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THE EFFECT OF FOOD INGREDIENTS ON THE OXYGEN BARRIER PROPERTIES OF RETORT MATERIALS

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THE EFFECT OF FOOD INGREDIENTS ON THE OXYGEN
BARRIER PROPERTIES OF RETORT MATERIALS

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
Amanda Michelle Ward
August 2012

Accepted by:
Dr. Scott Whiteside, Dissertation Chair
Dr. Ronald Thomas
Dr. Duncan Darby

ABSTRACT

An unexplored area in research is addressing how retorted food ingredients interact with retort packaging's oxygen barrier. Ten common food ingredients (whey protein isolate, soy protein isolate, bovine gelatin, fish gelatin, high molecular weight fish gelatin, water, air, oil, potato starch, and hydroxypropyl methylcellulose) were assessed to find their effect on the barrier properties of CPP, PET, and high barrier commercial retort pouches. OxySense Gen III 300 and Mocon OxTran 2/21 were used to evaluate the samples. CPP pouches were first assessed with the OxTran 2/21 and indicated that treatments affected the OTR's of the film materials. However, results from the OxySense show that there is not a difference in oxygen ingress over time. Oil increased film permeability on all pouch materials tested and allowed for a higher OTR and faster oxygen ingress.

DEDICATION

I am lucky and honored to call Cathy Ward my mother who let me grow wings and become the successful and grounded woman I am today.

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CHAPTER I

INTRODUCTION

The basic functions of food packaging are containment, protection, convenience, communication, and preservation (Osborn & Jenkins, 1992). Manufacturers use metal, plastic, paper, and glass to package food. Packaging must act as an oxygen barrier when used to package many oxygen sensitive foods. Generally, less oxidation leads to longer shelf life of packaged food products (Sacharow & Griffin, 1980).

Low Acid Canned Foods (LACF) create an ideal habitat for microbial growth. The Food and Drug Administration (FDA) mandates sterilization of low acid foods before consumption (21 CFR PART 113, 2012). High pressure and temperature treatments like retort processing ensure sterilization. Sterilization, historically performed in metal cans, has migrated towards flexible plastic packaging materials. This process is very harsh on packaging materials, especially flexible packaging, and can cause oxygen barriers to diminish (Blackistone & Harper, 1995).

There are many benefits to using plastic packaging materials, however, it has its limitations. To be competitive against glass and steel cans, they must maintain their barrier properties, be temperature stable, be heat sealable, be compatible with food, and be mechanically stable (Subramanian, Srivatsa, Nirmala, & Sharma, 1986). Flexible packaging materials are typically comprised of multiple layers to achieve all of these qualities

An unexplored area in research is addressing how retorted food ingredients interact with retort packaging materials and affect the oxygen barrier of packaging

materials. In recent research performed by Dharman (2011), additional layers were observed on the inner lining of flexible packaging film after the retort process. This phenomenon occurred during the retort process and effected the measurements on oxygen permeation devices. No research has been focused on investigating the effect of food ingredients on the oxygen permeability of retortable materials via the creation of an additional biofilm layer.

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CHAPTER II

LITERATURE REVIEW

Shelf Stable Foods

Food packaging can be generalized into three categories—frozen, refrigerated, and shelf stable. Typically, frozen and refrigerated foods are minimally processed. Foods in these categories can be submerged in hot water or blanched with hot gasses or steam. This minimalizes the amount of entrapped gasses within the food and prevents further enzymatic activity that can reduce the quality of the food (Gavin & Weddid, 1995).

The Food and Drug Administration (FDA) regulates shelf stable foods according to their water activity (A_w) and acidity (pH). A_w is related to the amount of moisture available in a food. Examples of foods that have an A_w less than 0.85 include raisins and potato chips. Heat is applied to prepare the food and the water activity is reduced to a point where microorganism cannot grow, thus they do not need additional thermal processing (Gavin & Weddig, 1995).

Shelf stable foods having A_w greater than 0.85 are regulated by the FDA's CFR part 113 (2012). Figure 1 depicts the relationship between the different classifications in shelf stable foods and their respective processing. High water activity is optimal for microorganism of public health importance to grow (Blackstone & Harper, 1995). These foods must be additionally treated and/or processed to prevent their microbial growth. Shelf stable foods with high A_w greater than 0.85 are broken down according to their pH

levels into three subcategories low acid, acidified, and naturally acidic (Gavin & Weddig, 1995).

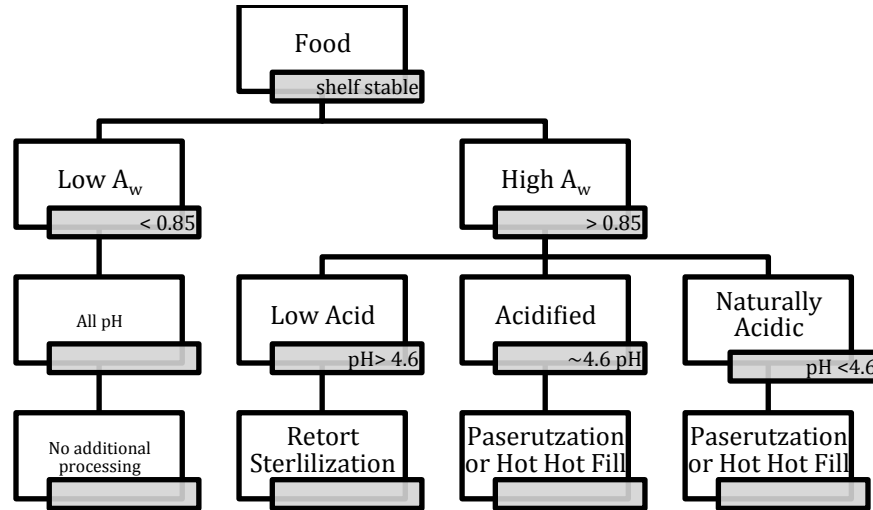


Figure 1. Relationship between A_w , pH, and processing.

Naturally acidic foods have pH values naturally below 4.6. This food category includes berries, cherries, pineapples, plums, or any food that has a pH below the 4.6 pH threshold. Acidified foods are moderately acid foods that have had extra acid added to lower the pH below 4.6. Foods that need additional acid include anything pickled or marinated like tomatoes, sweet potatoes, carrots, or any food whose pH value is adjusted to around the 4.6 threshold (Gavin & Weddig, 1995).

During processing these foods must maintain a pH level below 4.6 for up to 24 hours after processing (FDA, CFR part 113, 2012). Both acidified and naturally acidic foods can use minimal thermal processes like hotfilling or pasteurizing to limit the growth of spores and microbes (FDA, CFR part 114, 2012). These spore and microbes are typically yeasts and molds that spoil food and shorten shelf life.

Low Acid Canned Foods (LACF) are determined by the FDA (CFR part 114, 2012) to be anything but non-alcoholic beverages that have an equilibrium (24 hours after processing) pH value higher than 4.6 and a water activity above 0.85. This food category is now called Low Acid Foods (LAF), as the industry is migrating towards flexible packaging materials (Blackstone & Harper, 1995). Shelf stable foods in this category are optimal for microbial growth, therefore these foods must be thermally processed so they become commercially sterile. Thermal processing is considered to reach commercial sterility when the packaged food products are free from microorganisms of public health significance and any other microorganisms capable of reproducing in the food in non-refrigerated conditions. This is achieved when food is sealed in an airtight container and receives a sterilizing heat treatment to destroy harmful microbes and spores. Sterilization is done via a retort sterilization process.

The FDA mandates that this additional processing for LAF is necessary because of *Clostridium botulinum* (Botulism). *Clostridium botulinum* is considered of public health importance because it produces deadly toxins and can withstand a variety of climates world-wide due to its ability to form spores. It has been determined to be the direct cause of several foodborne deaths due to improperly processed foods (www.fda.gov, 2009). These deadly spores can grow in an A_w at or above 0.85 and pH above 4.6 and can survive in temperatures up to 100°C (212°F). *Clostridium botulinum* is also an anaerobic bacteria that can thrive in retort pouch conditions (low oxygen). Proper heat treatment above 100°C (212°F) is needed to effectively destroy these microorganisms (Gavin & Weddig, 1995).

