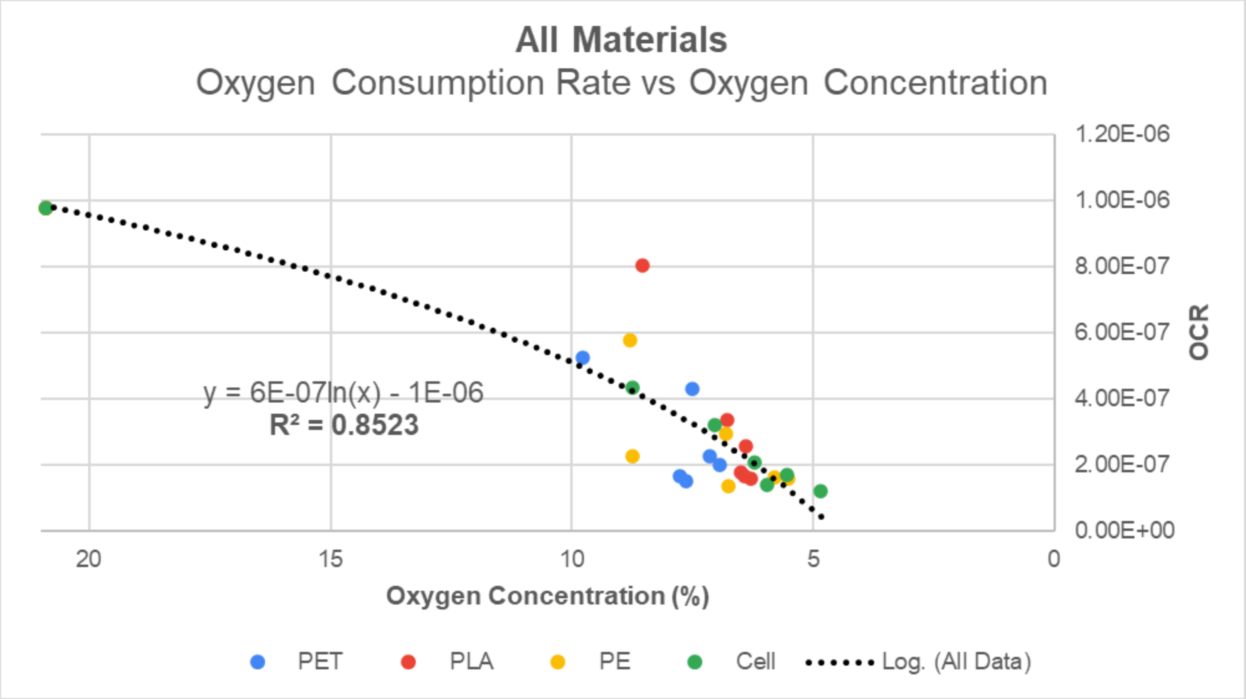


Figure 4.24: Oxygen Consumption Rate vs Oxygen Concentration for All Materials

Figure 4.24 shows the oxygen consumption rate at various oxygen concentrations across all packaging materials. The data fits well to the logarithmic curve Y = 6.3947E-07 ln(x) - 2.4579E-06 (R^2 = 0.8523) showing oxygen consumption to be a first order reaction. The equation shown here was used as a correction factor and applied to the OCR calculated in equation 3.6. This allowed the nonlinear nature of the impact of O_2 concentration on OCR to be better expressed.

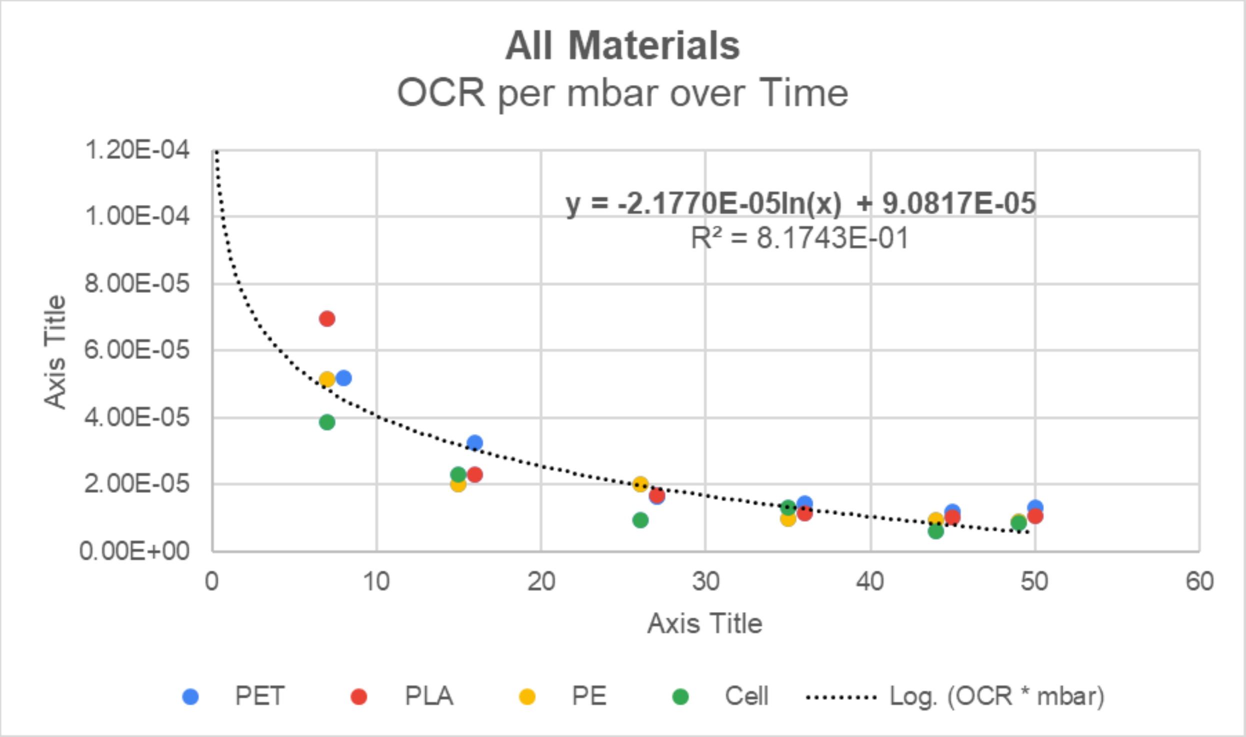


Figure 4.25: Oxygen Concentration per Oxygen Concentration over Time

Figure 4.25 shows the OCR per millibar of oxygen in the headspace ($OCR_{mbar, HS}$) of each material over time. The decrease in $OCR_{mbar, HS}$ may be attributed to a combination of moisture migration, non-linear reaction rate orders, and a reduction in the concentration of oxidizing compounds. These factors are discussed in section 5.3.

The combined effect of these influences is enough to make an impact on the final predicted shelf. The $OCR_{mbar, HS}$ at 10 days is 5.30E-05, while at 50 days it is 1.04 E-05.