Retort Process

Safety is a primary concern for consumers and manufacturers because of microorganisms, macroorganisms, and the migration of vapor, exposure to radiation, and chemical interactions within the package (Katan, 1996) can all spoil food and harm the consumer. Thermal processing, chemical treatments, or radiation can be used to ensure safety but typically, thermal processing is used.

In order for thermal processing to be successful, food must be enclosed in a container and exposed to high temperatures. The microorganisms that are harmful to humans are killed by high temperature processing and hermetically sealed in a package prevents the reentry of additional bacteria (Blackstone & Harper, 1995). The time and temperature needed for this process depends mostly on the specific food product characteristics and the package. Factors that must be considered include the product preparation methods, density, viscosity, weight, acidity, headspace, and water activity (Gavin & Weddig, 1995) in addition to the container and the type of retort used.

Retorts are the primary vessels used in thermal processing for LACF. The retort is a large pressure cooker whose temperature and pressure are precisely controlled throughout the sterilization process. The two main types of retorts are continuous and batch. In continuous retort processing, packages are filled, sealed, processed, cooled, and unloaded without stopping. Continuous retorts are only used with round rigid packages because there is a constant rolling of the containers. However, many types of batch retorts are used. Batch retorts must be loaded and unloaded before and after every process (Gavin & Weddig, 1995).

Still retorts are batch-type vessels that do not rotate or oscillate the packages inside the process vessel. Packages can either be stacked or loosely placed into various secondary containers and then placed into the system. The two types of still retorts are distinguished by their overpressure or pure steam pressure processes. In both systems, steam is initially used to purge the machine of entrapped air, allowing for even heating and faster process times (Gavin & Weddig, 1995). Steam is also the primary heat source as it condenses onto the packaging material and releases latent heat into the package (Richardson, 2001).

In pure steam still retorts, only saturated steam is used to increase the pressure and temperature within the retort. In overpressure retort system, extra pressure (steam and air) is added throughout the cycle. The overpressure prevents the deformation and rupturing of flexible containers and packaging due to heat expansion primarily during the cooling phase of the retort process (Gavin & Weddig, 1995).

Retort vessels can also agitate with discontinuous container handling, meaning the product is moving in the vessel during the retort cycle but still must be loaded before and unloaded after every retort process when the retort is not running. In this type of retort system, the packages can oscillate back-and-forth, rotate end-over-end, or rotate side-over-side allowing for continuous movement of the package. The agitation of the product allows for faster heating time (Gavin & Weddig, 1995).

Properties of Retort Packaging Materials

Historically, cans were the primary retort container of choice for retortable foods. They are rigid and strong, so internal expansion during the heating process will not

permanently distort them. They also maintain their hermetic seal throughout the retort process and the duration of their shelf life. Because they are metal, they are also excellent barriers to moisture and gasses (Sacharow & Griffin, 1980). However, manufacturers are moving away from metal cans because of the cost associated with their transporting and storage.

Flexible retort materials became an area of interest to the US military in 1975. The Department of Defense combat unit was looking to change US soldier rations. Meals Ready to Eat (MRE) were considered the first foods to be sterilized in flexible packaging. They utilized the barrier properties of aluminum foil and incorporated it via laminations into the packaging material. By 1986, they became standard issue to all soldiers in the US military (Blackstone & Harper, 1995).

There are many benefits to using plastic packaging materials. Plastic packages maintain their integrity throughout the handling process and form rigid, flexible, and moldable packages. They are economically more efficient than cans and glass jars because shipping costs (Williams, Steffe, & Black, 1982) and cook times (Fetherstone, 2011) are lower due to the lighter material and thinner profile. Food packaged in flexible plastic pouches can also retain more of its organoleptic qualities and nutritional value due to the shorter cook times needed to reach sterilization temperatures.

However, in order for retorted films to be successful against glass jars and steel cans, they must maintain their barrier properties to gas and moisture, maintain a hermetic seal at high temperatures, be stable up to 150°C, be heat sealable, be compatible with food, be printable and be mechanically stable (Subramanian, Srivatsa, Nirmala, &

Sharma, 1986). Generally speaking, no single layered plastic material is capable of producing all of the necessary requirements for all products. Multilayered (3 or 4) flexible pouches are used to achieve the needed properties (barrier and others) and provide the required shelf life.

Multilayered pouches are often created via lamination. Lamination is the process of bringing two different materials together using heat, adhesives, and pressure. In multilayered flexible retort packaging, layers are divided into a food contact layer, a barrier layer, and a printable outer layer. Additional layers might also exist within a layer for various application requirements.

Food Contact Layers

The food contact layer in a retort pouch is typically cast polypropylene (CPP). This contact layer is heat stable at retort temperatures without breaking down and losing its hermetic seal. CPP is typically used in most retort pouch applications due to its heat sealable and does not migrate into food product, a requirement of the FDA (US Food and Drug Administration, 2007). However, CPP is a very poor oxygen barrier and is therefore laminated to other high barrier materials.

Barrier Layers

There are two general categories of retort barrier pouches; foil and non-foil. In foil retort pouches, an aluminum foil layer of 0.00035 inches (Whiteside, 2005) is utilized as the primary oxygen barrier. Retort pouches containing aluminum foil barrier layers

are not microwavable and therefore retort pouch manufacturers are developing new non-foil barrier materials.

Currently, some non-foil barrier layers used in retort applications are polyvinylidene chloride, nylon, ethylene vinyl alcohol (EVOH), and barrier coated PET. These films are good oxygen barriers, however their inherently high cost makes their use in packaging very limited (Hong & Krochta, 2006).

Polyvinylidene chloride/Saran

PVDC is a great barrier to gasses, fats, and liquids and is compatible with CPP, PET, and Nylon (Brody, 2005). It has twice the moisture barrier of EVOH, both during and after the retort process (Schirmer, 1988). However, it has a high chloride content which corrodes machinery, thus increases cost. It also has a narrow processing window because it is heat sensitive. In addition, films turn brown during processing, puncture easily, and are difficult to seal (Brody, 2011).

Nylon

Biaxially oriented nylon (BON) is typically used as an abrasion or impact layer for retortable pouches. In the absence of moisture, nylon has excellent mechanical and barrier properties over a range of temperatures as well as good resistance to chemical corrosion. Strong intermolecular forces and crystallinity create tough materials with high melting temperatures. However, nylon is hydrophilic and can gain up to 8% of its weight when in contact with water (Hernandez, Selke, & Culter, 2000), thus reducing its mechanical and resistance properties. Nylon is generally used for its flexibility and puncture resistance and is laminated between moisture barrier materials.

EVOH

EVOH films possess great oxygen barrier properties and good resistance to most oils, acids, and solvent while maintaining its barrier properties (Hernandez, Selke, Culter, 2000). It is easy to manufacture and can be processed with many different polymers. However, when exposed to water, the oxygen barrier greatly decreases (Mokwena, Tang, & Laborie, 2011). This is especially important in retort processing, as water (steam, water spray, or immersion) is used at the primary processing medium to sterilize packages. To prevent water uptake, barrier materials like CPP (Halim et al., 2009) and desiccants incorporated into adhesives are sometimes used to surround EVOH (Tsai & Wachtel, 1990).

Coatings

Surface coatings of aluminum oxide (AlOx), silicon oxide (SiOx), and modified Poly Acrylic Acid (Besela®) have been shown to significantly improve the barrier properties of PET films. However, their widespread usage is limited due to major limitations. These materials are relatively expensive due to the coating process being technically difficult (Hong & Krochta, 2006). Retort pouches containing AlOx and SiOx coatings have been shown to develop cracks and pinhole during the retort process and pouch handling procedures (Galotto, Ulloa, Guarda, Gavara, & Miltz, 2009; Dharman, 2011).