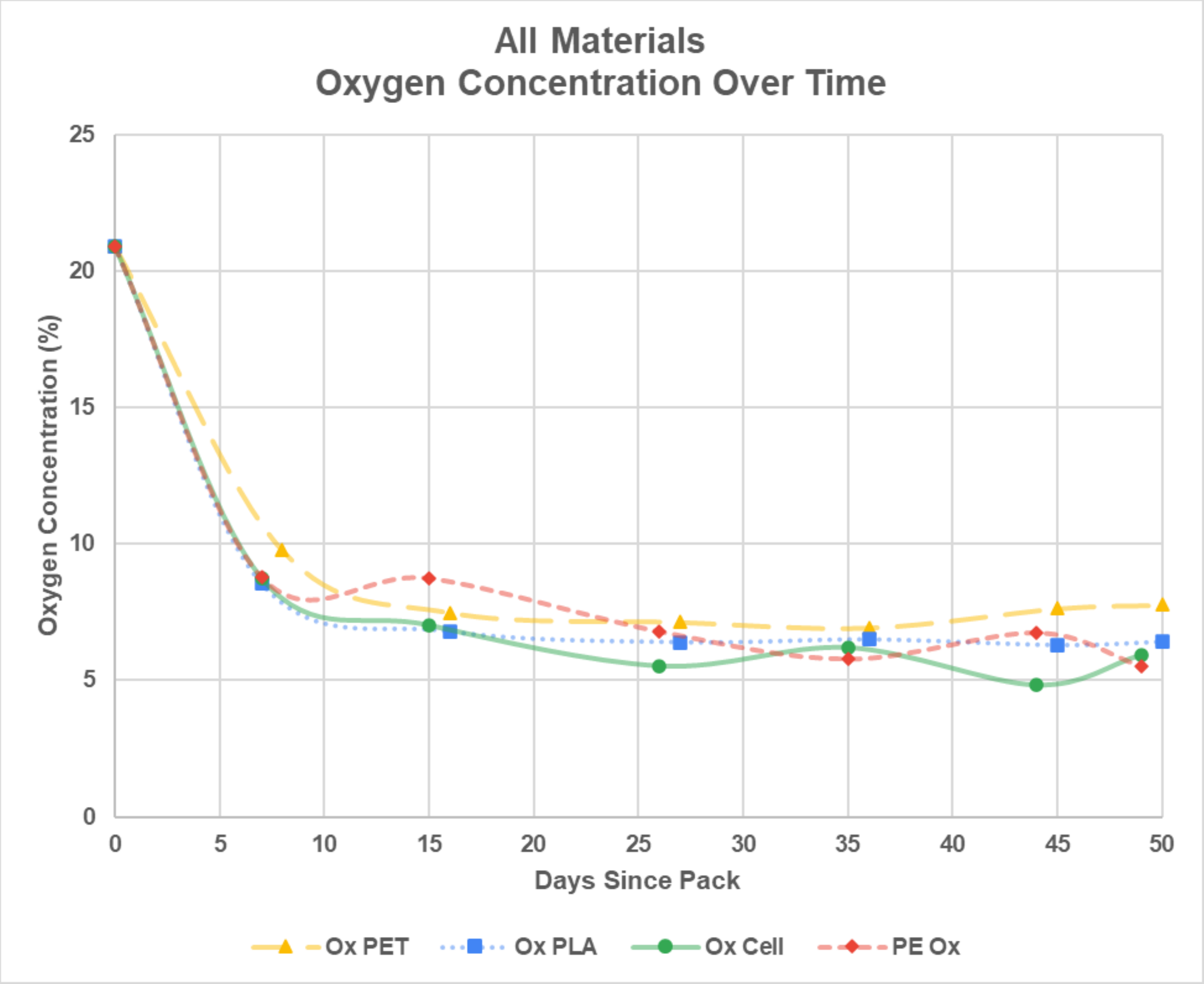


Figure 4.26 Average Oxygen Concentration over Time of All Materials

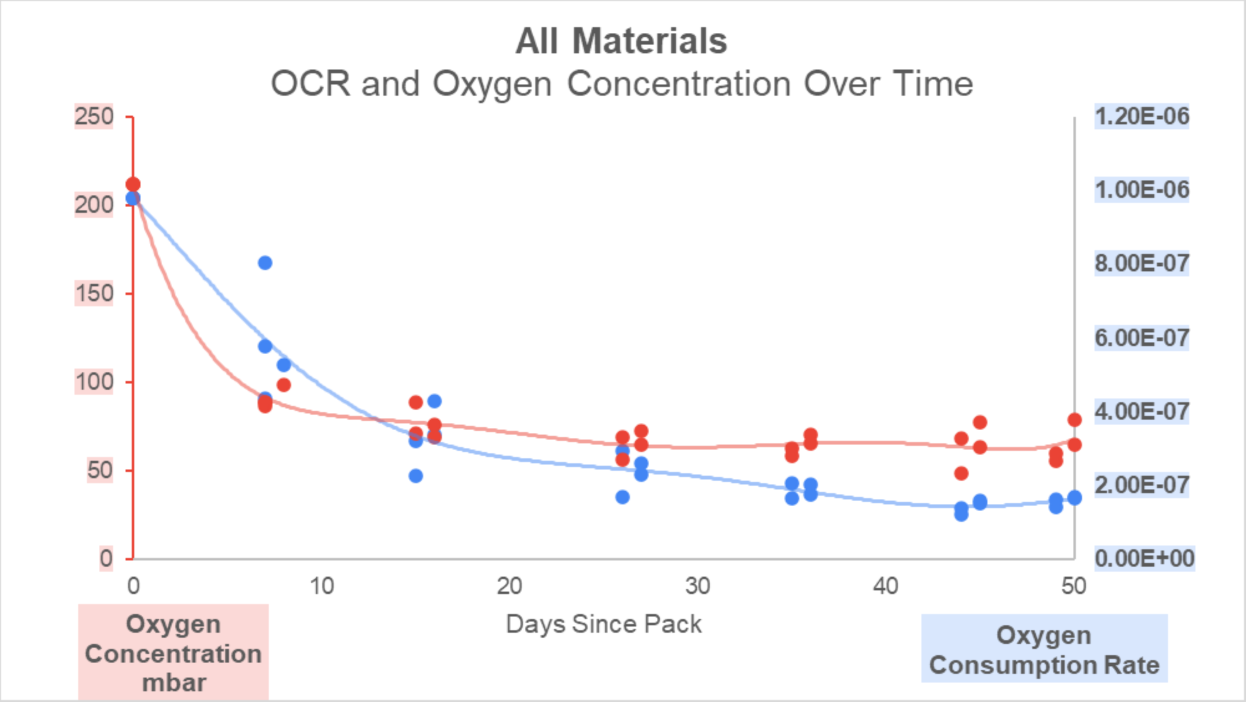


Figure 4.27: Average Oxygen Consumption Rate and Oxygen Concentration Over Time of All Materials

Figure 4.26 shows the concentration of oxygen in the headspace of each type of package over time. Figure 4.27 shows both the oxygen concentration and the oxygen consumption rate. Regardless of initial headspace volume, each set of pouches dropped quickly to about 90 mbar oxygen after 1 week and 65 mbar after 7 weeks. This is due to the first order rate law driving higher oxygen concentration pouches to oxidize more quickly than lower oxygen concentration pouches, as shown in Figure 4.28.

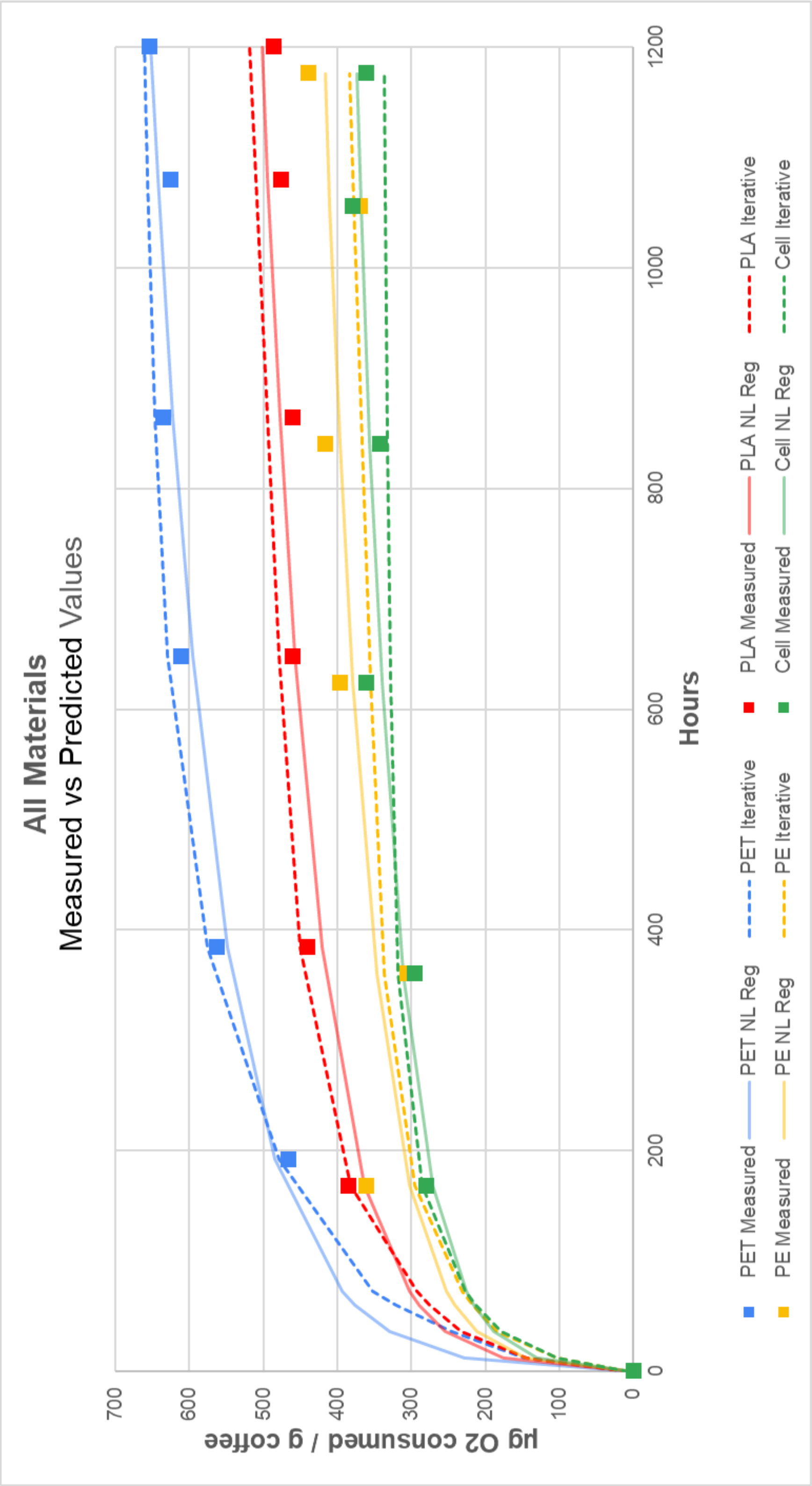


Figure 4.28: Measured and Predicted Shelf-Life Values for All Materials, Excluding Paper