Besela[®] film, a coated polyethylene terephthalate (PET), is an emerging technology similar to AlOx and SiOx. Besela[®] has oxygen barrier properties similar to SiOx. However, it is more heat resistant and has better mechanical properties than its

counterparts. In addition, it maintains a better barrier after retorting and prevents pinholes even after considerable flexing.

Outer Layer

The outer layer of retort pouch films must be able to withstand the moisture and pressure during the retort process, be printable, and have impact resistance. Polyethylene terephthalate (PET or polyester) is a clear film that is stiff yet strong, and absorbs very little water, thus making it ideal for the outer layer of retort flexible films (Mitsubishi Polyester Film, 2011). Its clarity and hydrophobicity makes it ideal for printing. Its stiffness makes its ideal for surface modifications which improve its barrier properties. PET is only sealable at its high melt temperature (250°C) so it is typically laminated to a layer with a much lower seal temperature. PET can also be used as a barrier layer that is placed between two additional layers (Lange & Wyser, 2003).

Natural Film Formers

Biopolymers are typically sourced from marine, animal, and plant microbial sources (Vasile & Zaikov, 2009). Research is focused on finding biopolymers that can be used as alternatives to petroleum based plastics. Due to biopolymers being natural film formers and possessing excellent oxygen barrier properties, they are typically used as coatings or in laminations. However, their hydrophilic nature greatly affects their oxygen barrier and mechanical properties, and often making them unsuccessful competitors to traditional petroleum based plastic. Research is needed to determine if biopolymers, when used as food additives, can create an additional barrier layer and improve the oxygen permeability of retorted pouches.

Protein Films

Proteins are complex polymers made up of 21 different amino acids bonded together via amide bonds. Altering the amino acid sequence, the amount of amino acids, and the length of the polypeptides allows the production of numerous proteins, all with unique properties (Damodaran et al., 2008). This molecular diversity provides almost limitless combinations of film-forming materials. Proteins are typically used to make films because they are edible, they supply nutrition, they have good mechanical, barrier, and visual properties (Janjarasskul & Krochta, 2010). Gelatin, soy, and milk proteins are all common sources of these films.

Gelatin is a hydrocolloid that is widely used in the food, pharmaceutical, and biomedical industries. Gelatin is primarily obtained from animal sources, with a small percentage sourced from marine animals. Fish Gelatin (FG) originates from fish skins, bones, and fins. FG has lower proline and hydroxyproline amino acid levels compared to pigs and cows. Karim and Bhat (2008) suggest that this caused the lower gel modulus, gelling, and melting temperatures.

Gelatin based films are good barriers against oxygen and aromas at low and intermediate relative humidity's. They are also brittle, so plasticizers are often added to increase the film toughness and flexibility (Cao, Yang, & Fu, 2009). FG films typically have poor barrier properties due to their hydrophilic nature (Arnesen & Gildberg, 2007) which can be improved by cross-linking, blending, and mixing with fibers or clay (Martucci & Ruseckaite, 2010).

Soy proteins are available in three different concentrations, flour (SPF), concentrate (SPC), and isolate (SPI). They are made up of albumins and globulins. Globulins are responsible for the hydrogen and hydrophobic bonding. The disulfide bonds in Albumins are responsible for the binding of the polypeptide subunits (Guerrero & de, 2010).

When SPI is heated, the albumin and globular proteins unfold, denature, and form new disulfide, hydrophobic, and hydrogen bonds upon cooling. This creates films with good barrier properties to O₂ and lipids. SPI films are poor moisture barriers (Janjarasskul & Krochta, 2010). They are typically applied as coatings on fruits, cheeses, and meats to prevent oxidation. Recent research has focused on modifying SPI in order to improve its properties (Wan, Kim, & Lee, 2005).

Milk is made up of lipids, proteins, carbohydrates, vitamins, and other minerals. Protein makes up approximately 30-36 g/L of milk. Milk proteins fall into two categories caseins and whey proteins. These two fractions are easily separated and historically whey protein was considered a waste. Today, whey protein can be concentrated into whey protein concentrate (WPC) and whey protein isolate (WPI) both of which have good nutritional properties (Damodaran et al., 2008).

Whey proteins have gained interest because they are a byproduct of cheese production and are typically wasted. WPI are typically used in food and film forming applications because they denature above 90°C (Damodaran et al., 2008). As coatings, they have excellent barrier properties to O₂, aroma, and oil. As stand-alone films, they

produce opaque films that are too brittle for most flexible applications (Sothornvit & Krochta, 2000).

Hong & Krochta (2004) studied the effects of WPI coatings on LDPE. A 10% (w/w) WPI solution plasticized with glycerol was prepared and cast onto a LDPE film. They found that the oxygen barrier properties of WPI depended on temperature and relative humidity (RH). At RH less than 25%, films achieved the desired barrier properties and could potentially be used as a barrier layer sandwiched between 2 moisture barriers.

In 2006, the same authors assessed the oxygen barrier properties of WPI and WPC coated PP films. They resulting WPI/glycerol and WPC/glycerol coated PP films improved the oxygen and moisture barrier properties. Similar to their previous research, the barrier properties of these films were also dependent on temperature and RH. These effects were due to the thermal expansion and increased molecular motion (Callister, 2007), and swelling effect on hydrophobic polymers (Hernandez-Izquierdo & Krochta, 2008), respectively.

Carbohydrate Films

Carbohydrates make up more than 90% of plant matter and are readily available and inexpensive. Furthermore, their diverse size, shape, and molecular makeup allow for variations in physical, organoleptic, and mechanical properties. The class carbohydrates present themselves in nature as monosaccharides, oligosaccharides, or polysaccharides (Damodaran et al., 2008).

Polysaccharides possess longer chains polymerized from monosaccharides or disaccharides that are joined together by glycosidic bonds. They typically have between 100–3,000 repeating units (Damodaran et al., 2008). The hydroxyl and other hydrophilic groups in the repeating units allow for bonding. Heating disrupts these long chains and reforms them during the casting, evaporating, and cooling process. Because of this hydrogen and hydrophilic bonding, polysaccharide films, in general, are very sensitive to water and lose their mechanical and barrier properties.

However, they are often studied as potential film formers because they are abundant, inexpensive, and edible. They are easily modified by the addition of salts, pH changes, solvents, heat, crosslinking agents, and nanotechnology (Janjarasskul & Krochta, 2010). Their films generally make good barriers to gasses like O₂ (Baldwin, Nisperos-Carriedo, & Baker, 1995).

A cellulose derivative like hydroxypropyl methylcellulose (HPMC) has also been used as a film former (Janjarasskul & Krochta, 2010). When applied to foods it provides barrier properties against O₂, water vapor, and oil. HPMC is a very versatile cellulose derivative. It is typically used because it is an excellent film former. The FDA (21 CFR 172.874, 2012) has approved the use of HPMC as a food additive and the JECFA has verified its safety (George A., 2007). HPMC has some limitations, like most polysaccharide films, it has a low moisture resistance.

Starches are very common food additives and make up approximately 70-80% of the calories humans eat each day. Starches are made up of two polymers amylose and amylopectin (Damodaran et al., 2008). When cast, these films are self-supporting

(Janjarasskul & Krochta, 2010). As films, they possess excellent barriers to gasses. Starch films are used as a coating to preserve fresh fruits (García, Martino, & Zaritzky, 1998) vegetables, and nuts. Potato amylopectin is unique in that it has small amounts of phosphate ester groups (Damodaran et al., 2008). In addition, potato starch is considered easy to work with because it readily dissolves in water, allowing for homogeneous solutions (Osés, Fernández-Pan, Mendoza, & Maté, 2009).

Food Additives

The natural film-formers above are also frequently used as food additives. Their primary purpose is to deter oxidative rancidity and spoilage. Another common household food additive is lemon juice because the ascorbic acid in the juice can prevent rapid oxidation of cut fruit. Butylated Hydroxyanisole is an industrial preservative that prevents rancidity in foods with high fat and oil content and prevents foods from changing flavors, colors, and smells (Branen, 1975).

Oxidation

Food oxidation is an irreversible process causing food to spoil and become rancid. The two types of rancidity are hydrolytic and oxidative. Hydrolytic rancidity occurs with high moisture and heat. Oxidative rancidity occurs when oxygen interacts with unsaturated fatty acids. This is also known as lipid oxidation (Damodaran, Parkin, & Fennema, 2008).

Lipids enhance the organoleptic properties of food including taste, color, smell, and feel (German, 1999). In the presence of oxygen, the fatty acid chains undergo a

process where hydrogen molecules are replaced with oxygen molecules. This process converts fatty acids into smaller functional groups like aldehydes, alkanes, esters, and alcohols that are more easily decomposed (Stauffer, 1999). These small, decomposed molecules create molecular fragments that interfere with flavor, decrease nutritional value, and produce the aromas associated with rancidity (Damodaran et al., 2008). This ultimately decreases shelf life (Waterman & Macy, 2009) of products.

Measuring Oxygen Transmission Rate

The Oxygen transmission rate (OTR) of packaging materials is often tested with MOCON Ox-Tran 2/21 (Mocon, Minneapolis, MN, USA) oxygen permeation instruments. It precisely controls the temperature and relative humidity and can measure and detect oxygen, carbon dioxide, and nitrogen in minute amounts (parts-per-billion sensitivity). Film samples are removed from packaging material and are securely clamped into a diffusion cell. This is a destructive test and the package cannot be reused. All residual oxygen is then removed from the chamber. When zero percent oxygen is established, pure oxygen is introduced into one side of the chamber opposite to the sensor. The sensor then records the diffusion of oxygen through the material. This process cannot be repeated for the same sample and can take up to 48 hours per sample.

Measuring Oxygen Ingress

Real time oxygen ingress that is non-invasive and passive can be measured with an OxySense Gen III 300 system (OxySense, Inc., Dallas, TX). A picture of the equipment is shown in Figure 2. This system consists of two parts, an oxygen sensor,

and a master box that evaluates and interprets the findings. The oxygen within an enclosed system is measured without destroying or altering the internal environment (Saini, 2008). This is an added benefit as the same samples can be repeated

Oxygen concentration measurements are possible based on fluorescence quenching. The OxyDot[®] (Dot) is comprised of an oxygen sensing dye that is immobilized in polymer that can withstand high temperature and pressure processes yet is permeable to gas. The Dot absorbs blue light emitting diode (LED) light and fluoresces light in the red region. Figure 3 represents the fluorescence decay over time. When oxygen is absent the Dot will emit an intense red light for 5 μ s whereas when oxygen is available the light intensity and emission is decreased to \sim 1 μ s. The decrease in intensity and emission can be calculated to accurately provide the amount of oxygen available



Figure 2. OxySense GenIII 300 Equipment.

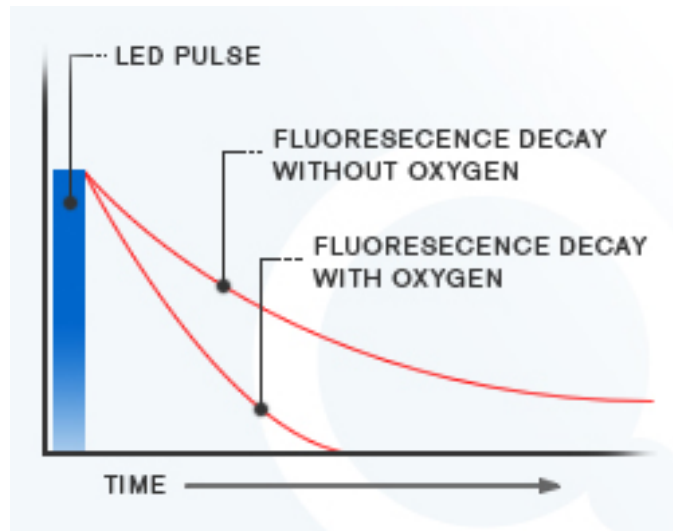


Figure 3. Graphical representation of Fluorescence decay with and without oxygen.

within 5% accuracy of the reading. The Dot does not consume oxygen in the process and the test can be repeated quickly (5 seconds) and indefinitely (Saini, 2008).

However, Figure 3 does not include the effect of oxygen partial pressure on the results. Figure 4 depicts the relative fluorescence in ambient at and 20°C at different pressures (Siani, 2008). Pressure of oxygen at sea level is equivalent to 212 mBar. This is derived from the fact that 1 atmosphere (atm) at sea level is equivalent to 1013.25mBar. The oxygen concentration at sea level is 20.9% and is multiplied by the mBar at sea level to obtain O₂ partial pressure, ~212mBar (Analox Sensor Technology Ltd., 2009). Because there is a correlation between pressure and fluorescence, pressure measurements are included in the percent oxygen calculations.

Fluorescence decay curves for differing concentrations of oxygen

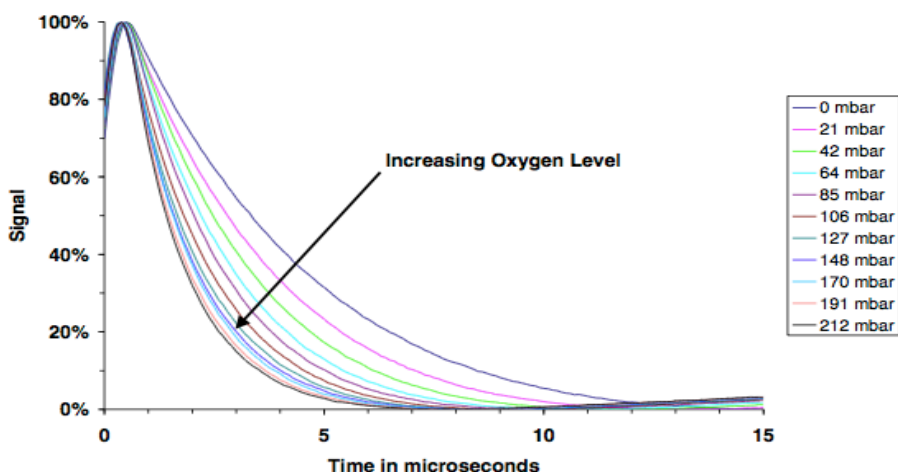


Figure 4. OxySense fluorescence decay curves for different oxygen concentrations after a 1 μ s LED pulse. Oxygen concentration was performed in air at 20 $^{\circ}$ C.

Purpose

Over the past few decades, there has been increased use of laminated flexible retort packaging materials for low acid shelf stable foods. These laminations films must be sealable, stiff, flexible, heat resistant and provide a barrier to moisture and oxygen. No single film layer provides all of these necessary functions, so multilayered films are used to provide adequate protection.

The barrier to oxygen is of significant importance in food packaging. Oxygen causes rancidity and can decrease the nutritional value and quality of food thereby reducing food product shelf life. The amount of oxygen in a package directly relates to the shelf life of many foods. In previous research, it was found that food ingredients affected retort materials, specifically their oxygen permeability. This research was

focused on assessing how food ingredients affected the oxygen barrier of retortable flexible packaging materials.

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CHAPTER III

MATERIALS AND METHODS

Materials

Hydroxypropyl methylcellulose (HPMC) grade AN15 was donated by Samsung Fine Chemical, LTD (Incheon, Korea). Dry OU Kosher Certified fish gelatin (FG), lot# 4125KD, and OU Kosher Certified high molecular weight fish gelatin (HMWFG), lot# 4092 HMWD, were purchased from Norland Products Incorporated (Cranbury, NJ). Bovine skin gelatin (BG), Type B, and potato starch (starch) were purchased from Sigma Chemical Company (St. Louis, MO). Soy protein isolated (SPI) was purchased from MP Biomedicals, LLC (Solon, OH). Whey protein (WPI) with a protein content of at least 11%, was purchased from Spectrum Chemicals (Gardena, CA). Corn oil (ACH Food Companies, Inc.) peanut oil, and corn oil was purchased from a local grocery store.