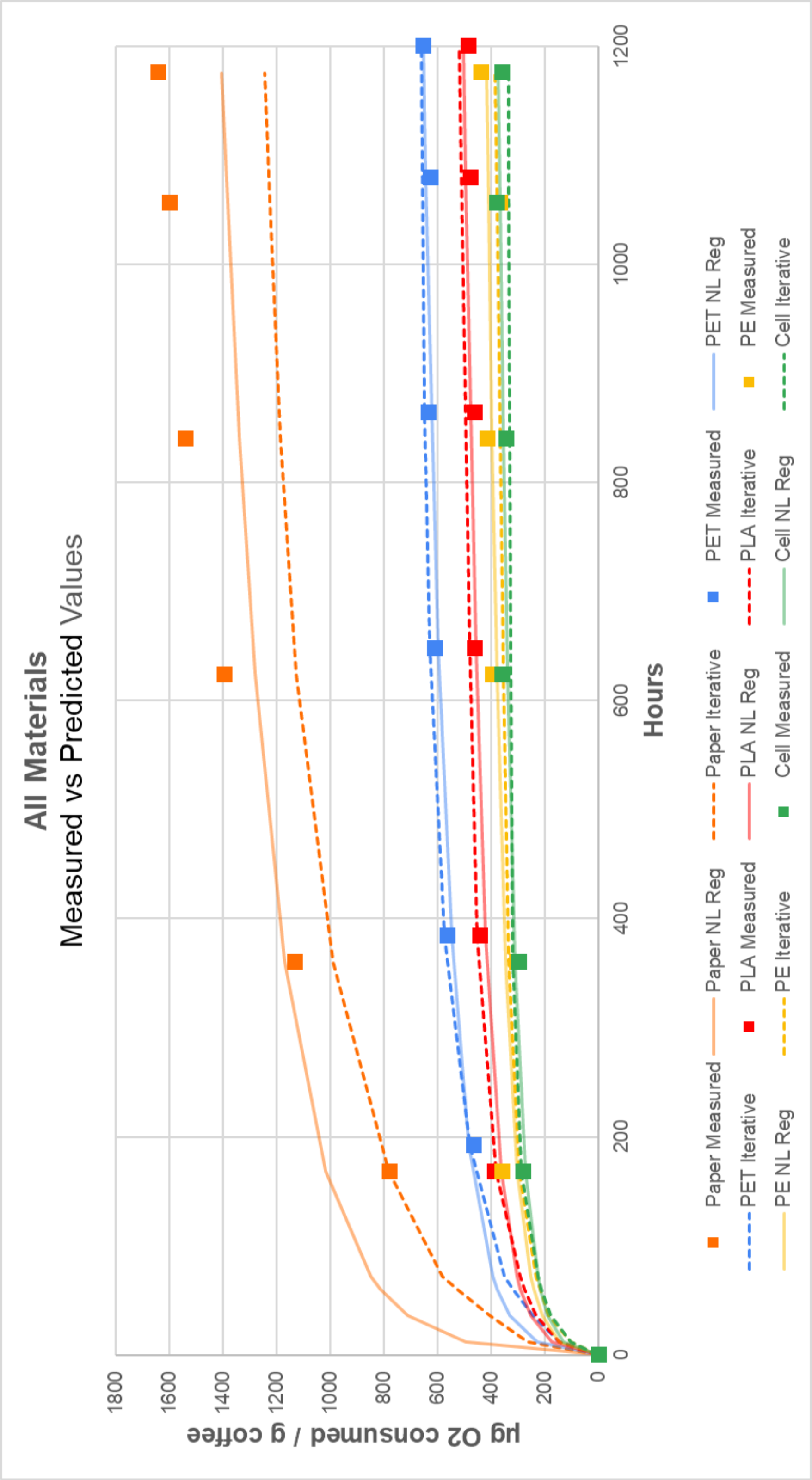


Figure 4.29: Measured and Predicted Shelf-Life Values for All Materials, Including Paper

Material	**Low Rigor** (300 µg O_2 / g coffee)	**Medium Rigor** (225 µg O_2 / g coffee)	**High Rigor** (150 µg O_2 / g coffee)
mPET	497	283	69
mcellophane	545	309	72
mPLA	208	126	37
mPE	221	130	38
Paper	332	192	51

Table 4.6 Expected Shelf Life (Days) of Coffee Systems at Low, Medium, and High Rigor

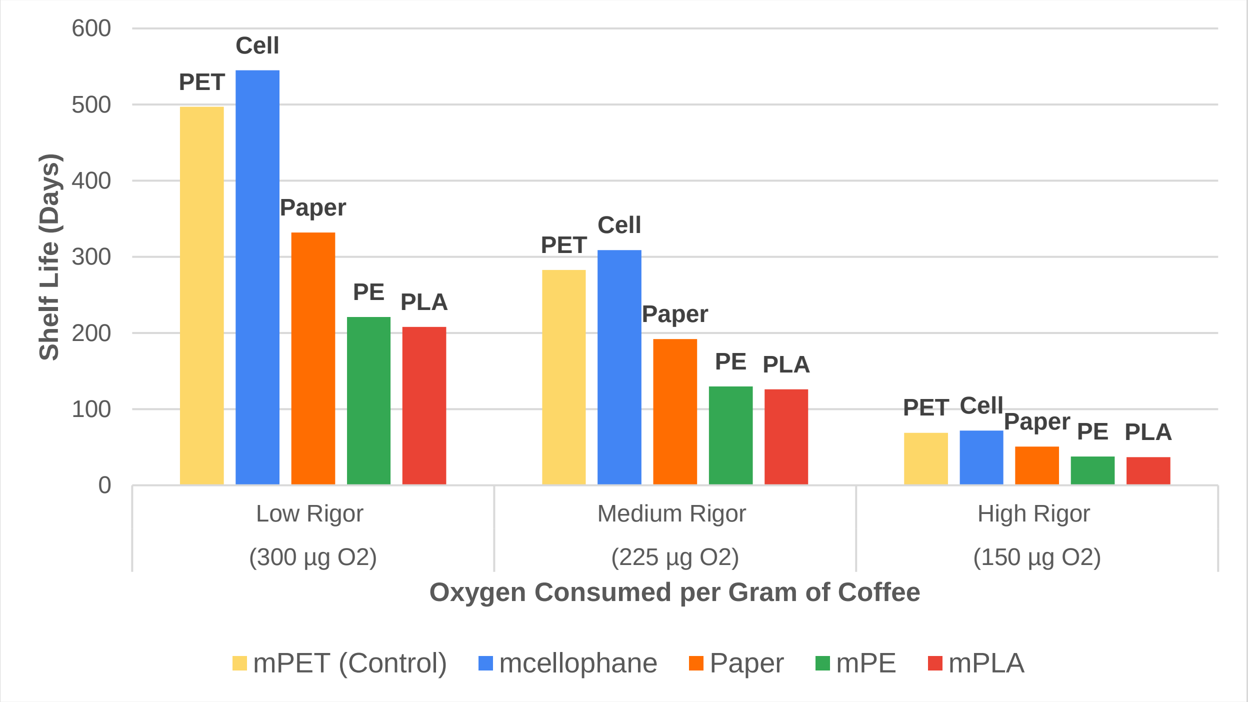


Figure 4.30 Expected Shelf Life (Days) of Coffee Systems at Low, Medium, and High Rigor

Table 4.6 and Figure 4.30 show the expected shelf life at a low, medium and high degree of rigor for coffee packaged as described in section 3.7. No systems were capable of making a six-month shelf life claim using a high rigor end of life condition. Six-month label claims could be made at medium rigor for the mPET and mcellophane packages, and conditionally for the paper packaging- see section 5.5 for discussion. The mPET, mcellophane, mPLA, and mPE packages, and conditionally the paper package, could claim a six-month shelf life at a low rigor.

CHAPTER FIVE

FURTHER DISCUSSION

5.1 Discussion of Results

The data shown above demonstrates the oxygen uptake and carbon dioxide release characteristics of coffee over time. The OCR of this coffee was 9.80E-07 g_{O2} / g_{coffee} / day / mbar, a value which aligns with previous literature (Witik, 2019; Cardelli-Friere 2004; Yeretzian, 2017). From the above data it is clear that the initial concentration of oxygen in the headspace is the largest factor in determining shelf life, as has been previously reported (Witik 2019, Cardelli-Friere 2004, Yeretzian, 2017). It can also be seen that moisture has a moderate effect on OCR, and that temperature has a small effect on the OCR with Q_{10} numbers of 1.161 and 1.469 respectively. These numbers match what has been shown in previous studies (Anese, 2006). OCR was found to roughly fit a first order reaction rate with respect to oxygen, though this rate decreased over time. Each gram of coffee released between 1.04 and 1.86 on average, values which align with previous studies (Shimoni, 2007). Carbon dioxide release was found to be highly variable from sample to sample, generating a P-value of less than 0.05 in a repeated measures ANOVA. This is likely due to human error during the grinding and packaging processes. An iterative shelf life modeling system was created and found to accurately predict the shelf life of coffee within the normal parameters of oxygen uptake for the mPET, mcellophane, mPLA, and mPE packages. The shelf life predictions for the paper packaging diverged from measured data and so the model was deemed inappropriate for low barrier value packaging systems. When a “real-world” small producer coffee system was modeled with the iterative calculations, none of the selected materials were able to generate shelf lives of 180 days or more at a high level of sensory rigor (less than 150 µg O_2 consumed per gram of coffee).

mPET, mcellophane, and conditionally paper were able to sustain a shelf life of 180 days or more at a medium level of sensory rigor (less than 225 µg O_2 consumed per gram of coffee). All materials were able to sustain a 6-month shelf life at a low level of sensory rigor (less than 300 µg O_2 consumed per gram of coffee).

5.1 Statistically significant difference in CO2 levels

The apparent statistically significant effect of packaging type on the milliliters of CO_2 released could have several explanations. The most probable is simply due to human error during the packaging of coffee. In order to achieve an efficient packaging process, 10 pouches were prepared and filled at a time before all being sealed together. This entire process took only a few minutes, it is certain that some pouches degassed more than others before sealing. In addition, some iterations of this process were slower than others, leading to additional variation in initial CO_2 concentrations.

Another possibility for the discrepancy in CO_2 release is that some packages had poor seals, allowing CO_2 to escape. This is unlikely as each package was manually observed for leaks before sampling. This is not true for paper, which was known to have leaks. It is possible that the difference in average headspace sizes caused an overpressure effect which discouraged $CO_{2,}$ release. This is unlikely because the pouches did not feel as though they were significantly pressurized, and because the nitrogen flushed samples did not produce less CO_2 than the non-MAP samples.

5.2 CO_2 Release disrupts STP

It is probable that the release of CO_2 into sealed pouches increased the internal pressure of these pouches. In theory, this deviation from STP conditions could result in incorrect calculations. However, the increase in internal pressure was assumed to be relatively small as the sides of the pouches were loose and able to be deformed easily. Thus no transformation of the data to STP conditions was performed before calculations were done.

5.3 Moisture Migration Confounds OCR

During the earliest hours of this experiment, a higher than expected OCR was observed. This value quickly drops to match the anticipated value. The PET samples demonstrated this trend more pronouncedly than did other groups. Witik et al noted the same phenomenon in their work and hypothesized that this was due to the moisture migration of water from the outside to the inside of the coffee bed. In their words, "The apparent aw of [recently packed coffee pouches], which were shortly exposed to moist air, was significantly higher than the equilibrium aw, which was shown to take hours to reach." (Witik, 2019). After the coffee beans were removed from the freezer and allowed to rise to ambient temperature, the PET samples were packed first. It is possible that these beans were still slightly cooler than room temperature and so absorbed moisture from the air more quickly than did the other samples, thereby increasing the initial OCR.

5.4 Moisture Sorption Isotherm

During the development of a moisture sorption isotherm for this product, Aw values of 0.010, 0.225, 0.430, 0.540, 0.750, 0.850, 0.920 were captured. This means that the initial Aw value of 0.1184 falls in a sizable gap between the first and second data points. It is probable that if an inflection point were to be observed, it would be between these two values. However, because a higher R^2 value is achieved through curve fitting using an exponential equation than a third degree polynomial, and because the literature suggests a type III BET curve (exponential), it is likely that this inflection point does not exist or does not impact modeling outcomes.

Additionally, although a moisture sorption isotherm was performed to develop this model, the author does not believe it is necessary to characterize other products. The literature has shown rather consistent moisture uptake behavior across a variety of coffee varieties and roast levels, and so these values can be safely estimated. One such estimation is given in Witik, 2019.

5.5 High Moisture Testing on Paper Structure

The actual and theoretical consumption characteristics of coffee in the paper pouches were quite different, with the theoretical values of oxygen consumption being significantly lower than expected. One reason for this may be the way in which barrier values were calculated for this study. Although paper structure barrier values are usually taken via TAPPI standards, polymer structure barrier values are usually taken via ASTM standards. The barrier values used for the paper structure in this study were calculated via ASTM methods for consistency across products. However, this may have misrepresented the actual values demonstrated by the pouch during testing. For these reasons, any calculated results from the paper system should be viewed with a lower level of confidence than other packages. This is why the paper packaging was given only a conditional 6-month shelf life at medium and low rigors in section 4.4.

5.6 Q10 light limitation

It is well known that light can drive oxidative reactions in food systems (Labuza, 2009). During the Q_{10} experiment performed in this study, some sample sets were stored in rooms with overhead lights while other samples were stored in dark temperature controlled chambers. Although this is acknowledged as a potential confounding variable, the author believes it is unlikely to have a significant impact.

5.7 Volume of packs

During the headspace volume determination, it was found that the paper pouches could not be measured via the Archimedes principle without being destroyed. This was mitigated by destructively testing several pouches initially and estimating headspace values based on the increases in other pouches after this time.

5.8 Oxygen Consumption Rate per Oxygen Concentration Decreases over Time

The decrease in OCR per millibar over time may be explained in several ways. First, as discussed above, the ingress of moisture from the outside layer to the inside of the coffee grounds likely contributes to a higher than expected OCR at a given oxygen concentration and moisture content. This may contribute to the sharp decrease in OCR seen in the first 10 days. It is also possible that the reaction rate of coffee oxidation, with respect to oxygen, is not purely first order. This can be seen when examining a graph displaying the OCR of coffee at various concentrations of oxygen (as in figure 4.24). Although this data is better fitted to a linear regression than an exponential or logarithmic regression, there is an observable trend towards higher than calculated OCR values at higher oxygen concentrations (~100 mbar). A third reason for the decrease in OCR per millibar oxygen over time could be due to the decreased availability of lipids and other oxidizers over time. If enough of these compounds oxidize, it is possible that they could become the rate limiting factor in this system. However, the similarity in OCR decreases between the mPET system (634 µg O_2 consumed after 50 days) and mcellophane (373 µg O_2 consumed after 50 days) suggests that this is not the case.

5.9 Recommendations

Based on the results of this study, metallized cellophane may be a good choice for producers looking to package roasted and ground coffee with a bio-based material. Further considerations would need to be made concerning cost, printability, and practical waste stream considerations.

CHAPTER SIX

CONCLUSIONS

6.1 Conclusions

The oxygen consumption characteristics of coffee was observed across five materials, namely mPET, mPLA, mPE, and mcellophane, and paper. A shelf life model was developed which captured the behavior of coffee in each environment and accurately predicted the end of life values for all materials except paper. It was shown that moisture and the partial pressure of oxygen have the greatest effects on oxygen uptake, and that these values change in their degree of influence over time. The oxygen transmission rate of the packaging materials was shown to highly influence the estimated shelf life. The control material (mPET) and mcellophane were generally found to be more suitable for protecting RG coffee than mPLA and mPE.

6.2 Future Work

6.1.1 Supply Chain Modeling

In order to better simulate packages moving through a supply chain, procedures such as temperature abuse or repeated flex testing (Gelboflex) are sometimes used. A follow up study examining the effect of these factors on the efficacy of various materials could be useful.

6.1.2 Correlation of Oxygen Consumption and Shelf Life for Specialty Grade Coffee

With the rise of specialty grade coffee, more work is needed to ensure that other factors such as non-oxidative reactions will not result in unacceptable coffee sooner than expected. Of particular usefulness would be a study which conducted weekly sensory analysis of specialty grade coffee while closely following total oxygen consumption.

APPENDICES

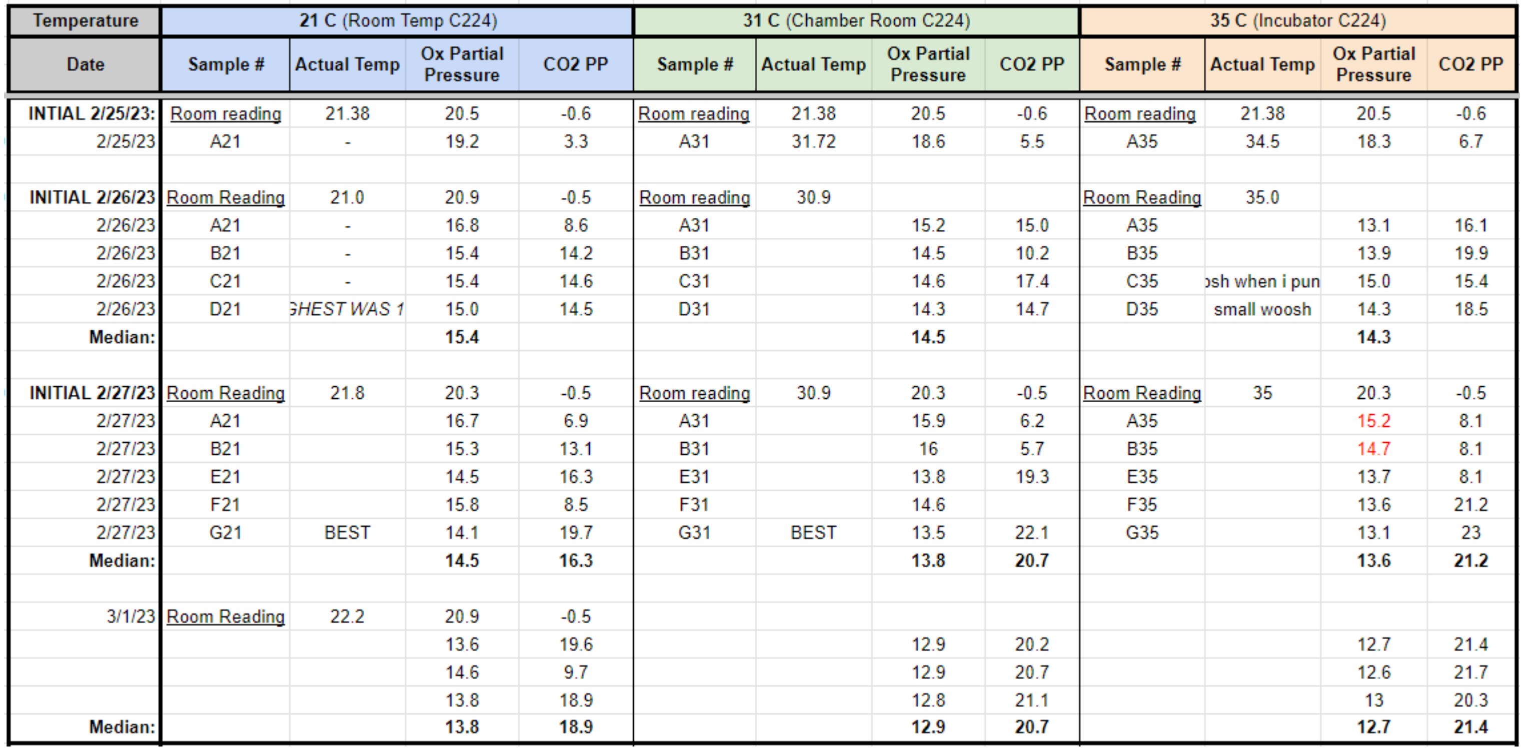
APENDIX A

Heat Seal Parameters

Material	Heat (Fº)	Dwell	Pressure
mPET	285	3.5	40
mPE	290	2	60
mcellophane	290	2	60
mPLA	290	2	40
Paper	300	3.5	60