Extrel[®] 487 Impact Copolymer Polypropylene 3.0 gauge film was purchased from Tredagar Film Products (Richmond, VA). 7000 series uncoated PET 92 gauge film was donated by Mitsubishi Plastics, Inc (Toyoko, Japan). Trial films consisting of 0.5 μ m AlOx/12 μ m PET/0.5 μ m AlOx // 15 μ m BON // 70 μ m CPP) was donated by Ampac[®] (Cincinnati, OH). OxyDots[®] and General Electric RTV 118 adhesive were purchased from OxySense (Las Vegas, NV).

Methods

Solution Preparation

Aqueous solutions were prepared by dissolving 3g of food ingredients per 100mL of degassed, deionized, and distilled water with magnetic stirring at 90°C for 30 minutes. In solutions with both a food ingredient and oil, 3mL of oil was added after 25 minutes of magnetic stirring at 90°C. These solutions were heated and stirred for an additional 5 minutes. All solutions were removed from the hot plate after 30 minutes and allowed to cool to room temperature with magnetic stirring continued for at least 8 hours.

Sample Preparation

Pouches were created from rolled stock film. Films were cut into 4in x 8in rectangles. OxyDots[®] were applied to the flat film using General Electric RTV 118 adhesive. The adhesive was allowed to cure for a minimum of 90 minutes (OxySense, 2011). Films were fabricated into three-sided seal pouches using a Fuji impulse sealer (Toyo Jidoki CO., Dalian, China). CPP films were sealed at 120°C for 1.5 seconds and cooled for 2 seconds before jaw released. AmPac trial films and PET films were sealed at 160°C for two seconds and cooled for five seconds.

150mL of the prepared treatment solutions were added to each pouch. Pouches were manually sealed with minimal headspace. Six replicates were made for each sample. Pouches were processed in a two-basket Surdry Retort Model A0-142 (Surdry, Spain) for 30 minutes at 38psi/250°C in static water spray mode. Pouches were allowed to cool for at least 8 hours over night in ambient temperature (25°C, 50%RH).

Difficulties arose during the removal of oxygen from the pouches. All preliminary tests were performed on CPP pouches. The use of dry ice to flush the pouches of oxygen created sizeable headspace. A septum was then applied and nitrogen was flushed into pouches. Headspace was then removed through a needle-vacuumed system. The process was repeated twice. It was found that oxygen migrated into the pouches via the septum. Silicon sealant was used to plug the septum. It was then found that pouches with aqueous solution had a rapid influx of oxygen (<24hours). The best methods for oxygen measurement were to drain each pouch after overnight cooling. Empty pouches were resealed with the Fuji impulse sealer. A septum was applied and pouches were flushed with a nitrogen gas tank with a gas pressure regulator set at ~116.03psi (800 kPa) for 20 sec/pouch, see Figure 5.

Test OxySense measurements were taken (not recorded) at this time. If the reading was greater >3.00%, pouches were vacuum suctioned until maximum headspace was removed. This was repeated until the headspace was below 3% oxygen. An additional seal below the septum puncture was added to prevent leakage through the septum. In Figure 6, the left represents a pouch (treated with air) that was removed from the retort. In the same picture, the pouch on the right has had its contents removed, has had a septum applied, has been flushed, and has been sealed below the septum.

The samples were labeled as follows; film material, ingredient, sample number (CPP BG-001). Some samples did not survive the post retort resealing process. To ensure a sufficient number of test samples were available for analysis, additional

samples were made and processed. These additional samples were coded with the word 'redo'; film material, ingredient, redo-sample number (CPP BG redo-001).



Figure 5. Picture of a nitrogen tank pressure gauge.



Figure 6. Post retort sealing process.

Oxygen Permeability

The oxygen transmission rate (OTR) of the CPP films were tested using a MOCON Ox-Tran 2/21 (Mocon, Minneapolis, MN, USA) oxygen permeation instrument in accordance to the ASTM D3985. Oxygen permeability's of CPP films were assessed at 23°C and 0% relative humidity. Samples were manually wiped with a clean paper towel and dried overnight for a minimum of 8 hours in ambient conditions (25°C, 50% RH). Two 1.5" by 1.5" inch samples were taken from opposing sides of the pouch.

Data fits of OxySense® Date

The objective of this research was to assess the effect of food ingredients on packaging materials' oxygen barrier properties. Due to the preparation procedure previously described, samples had varying oxygen concentrations at the start of data collection. For this reason, slope comparisons were made using Statistical Analysis Software (SAS).

During the evaluation of the data, some samples were found to have very rapid ingress of oxygen consistent with leaking pouches. These samples were eliminated for further analysis due to leaks. Other samples were eliminated from further analysis due to dot failures. Some of the oils used were found to have a damaging effect on the Oxydots themselves. See appendices A-C for details.

Measurements for time and percent oxygen for all OxySense samples and treatments were evaluated in SAS. Each sample was fit with either a second or a third order polynomial best fit trendline. A trendline is a tool used to evaluate the relationship between dependent and independent variables, in this case percent oxygen and time,

respectively. This type of analysis can project the development of data. PET samples revealed a second order polynomial fit and CPP samples portrayed a third order polynomial fit after analysis. Second ($y=a+bX+cX^2$) and third order ($y=a+bX+cX^2+dX^3$) polynomial coefficients (b, c, d) represent the slope of that specific segment. Where "b" is the linear slope, "c" is the quadratic slope, and "d" is the cubic slope. The coefficients were analyzed via ANOVA ("d" only in CPP data). The confidence interval was set at 95% ($P<0.05$). Data was assessed based on these parameters.

However, neither polynomial line portrayed the natural behavior of permeation. The nature of oxygen permeation into a pouch is to ultimately reach equilibrium with the atmosphere outside of the pouch (ambient air at roughly 21% oxygen). Second degree polynomials should not show a local maximum and then a reduction in oxygen headspace in the pouch. A third degree polynomial trendline should not show a local maximum and then an increase in oxygen headspace. However, these trendlines can be used to make significant ($p<0.05$) comparisons based on their linear, quadratic, and cubic slopes.

Statistical Analysis

Statistics on a completely randomized design were performed with the analysis of variance (ANOVA) using SAS (version 9.1, SAS Institute Inc., Cary, NC, USA) and differences among mean values were processed by Least Significant Differences (LSD). Significance was defined at a level of $P < 0.05$.

CHAPTER IV

RESULTS & DISCUSSION

The focus of food packaging is to minimize the amount of food loss, and to provide safe quality foods (Lee, Son, & Hong, 2007). Maintaining a barrier during storage is necessary because the diffusion of gas and food ingredients greatly affect food quality (Janjarasskul & Krochta, 2010). Oxygen and other gasses permeate through packaging materials via micro-cracks and channels, nano-scale defects, pinholes, diffusion, and solubility (Barker, et. al, 1995). Barrier coatings and laminated layers reduce this problem. The objective of this research was to assess how different food ingredients affect the barrier properties of retort packing material.

Oxygen Transmission Rate

Abbreviations for food ingredients that were used to treat the CPP films can be found in Table 1. Figure shows the Oxygen Transmission Rate (OTR) in $\text{cc}/[\text{m}^2\text{-day}]$ at 23°C and $0\%\text{RH}$ for CPP treated with different food ingredients. Note that two samples, EVOO and BG, did not produce duplicate OTR values because cleaning with detergent was not performed. In previous research performed by Dharman (2011), a layer was formed during the retort process that interfered with the Ox-Tran 2/21 process and readings could not be made. When the layer was removed by cleaning with detergent and water, measurements could be taken. In this research, cleaning, beyond the minimal wiping off excess dripping liquids, was withheld to prevent the removal of any potential layers.

Table 1. Food ingredient list used as treatments on CPP retort films analyzed with a Mocon OxTran 2/21.