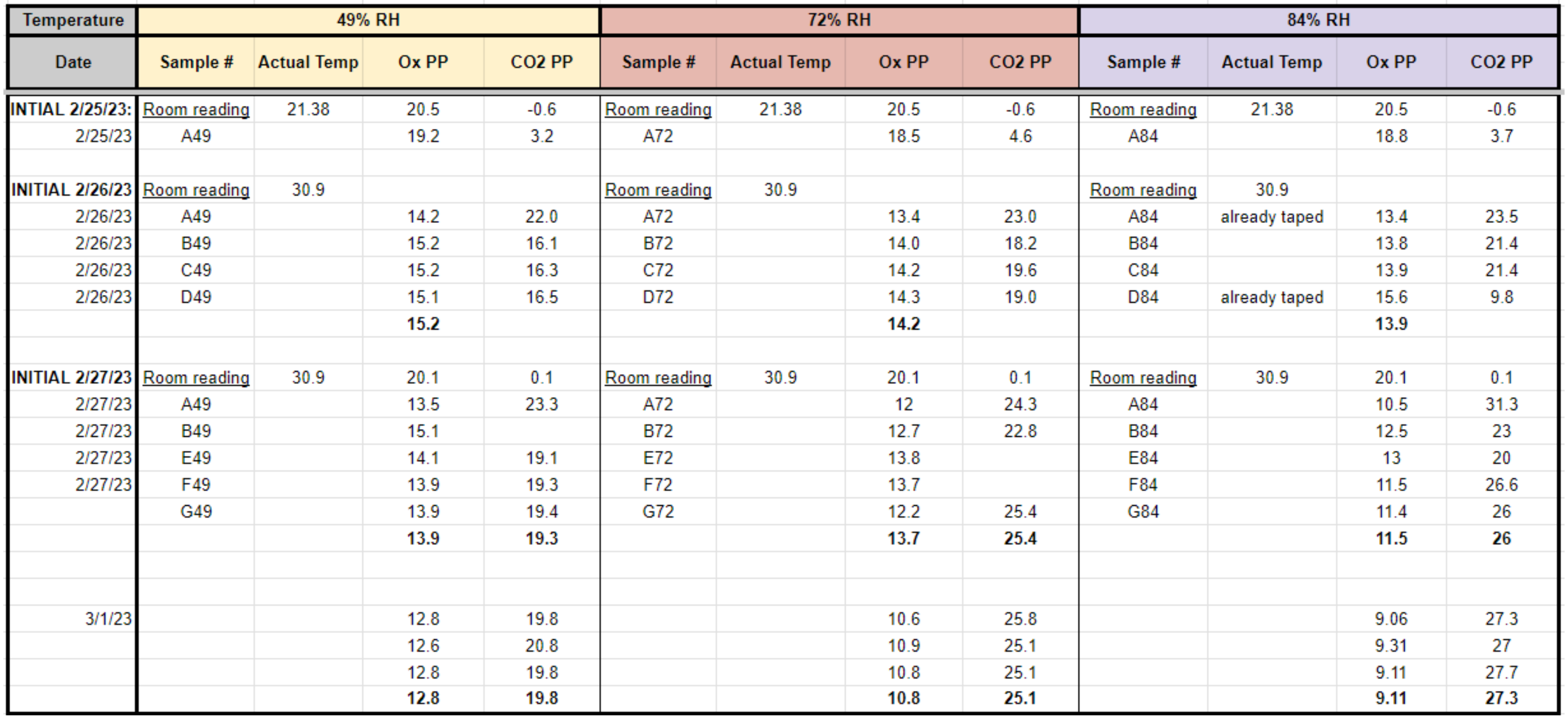
APENDIX B

Raw Data Q10 (1/2)



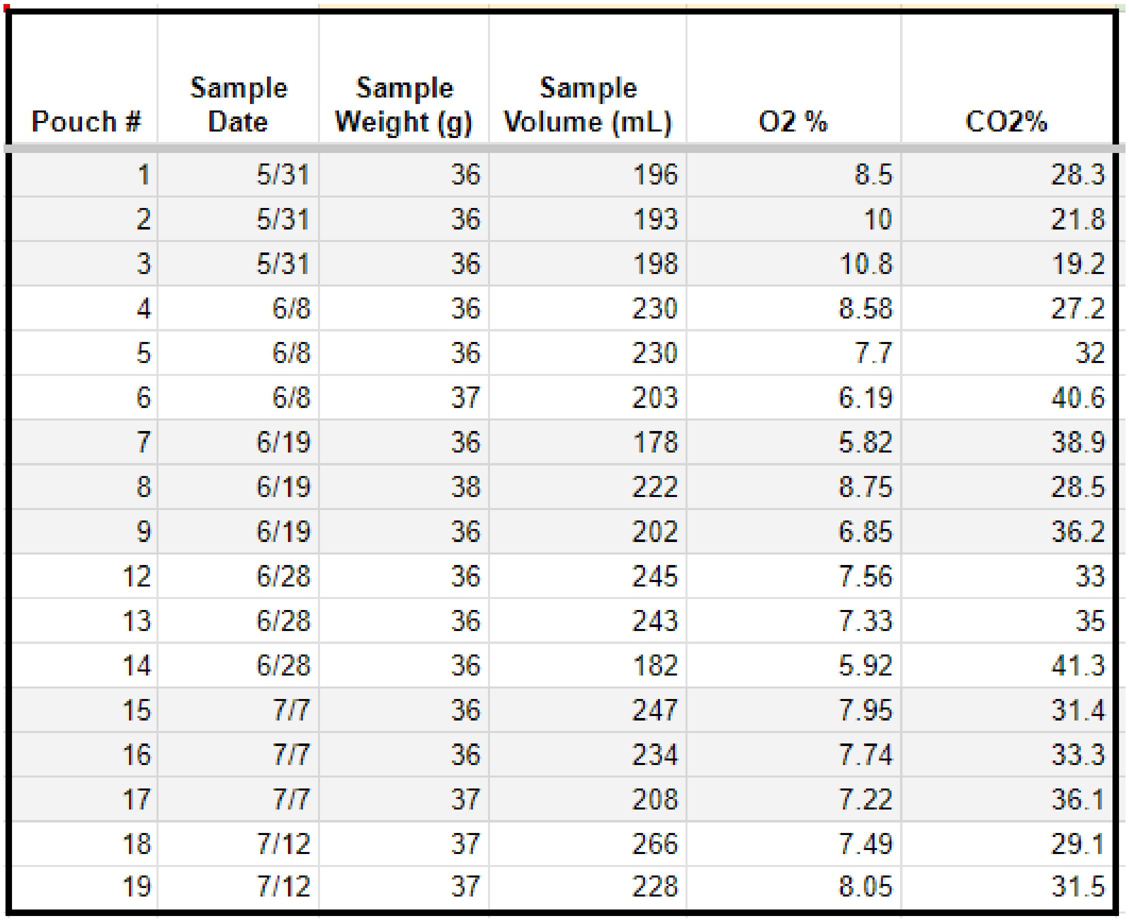
Temperature	21 C (Room Temp C224)				31 C (Chamber Room C224)				35 C (Incubator C224)			
Date	Sample #	Actual Temp	Ox Partial Pressure	CO2 PP	Sample #	Actual Temp	Ox Partial Pressure	CO2 PP	Sample #	Actual Temp	Ox Partial Pressure	CO2 PP
INTIAL 2/25/23:	Room reading	21.38	20.5	-0.6	Room reading	21.38	20.5	-0.6	Room reading	21.38	20.5	-0.6
2/25/23	A21	-	19.2	3.3	A31	31.72	18.6	5.5	A35	34.5	18.3	6.7
INITIAL 2/26/23	Room Reading	21.0	20.9	-0.5	Room reading	30.9			Room Reading	35.0		
2/26/23	A21	-	16.8	8.6	A31		15.2	15.0	A35		13.1	16.1
2/26/23	B21	-	15.4	14.2	B31		14.5	10.2	B35		13.9	19.9
2/26/23	C21	-	15.4	14.6	C31		14.6	17.4	C35	ɔsh when i pun	15.0	15.4
2/26/23	D21	*ƷHEST WAS 1*	15.0	14.5	D31		14.3	14.7	D35	small woosh	14.3	18.5
Median:			**15.4**				**14.5**				**14.3**	
INITIAL 2/27/23	Room Reading	21.8	20.3	-0.5	Room reading	30.9	20.3	-0.5	Room Reading	35	20.3	-0.5
2/27/23	A21		16.7	6.9	A31		15.9	6.2	A35		15.2	8.1
2/27/23	B21		15.3	13.1	B31		16	5.7	B35		14.7	8.1
2/27/23	E21		14.5	16.3	E31		13.8	19.3	E35		13.7	8.1
2/27/23	F21		15.8	8.5	F31		14.6		F35		13.6	21.2
2/27/23	G21	BEST	14.1	19.7	G31	BEST	13.5	22.1	G35		13.1	23
Median:			**14.5**	**16.3**			**13.8**	**20.7**			**13.6**	**21.2**
3/1/23	Room Reading	22.2	20.9	-0.5								
			13.6	19.6			12.9	20.2			12.7	21.4
			14.6	9.7			12.9	20.7			12.6	21.7
			13.8	18.9			12.8	21.1			13	20.3
Median:			**13.8**	**18.9**			**12.9**	**20.7**			**12.7**	**21.4**

Raw Data Q_{10} (2/2)