Treatment	Abbreviation
Stock film; Not retorted	None
Bovine Gelatin	BG
Fish Gelatin	FG
High Molecular Weight Fish Gelatin	HMWFG
Hydroxypropyl Methylcellulose	HPMC
Canola Oil	Ca. Oil
Soy Protein Isolate	SPI
Potato Starch	Starch
Water	H ₂ O
Whey Protein Isolate	WPI
Peanut Oil	P. Oil
Corn Oil	Co. Oil
Extra Virgin Olive Oil	EVOO

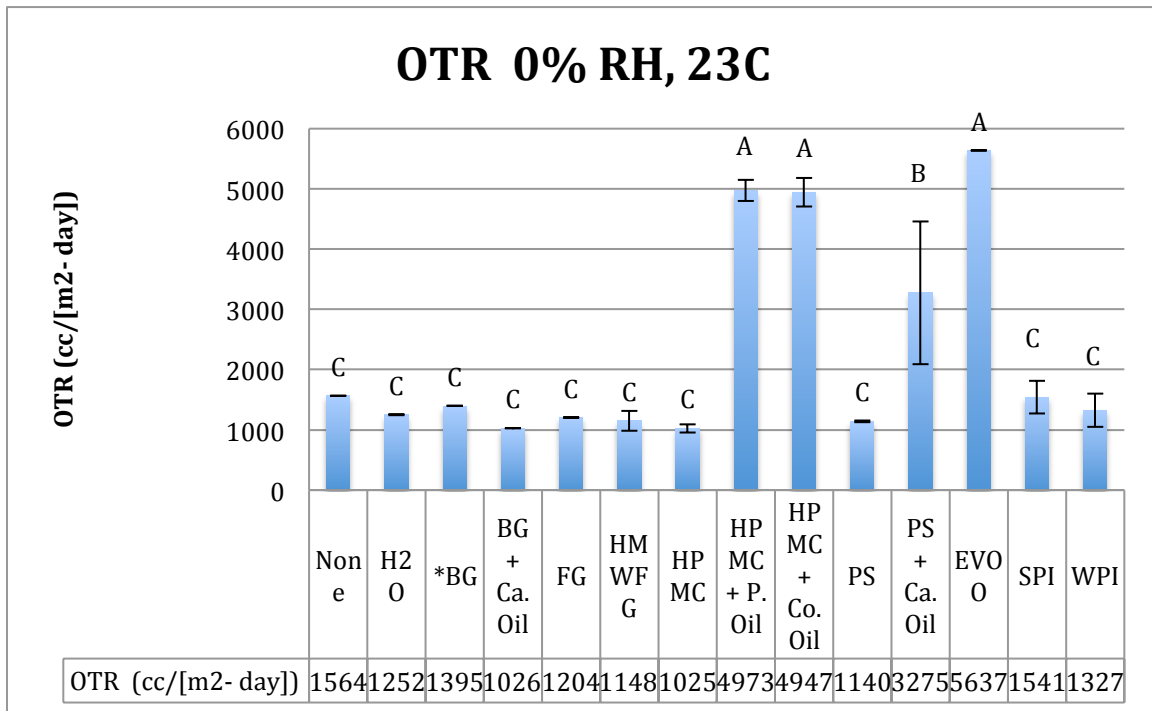


Figure 7. The OTR of CPP treated with different food ingredients and retort sterilization compared to a control (non retorted).

Standard deviation was high for some measurements. Samples were taken from both the top and bottom side of the post retorted pouch. The side of the pouch in contact with the retort tray created a puckering pattern on the film during processing that would no longer lay flat. This increased the area of the film and thinned the material in places. Standard practice mandates that test specimens be free of wrinkles, defects, creases, pinholes (ASTM D3985, 2011), and be flat and tight to acquire good measurements (Mocon, Inc, 2012). It is possible that puckering pattern of the retorted film prevented a tight and flat fit. In addition, the residue on the film may have may have inhibited a good seal on the tests described allowing for the leaking of oxygen around the edge of the sample into the Mocon Ox-Tran's measurement chamber.

The barrier properties of CPP improved after retorting (see Table). Tredagar 487 CPP has a crystallization temperature around 113°C/ 235.4°F. The retort cooking process typically sterilizes food at 121.1°C/250°F and then slowly cools over approximately 60 minutes down to 25°C. This slow cooling process allows CPP to more fully crystallize and become a slightly better barrier (Callister, 2007).

HMWFG, SPI, and WPI have no significant effect ($p < 0.05$) on the CPP films. Different oils were chosen to evaluate using Mocon Ox-Tran 2/21 analyses. Fatty acid saturation affects the sorption of oil into packaging films. As unsaturation increases, sorption declines because the increase in double bonds decreases chain flexibility in the oil and makes it more difficult for oils to sorb into a polymers free space (Caner, 2011). **Error! Reference source not found.** represents the fatty acid contents in the oils chosen. However, it can be seen in Table

Table 2. OTR results (cc/[m2-day]) for CPP pouches at 23±2°C and 0±2%RH. Retorted pouches with different food ingredients were compared to non-retorted CPP.

Treatment	OTR (cc/[m2- day])	Significant Difference
None	1564 ± 1.864	C
H ₂ O	1252 ± 8.606	C
FG	1204 ± 2.355	C
BG	*1395	C
BG + Ca. Oil	1026 ± 0.697	C
HPMC	1025 ± 69.276	C
HPMC + P. Oil	4973 ± 173.128	A
HPMC + Co. oil	4947 ± 239.181	A
PS + Ca. Oil	3275 ± 1188.456	B
WPI	1327 ± 277.186	C
Starch	1140 ± 12.728	C
HMW FG	1148 ± 166.170	C
EVOO	*5637	A
SPI	1541 ± 272.943	C

Mean ± standard deviation. *n=1, all others n=2. Treatments with different letters are significantly different (p<0.05).

Table 3. Fatty acid polyunsaturated, monounsaturated, total unsaturated, and saturated fatty acid content.

Types of Vegetable Oil (%)	Polyunsaturated Fatty Acids (%)*	Monounsaturated Fatty Acids (%)*	Total Unsaturated Fatty Acids (%)* **	Saturated Fatty Acids (%)*
EVOO	25	55	80	20
Co. Oil	59	24	83	13
Ca. Oil	33	55	88	7
P. Oil	32	46	78	17

All values approximated* Values are given as a percent of total fat; ** total unsaturated fatty acids = polyunsaturated fatty acids + monounsaturated fatty acids (*Fats, cooking oils and fatty acids*, 2010).

that the degree of saturation did not effect the OTR of CPP film, thus OxySense evaluation was performed only on Corn oil.

OTR significantly ($p < 0.05$) decreased in EVOO, HPMC/P. Oil, and HPMC/Co. Oil samples. Oil had a negative effect on polypropylene due to sorption and plasticization. Sorption occurred when molecules from inside the pouch migrated into the CPP packaging material. Sorption caused plasticization, the modification of polymeric materials. Plasticization is typically used to improve the mechanical and barrier properties of films (Hernandez-Munoz, Catala, & Gavara, 1999). However, unwanted plasticization can adversely affect the shelf life of foods. CPP readily sorbs oil into its matrix, due to the chemical similarities between CPP and oil. CPP, like oil, is hydrophobic and has an affinity fo certain oils (Caner, 2011).

Figure represents a spherulite, a small crystal grouped around a central point. The lamella (polymer chains) are organized and tightly packaged naturally inhibiting permeation and migration. Amorphous regions are open areas of free volume that encourage permeation and migration. When oil is sorbed into CPP, the oil enters the amorphous regions (Wang & Storm, 2006) and the area is expanded. The oil relaxes the polymer, promoting polymer swelling by creating an increased free volume, and decreasing crystallinity. When there is less crystallinity, there is more free volume. Ultimately, this increased space allows for the permeation of oxygen through CPP.

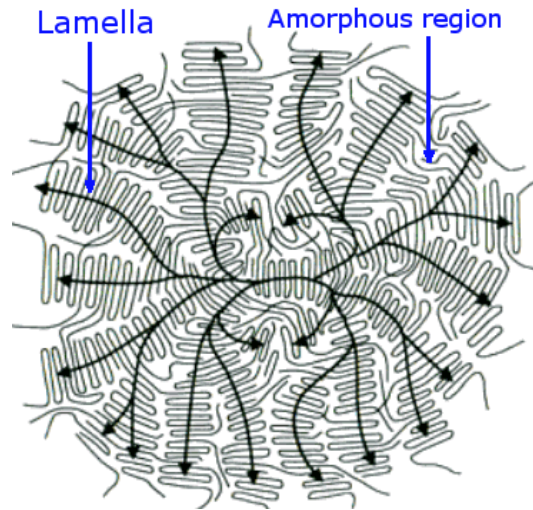


Figure 8. Spherulite (Wikipedia, 2012)

HPMC was investigated as a food ingredient because it is often used to stabilize oils in food formulations. An emulsion is the distribution of one liquid in another when the two are not miscible or soluble. Emulsions are thermodynamically unstable, and try to separate in order to minimize the area in contact with each other (Camino & Pilosof, 2011). Stabilizers are often added to aid in this process. According to Camino & Pilosof (2011), emulsions need to have a droplet size less than 1 μ m to maintain proper distribution. Weiss et al. (2006), suggested that this can only be achieved by high-pressure homogenizers, high shear stirring, or by ultrasound generators. Figure shows that HPMC was not an effective stabilizer for P. Oil and Co. After the retort process there was separation in the HPMC mixtures. An inappropriate amount of HPMC and/or solution preparation process would cause the emulsification to break during the harsh retort process. It is likely that this separation caused the oil to contact a greater area of the CPP pouches, causing plasticization and higher OTR values.

Aqueous BG and aqueous BG & Ca. oil were tested. BG aqueous solutions increased the OTR of CPP retorted films (Figure). However, aqueous BG+ Ca. oil slightly improved the OTR of retorted films. BG has a high capability to emulsify oil (Karim & Bhat, 2008). At the tested concentrations, no separation of oil and BG was noted after retort. BG successfully encapsulated to oil, despite only using heat and magnetic stirring, and therefore did not have the opportunity to migrate into the CPP film.

If oil plasticized the film, free space could have increased allowing BG to migrate into the film. Once the cooling cycle began, BG could have recrystallized in the polymer matrix. It is more probable that there was a creation of a barrier layer. BG is a known film former with good barrier properties in the absence of water (Sobral, Menegalli, Hubinger, Roques, 2001). Because samples were dried without being cleaned, a BG layer could have been responsible for the slight improvement in OTR.

Starch did not significantly improve the OTR of CPP film. However, when used as an emulsifier for Ca. oil the OTR was significantly different ($p < 0.05$) from all other samples.

Oxygen Ingres

As stated in the previous section, O₂TR measurements were conducted on unwashed samples at 23°C and 0% relative humidity. These conditions do not represent how a package would behave in a more commercial environment. Therefore, OxySense testing was started without using soap or wiping the samples. The study was completed in ambient relative humidity (RH) and temperature, 50% and 25°C, respectively. CPP, PET, and an Ampac high barrier trial multilayer film were treated with ten common food

ingredients. Table 2 lists the food ingredients used to treat PET, CPP, and Ampac films. Oxygen ingress was recorded with the OxySense for all treatments.

The resulting oxygen ingress data for PET and CPP pouches were compared using SAS to calculate the curve fits that best described the data points. CPP and PET pouches were found to have second order and third order polynomial fittings, respectively. A second order polynomial line has two slopes, a coefficient linear (straight) and quadratic (downward curved). Third order polynomial lines have an additional cubic slope that has an upward curve section after the quadratic portion. Comparisons of PET treatments were made at the linear and quadratic slopes whereas CPP samples were compared at the linear, quadratic, and cubic slopes.

However, it is important to understand that neither 2nd nor 3rd order polynomial fitting truly represents oxygen ingress. Fick's first law states that the rate of diffusion will occur faster when a concentration gradient is farther apart. Molecules will travel from high concentration to low concentration at a rate that is proportional to the concentration gradient (Callister, 2007). In the CPP and PET samples, there was no true linear portion of the line because the slope starts very steeply and then gradually reaches equilibrium. However, the data can still be compared by using the linear slope as the data correlation is still statistically significant. For the duration of this discussion, linear slope refers to the initial "steep" ingress of oxygen.

Table 2. OxySense testing; PET, CPP, and Ampac films Treatments & Abbreviations.

Treatment	Abbreviation
Air	Air
Bovine Gelatin	BG
Fish Gelatin	FG
High Molecular Weight Fish Gelatin	HMWFG
Hydroxypropyl Methyl Cellulose	HPMC
Corn Oil	Oil
Soy Protein Isolate	SPI
Potato Starch	Starch
Water	H ₂ O
Whey Protein Isolate	WPI

After the linear slope comes the quadratic slope. The more drastic curving of the line, or the slowing of oxygen ingress, reflects this. However, it is understood that the curve downward is not the typical ingress of oxygen. This is also true for the cubic portion of the slope, oxygen ingress is unlikely to increase after reaching equilibrium as the cubic polynomials suggest. The analysis of oxygen ingress should fall between the two polynomial lines; so standard polynomial fittings are needed to explain the data.

CPP Pouches

Linear, quadratic, and cubic curve components were compared for all CPP pouches. Statistical analysis of these curves can be found in Table 3. None of the cubic sections of the pouches were significantly different. In addition, only one treatment was significantly different ($p < 0.05$) in both its linear and quadratic slopes.

Table 3. Statistical analysis of the linear, quadratic, and cubic slopes of CPP pouches.

Treatment	Linear Slope	Sig.	Quadratic Slope	Sig.	Cubic Slope	Sig.
Air	1.940 ± 0.094	B	-0.075 ± 0.005	B	0.001 ± 0.000	A
BG	1.944 ± 0.062	B	-0.073 ± 0.002	B	0.001 ± 0.000	A
FG	1.810 ± 0.352	B	-0.070 ± 0.016	B	0.001 ± 0.000	A
H ₂ O	1.929 ± 0.207	B	-0.077 ± 0.015	B	0.001 ± 0.000	A
HMWFG	1.803 ± 0.032	B	-0.068 ± 0.002	B	0.001 ± 0.000	A
HPMC	1.848 ± 0.134	B	-0.067 ± 0.008	B	0.001 ± 0.000	A
Oil	5.286 ± 1.481	A	-0.627 ± 0.711	A	0.021 ± 0.075	A
SPI	1.838 ± 0.194	B	-0.070 ± 0.010	B	0.001 ± 0.000	A
Starch	1.887 ± 0.119	B	-0.075 ± 0.011	B	0.001 ± 0.000	A
WPI	2.003 ± 0.168	B	-0.086 ± 0.008	B	0.001 ± 0.000	A

Significant difference (Sig.) at 0.05 level are indicated by different letters; Mean ± standard deviation.

In Figure 7, it can be seen that CPP pouches treated with oil reached ambient oxygen (~21%) in approximately 7 days compared to ~25 days for all other treatments. Linear and quadratic sections of oil samples showed a significant ($p < 0.05$) influx of oxygen. As stated above, oil is sorbed into CPP causing the plasticization that allowed for the massive increase in oxygen permeation. By the time these pouches reached ~21% oxygen oil had migrated through CPP and could be wiped off the outer surface of the enclosed pouch.

None of the other treatments significantly affected the oxygen ingress of CPP pouches. However, it should be noted that, after retort processing, HPMC and Starch samples were difficult to seal. These two solutions created a layer on the CPP pouches that required at least two heat seal attempts on the Fuji impulse sealer.