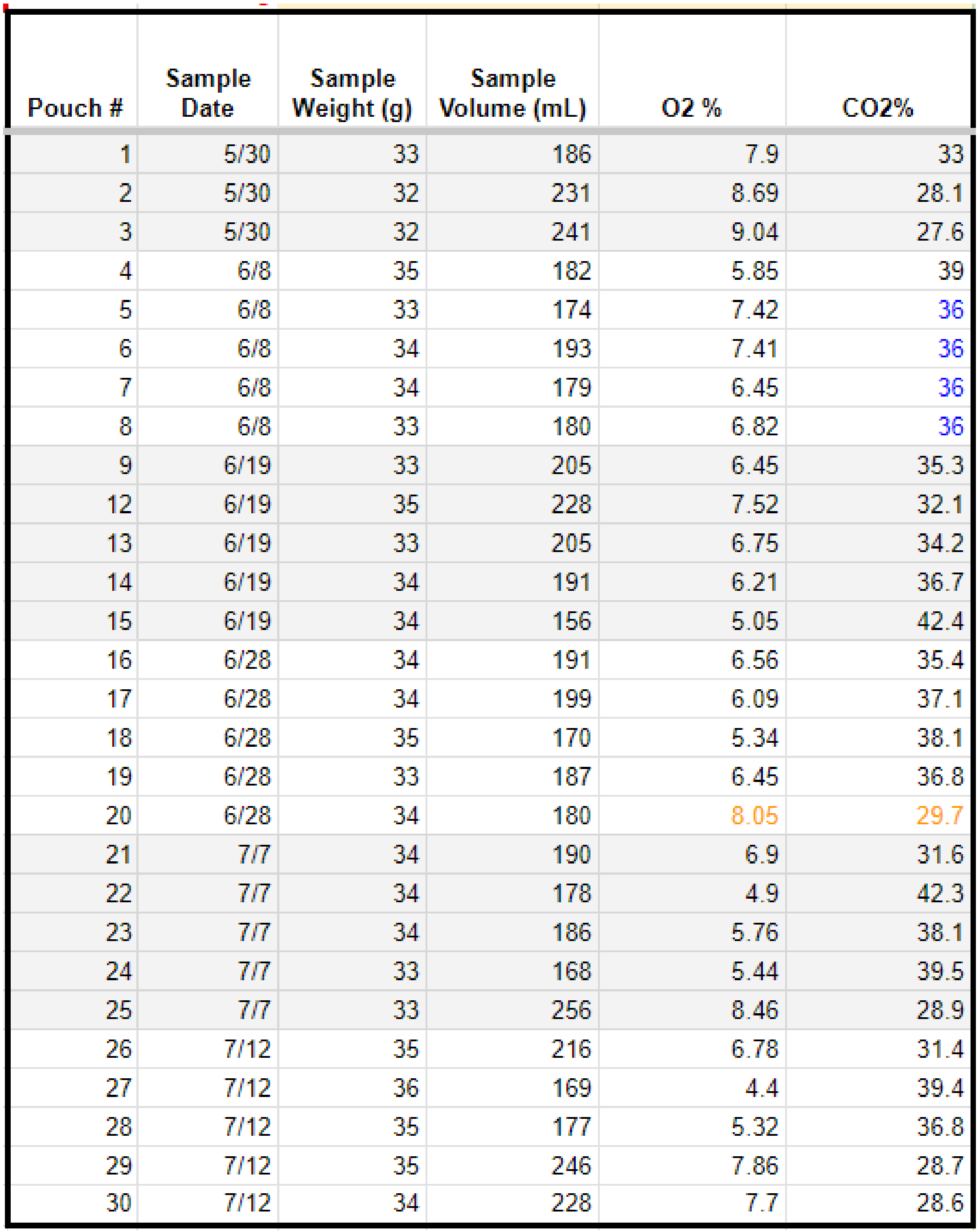
Temperature	49% RH				72% RH				84% RH			
Date	Sample #	Actual Temp	Ox PP	CO2 PP	Sample #	Actual Temp	Ox PP	CO2 PP	Sample #	Actual Temp	Ox PP	CO2 PP
INTIAL 2/25/23:	Room reading	21.38	20.5	-0.6	Room reading	21.38	20.5	-0.6	Room reading	21.38	20.5	-0.6
2/25/23	A49		19.2	3.2	A72		18.5	4.6	A84		18.8	3.7
INITIAL 2/26/23	Room reading	30.9			Room reading	30.9			Room reading	30.9		
2/26/23	A49		14.2	22.0	A72		13.4	23.0	A84	already taped	13.4	23.5
2/26/23	B49		15.2	16.1	B72		14.0	18.2	B84		13.8	21.4
2/26/23	C49		15.2	16.3	C72		14.2	19.6	C84		13.9	21.4
2/26/23	D49		15.1	16.5	D72		14.3	19.0	D84	already taped	15.6	9.8
			15.2				**14.2**				**13.9**	
INITIAL 2/27/23	Room reading	30.9	20.1	0.1	Room reading	30.9	20.1	0.1	Room reading	30.9	20.1	0.1
2/27/23	A49		13.5	23.3	A72		12	24.3	A84		10.5	31.3
2/27/23	B49		15.1		B72		12.7	22.8	B84		12.5	23
2/27/23	E49		14.1	19.1	E72		13.8		E84		13	20
2/27/23	F49		13.9	19.3	F72		13.7		F84		11.5	26.6
	G49		13.9	19.4	G72		12.2	25.4	G84		11.4	26
			13.9	**19.3**			**13.7**	**25.4**			**11.5**	**26**
3/1/23			12.8	19.8			10.6	25.8			9.06	27.3
			12.6	20.8			10.9	25.1			9.31	27
			12.8	19.8			10.8	25.1			9.11	27.7
			12.8	**19.8**			**10.8**	**25.1**			**9.11**	**27.3**

Raw Data (mPET Shelf Life)



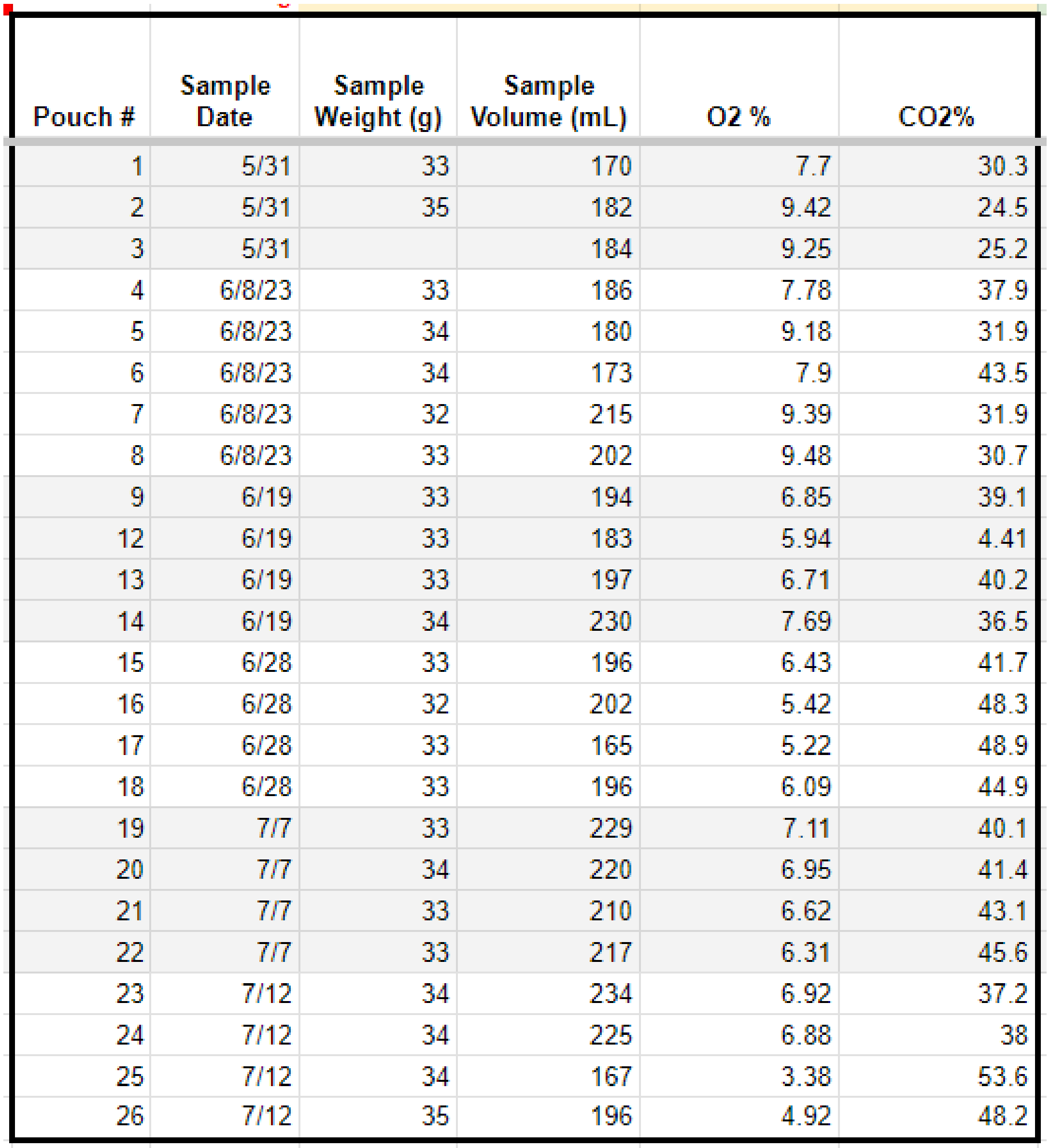
Pouch #	Sample Date	Sample Weight (g)	Sample Volume (mL)	O2 %	CO2%
1	5/31	36	196	8.5	28.3
2	5/31	36	193	10	21.8
3	5/31	36	198	10.8	19.2
4	6/8	36	230	8.58	27.2
5	6/8	36	230	7.7	32
6	6/8	37	203	6.19	40.6
7	6/19	36	178	5.82	38.9
8	6/19	38	222	8.75	28.5
9	6/19	36	202	6.85	36.2
12	6/28	36	245	7.56	33
13	6/28	36	243	7.33	35
14	6/28	36	182	5.92	41.3
15	7/7	36	247	7.95	31.4
16	7/7	36	234	7.74	33.3
17	7/7	37	208	7.22	36.1
18	7/12	37	266	7.49	29.1
19	7/12	37	228	8.05	31.5

Raw Data (mPLA Shelf Life)



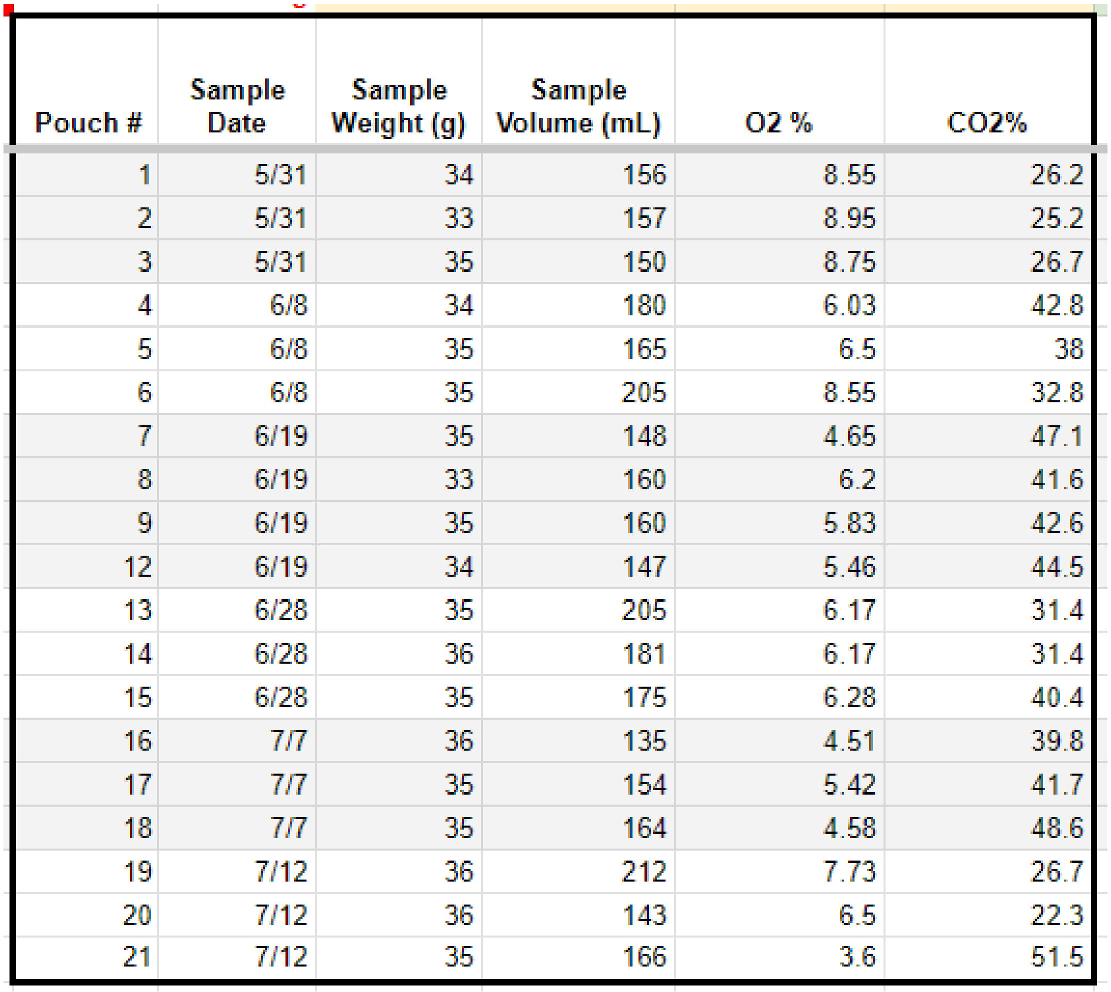
Pouch #	Sample Date	Sample Weight (g)	Sample Volume (mL)	O2 %	CO2%
1	5/30	33	186	7.9	33
2	5/30	32	231	8.69	28.1
3	5/30	32	241	9.04	27.6
4	6/8	35	182	5.85	39
5	6/8	33	174	7.42	36
6	6/8	34	193	7.41	36
7	6/8	34	179	6.45	36
8	6/8	33	180	6.82	36
9	6/19	33	205	6.45	35.3
12	6/19	35	228	7.52	32.1
13	6/19	33	205	6.75	34.2
14	6/19	34	191	6.21	36.7
15	6/19	34	156	5.05	42.4
16	6/28	34	191	6.56	35.4
17	6/28	34	199	6.09	37.1
18	6/28	35	170	5.34	38.1
19	6/28	33	187	6.45	36.8
20	6/28	34	180	8.05	29.7
21	7/7	34	190	6.9	31.6
22	7/7	34	178	4.9	42.3
23	7/7	34	186	5.76	38.1
24	7/7	33	168	5.44	39.5
25	7/7	33	256	8.46	28.9
26	7/12	35	216	6.78	31.4
27	7/12	36	169	4.4	39.4
28	7/12	35	177	5.32	36.8
29	7/12	35	246	7.86	28.7
30	7/12	34	228	7.7	28.6

Raw Data (mPE Shelf Life)



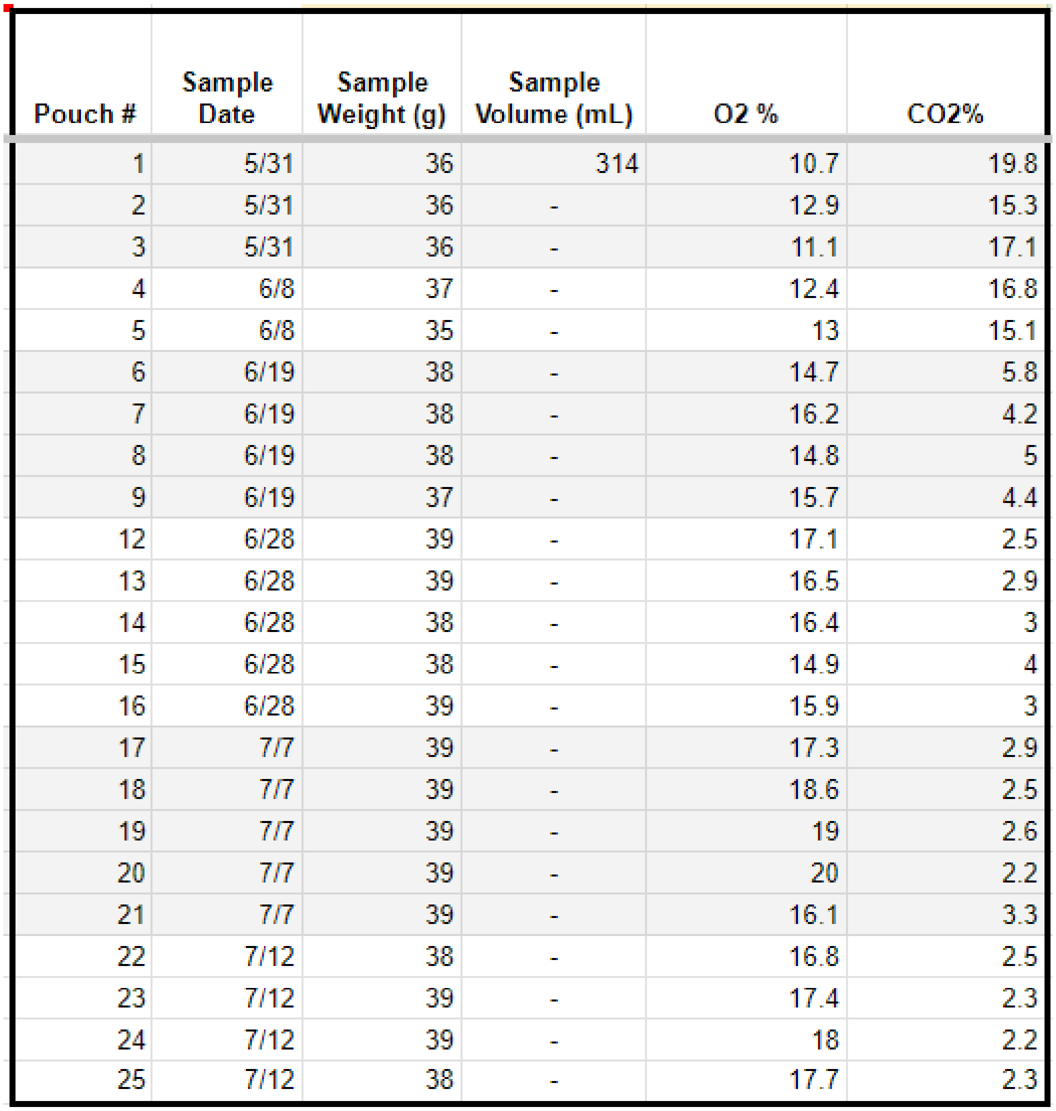
Pouch #	Sample Date	Sample Weight (g)	Sample Volume (mL)	O2 %	CO2%
1	5/31	33	170	7.7	30.3
2	5/31	35	182	9.42	24.5
3	5/31		184	9.25	25.2
4	6/8/23	33	186	7.78	37.9
5	6/8/23	34	180	9.18	31.9
6	6/8/23	34	173	7.9	43.5
7	6/8/23	32	215	9.39	31.9
8	6/8/23	33	202	9.48	30.7
9	6/19	33	194	6.85	39.1
12	6/19	33	183	5.94	4.41
13	6/19	33	197	6.71	40.2
14	6/19	34	230	7.69	36.5
15	6/28	33	196	6.43	41.7
16	6/28	32	202	5.42	48.3
17	6/28	33	165	5.22	48.9
18	6/28	33	196	6.09	44.9
19	7/7	33	229	7.11	40.1
20	7/7	34	220	6.95	41.4
21	7/7	33	210	6.62	43.1
22	7/7	33	217	6.31	45.6
23	7/12	34	234	6.92	37.2
24	7/12	34	225	6.88	38
25	7/12	34	167	3.38	53.6
26	7/12	35	196	4.92	48.2

Raw Data (mcellophane Shelf Life)



Pouch #	Sample Date	Sample Weight (g)	Sample Volume (mL)	O2 %	CO2%
1	5/31	34	156	8.55	26.2
2	5/31	33	157	8.95	25.2
3	5/31	35	150	8.75	26.7
4	6/8	34	180	6.03	42.8
5	6/8	35	165	6.5	38
6	6/8	35	205	8.55	32.8
7	6/19	35	148	4.65	47.1
8	6/19	33	160	6.2	41.6
9	6/19	35	160	5.83	42.6
12	6/19	34	147	5.46	44.5
13	6/28	35	205	6.17	31.4
14	6/28	36	181	6.17	31.4
15	6/28	35	175	6.28	40.4
16	7/7	36	135	4.51	39.8
17	7/7	35	154	5.42	41.7
18	7/7	35	164	4.58	48.6
19	7/12	36	212	7.73	26.7
20	7/12	36	143	6.5	22.3
21	7/12	35	166	3.6	51.5

Raw Data (Paper Shelf Life)



Pouch #	Sample Date	Sample Weight (g)	Sample Volume (mL)	O2 %	CO2%
1	5/31	36	314	10.7	19.8
2	5/31	36	-	12.9	15.3
3	5/31	36	-	11.1	17.1
4	6/8	37	-	12.4	16.8
5	6/8	35	-	13	15.1
6	6/19	38	-	14.7	5.8
7	6/19	38	-	16.2	4.2
8	6/19	38	-	14.8	5
9	6/19	37	-	15.7	4.4
12	6/28	39	-	17.1	2.5
13	6/28	39	-	16.5	2.9
14	6/28	38	-	16.4	3
15	6/28	38	-	14.9	4
16	6/28	39	-	15.9	3
17	7/7	39	-	17.3	2.9
18	7/7	39	-	18.6	2.5
19	7/7	39	-	19	2.6
20	7/7	39	-	20	2.2
21	7/7	39	-	16.1	3.3
22	7/12	38	-	16.8	2.5
23	7/12	39	-	17.4	2.3
24	7/12	39	-	18	2.2
25	7/12	38	-	17.7	2.3

LITERATURE CITED

1. Drobny, J. G. (2014). Processing methods applicable to thermoplastic elastomers. Handbook of Thermoplastic Elastomers

2. Association of Plastic Manufacturers. (2018). Plastics- The facts 2017. Brussels, Belgium: Association of Plastic Manufacturers.

3. Association of Plastic Manufacturers. (2017). Polyethylene Furanoate (PEF) - The Rising Star Amongst Today's Bioplastics. Brussels, Belgium: Association of Plastic Manufacturers.

4. Synvina. (2018). Blow moulding PEF bottle blowing - Synvina. Retrieved from Synvina website.

5. Ava-Biochem. (2019). Pairelox - paired electrochemical oxidation process for feasible industrial production of the crucial FDCA building block for the bioplastic industry. Muttenz, Switzerland: AVA-Biochem.

6. Synvina Bioplastics. (2017). Synvina receives interim approval from European PET Bottle Platform: PEF to be integrated in circular economy. Synvina News Release.

7. Lamberti, M., & Escher, F. (2007). Aluminium Foil as a Food Packaging Material in Comparison with Other Materials. Food Reviews International, 23(4), 407–433. https://doi.org/10.1080/87559120701593830

8. Robertson, G. L. (1998). *Food Packaging: Principles and Practice* (p. 130).

9. *What is Surface Energy? Formula & Definition*. (n.d.). Ossila. https://www.ossila.com/en-us/pages/a-guide-to-surface-energy

10. Robertson, G. L. (1998). Food Packaging: Principles and Practice (p. 131).

11. Muller, J., González-Martínez, C., & Chiralt, A. (2017). Combination of Poly(lactic) Acid and Starch for Biodegradable Food Packaging. Materials, 10(8), 952. https://doi.org/10.3390/ma10080952

12. Hu, Y., Daoud, W., Cheuk, K., & Lin, C. (2016). Newly Developed Techniques on Polycondensation, Ring-Opening Polymerization and Polymer Modification: Focus on Poly(Lactic Acid). Materials, 9 (3), 133. doi: 10.3390/ma9030133.

13. Auras, R., Harte, B., & Selke, S. (2004). An Overview of Polylactides as Packaging Materials. Macromolecular Bioscience, 4(9), 835–864. https://doi.org/10.1002/mabi.200400043

14. Oliveira, J. C., & Sarantopoulos, C. (1997). Mechanical Stress Resistance of Barrier Packaging Films.

15. Yeretzian, C. (2017). *Craft and Science of Coffee* (p. 348).

16. Witik, R. A., Phoutthasak, S., Collet, A., & Wyser, Y. (2019). Shelf life prediction of oxygen-sensitive products: The influence of moisture on prediction accuracy for freeze-dried coffee. Packaging Technology and Science, 32(7), 357–365. https://doi.org/10.1002/pts.2444

17. Wang, N., & Lim, L.-T. (2012). Fourier Transform Infrared and Physicochemical Analyses of Roasted Coffee. Journal of Agricultural and Food Chemistry, 60(21), 5446–5453. https://doi.org/10.1021/jf300348e

18. PITTIA, P., NICOLI, M. C., & SACCHETTI, G. (2007). EFFECT OF MOISTURE AND WATER ACTIVITY ON TEXTURAL PROPERTIES OF RAW AND ROASTED COFFEE BEANS. Journal of Texture Studies, 38(1), 116–134. https://doi.org/10.1111/j.1745-4603.2007.00089.x.

19. Agustini, S., & Yusya, M. K. (2020). The effect of packaging materials on the physicochemical stability of ground roasted coffee.

20. Aliotta, L., Seggiani, M., Lazzeri, A., Gigante, V., & Cinelli, P. (2022). A Brief Review of Poly (Butylene Succinate) (PBS) and Its Main Copolymers: Synthesis, Blends, Composites, Biodegradability, and Applications. Polymers, 14(4), 844. https://doi.org/10.3390/polym14040844

21. Mustățea, G., Ungureanu, E., & Belc, N. (2019). POLYLACTIC ACID (PLA) FOR FOOD PACKAGING APPLICATIONS – A SHORT OVERVIEW.

22. Platnieks, O., Gaidukovs, S., Kumar Thakur, V., Barkane, A., & Beluns, S. (2021). Bio-Based Poly (Butylene Succinate): Recent Progress, Challenges and Future Opportunities. European Polymer Journal, 110855. https://doi.org/10.1016/j.eurpolymj.2021.110855

23. Kim, Y. D., & Kim, S. C. (1998). Effect of chemical structure on the biodegradation of polyurethanes under composting conditions. Polymer Degradation and Stability, 62(2), 343–352. https://doi.org/10.1016/s0141-3910(98)00017-2.

24. Guerra, S., Lagazio, C., Manzocco, L., Barnabà, M., & Cappuccio, R. (2008). Risks and pitfalls of sensory data analysis for shelf life prediction: Data simulation applied to the case of coffee. LWT - Food Science and Technology, 41(10), 2070–2078. https://doi.org/10.1016/j.lwt.2008.01.011.

25. Cardelli, C., & Labuza, T. P. (2001). Application of Weibull Hazard Analysis to the Determination of the Shelf Life of Roasted and Ground Coffee. LWT - Food Science and Technology, 34(5), 273–278. https://doi.org/10.1006/fstl.2000.0732.

26. Mustățea, G., Ungureanu, E., & Belc, N. (2019). POLYLACTIC ACID (PLA) FOR FOOD PACKAGING APPLICATIONS – A SHORT OVERVIEW.

27. Tomé, L. C., Gonçalves, C., Boaventura, M., Lúcia Brandão, Mendes, A., Armando, Carlos Pascoal Neto, Gandini, A., Carmen S.R. Freire, & Marrucho, I. M. (2011). Preparation and

evaluation of the barrier properties of cellophane membranes modified with fatty acids. Carbohydrate Polymers, 83(2), 836–842. https://doi.org/10.1016/j.carbpol.2010.08.060.

28. Khanam, P. N., & AlMaadeed, M. A. A. (2015). Processing and characterization of polyethylene-based composites. Advanced Manufacturing: Polymer & Composites Science, 1(2), 63–79. https://doi.org/10.1179/2055035915y.0000000002

29. How2Recycle - How2Recycle. (2019). How2recycle.info. https://how2recycle.info/

30. Bayus, J., Ge, C., & Thorn, B. (2016). A preliminary environmental assessment of foil and metallized film centered laminates. Resources, Conservation and Recycling, 115, 31–41. https://doi.org/10.1016/j.resconrec.2016.08.024

31. Nicoli, M. C., Calligaris, S., & Manzocco, L. (2009). Shelf-Life Testing of Coffee and Related Products: Uncertainties, Pitfalls, and Perspectives. Food Engineering Reviews, 1(2), 159–168. https://doi.org/10.1007/s12393-009-9010-8.

32. Manzocco, L., Calligaris, S., Anese, M., & Nicoli, M.C. (2011). The stability and shelf life of coffee products.

33. ROSS, C. F., PECKA, K., & WELLER, K. (2006). EFFECT OF STORAGE CONDITIONS ON THE SENSORY QUALITY OF GROUND ARABICA COFFEE. Journal of Food Quality, 29(6), 596–606. https://doi.org/10.1111/j.1745-4557.2006.00093.x

34. Sunarharum, W.B., Williams, D.J., & Smyth, H.E. (2014). Complexity of coffee flavor: A compositional and sensory perspective. Food Research International, 62, 315-325.

35. Witik, R.A., Phoutthasak, S., Collet, A., & Wyser, Y. (2019). Shelf life prediction of oxygen-sensitive products: The influence of moisture on prediction accuracy for freeze-dried coffee. Packaging Technology and Science, 32, 357 - 365.

36. Hodge, J. E. (1953). Dehydrated Foods, Chemistry of Browning Reactions in Model Systems. Journal of Agricultural and Food Chemistry, 1(15), 928–943. https://doi.org/10.1021/jf60015a004

37. SHIMONI, E., & LABUZA, T. P. (2000). DEGASSING KINETICS AND SORPTION EQUILIBRIUM OF CARBON DIOXIDE IN FRESH ROASTED AND GROUND COFFEE. Journal of Food Process Engineering, 23(6), 419–436. https://doi.org/10.1111/j.1745-4530.2000.tb00524.x

38. Heiss, R., Radtke, R., Robinson, L. (1977). In Proceedings of the 14th ASIC Meeting, Colloquium on Coffee, Abidjan, 163–174.

39. Buffo, R. A., & Cardelli-Freire, C. (2004). Coffee flavour: an overview. Flavour and Fragrance Journal, 19(2), 99–104. https://doi.org/10.1002/ffj.1325

40. Hughes, S. W. (2005). Archimedes revisited: a faster, better, cheaper method of accurately measuring the volume of small objects. Physics Education, 40(5), 468–474. https://doi.org/10.1088/0031-9120/40/5/008

41. Labuza, T. P., & Dugan, L. R. (1971). Kinetics of lipid oxidation in foods. C R c Critical Reviews in Food Technology, 2(3), 355–405. https://doi.org/10.1080/10408397109527127