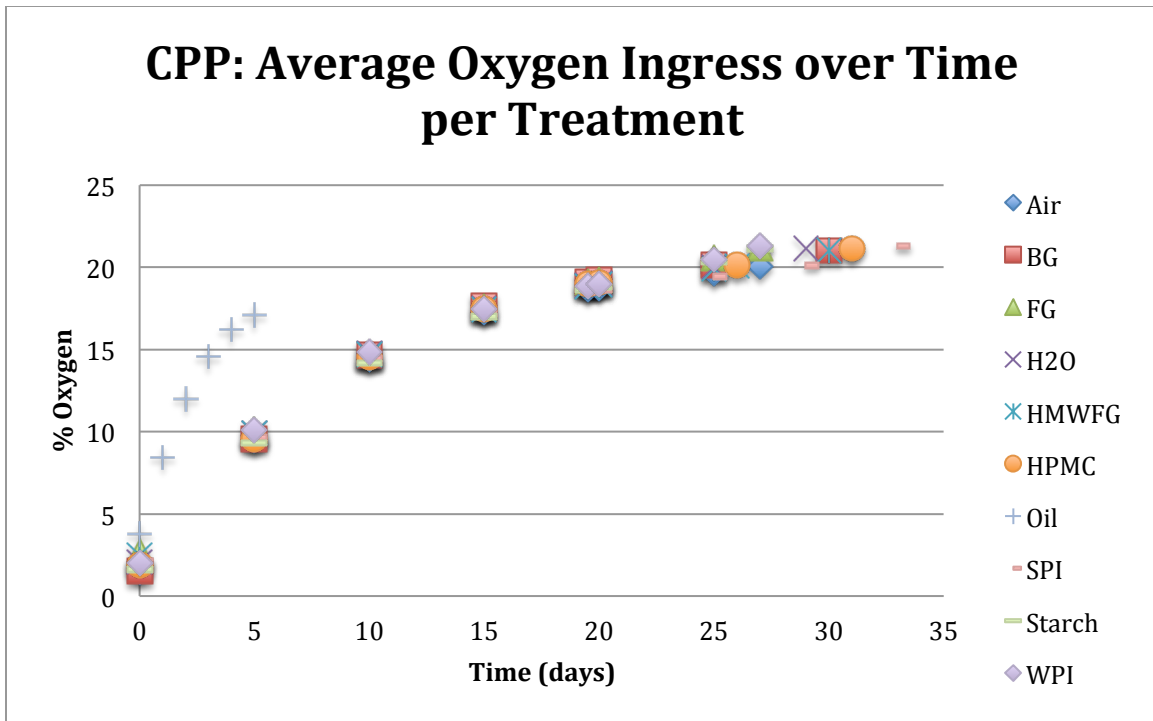


Figure 7. The average oxygen ingress over time (slope) for CPP pouches treated with 10 common food ingredients.

PET Pouches

PET pouches were evaluated with nine different food ingredients. Ingress showed a second order polynomial trendline and therefore significance was evaluated for linear and quadratic slopes. Figure 8 displays all of the treatments' average ingress of oxygen over time for PET pouches.

Linear Slope

Linear slopes were divided into four significantly different ($p < 0.05$) groups, with some treatments falling into multiple divisions. This list can be found in Table 4 and is

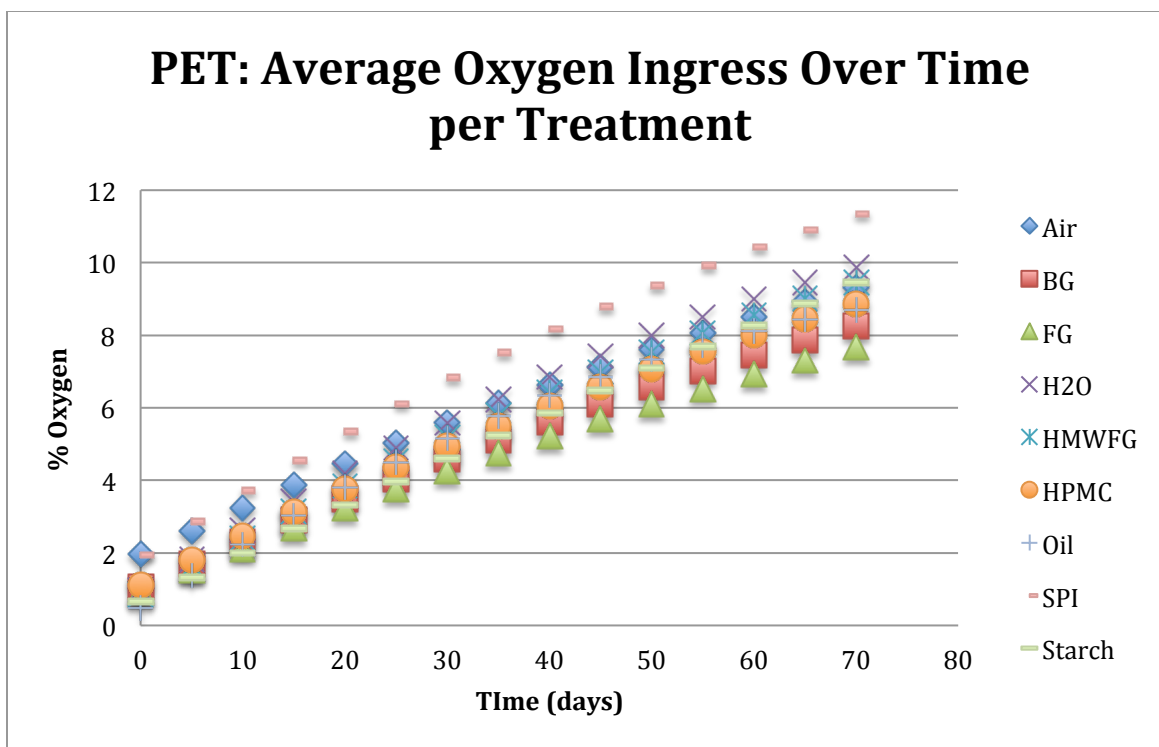


Figure 8. Oxygen concentration over time for retorted PET pouches treatments with 9 food ingredients. *WPI treatment was not evaluated

Table 4: SAS output for linear slopes organized from largest to smallest slope.

Treatment	Mean	t grouping		
*SPI	0.18493		A	
Oil	0.18411		A	
H ₂ O	0.17352	B	A	
HMWFG	0.16097	B	A	C
HPMC	0.14069	B	D	C
Starch	0.13591	B	D	C
Air	0.13271		D	C
BG	0.12842		D	C
FG	00.12137		D	

Significance ($p < 0.05$) represented by different letters. Significant difference at 0.05 level is indicated by different letters; *n=1, all others n>2.

arranged according to mean of slope. Graphical representations of the groupings can be found in Figure 9, Figure 11, Figure 12, and Figure 13.

Figure 9 represents the slopes in grouping A including Oil, SPI, H₂O, and HMWFG. This group has the steepest slope values. During the initial ingress of oxygen into PET pouches, these samples allowed for the greatest ingress of oxygen over time. In Figure 10, FG is added to grouping A to better visualize the difference in oxygen ingress. By adding FG as a comparison, it can be seen that group A have steeper slopes than FG.

Group B is represented in Figure 11. This group includes H₂O, HMWFG, HPMC, and Starch. This group is significantly different ($p < 0.05$) than groups A, C, and D. Figure 12 shows slope group C including HMWFG, HPMC, Starch, Air, and BG.

Figure 15 represents significantly different ($p < 0.05$) slopes D including HPMC, Starch, Air, BG, and FG. This group had the least amount of initial oxygen ingress. Error! Reference source not found.6 displays significant group D against water and HMWFG in Groups B and C. However, to best visualize the difference in the linear oxygen ingress, SPI (group A) was added to linear group D (Figure 17).

Quadratic Slopes

Quadratic slopes are also divided into four different groupings that are significantly different ($p < 0.05$) from each other. These groupings can be found in Table 5 from greatest to smallest mean. It is interesting to note that means for the quadratic slopes are negative. The more gradual slopes are in group A, whereas the steepest slopes are in Quadratic D, opposite to the linear slopes SAS output.

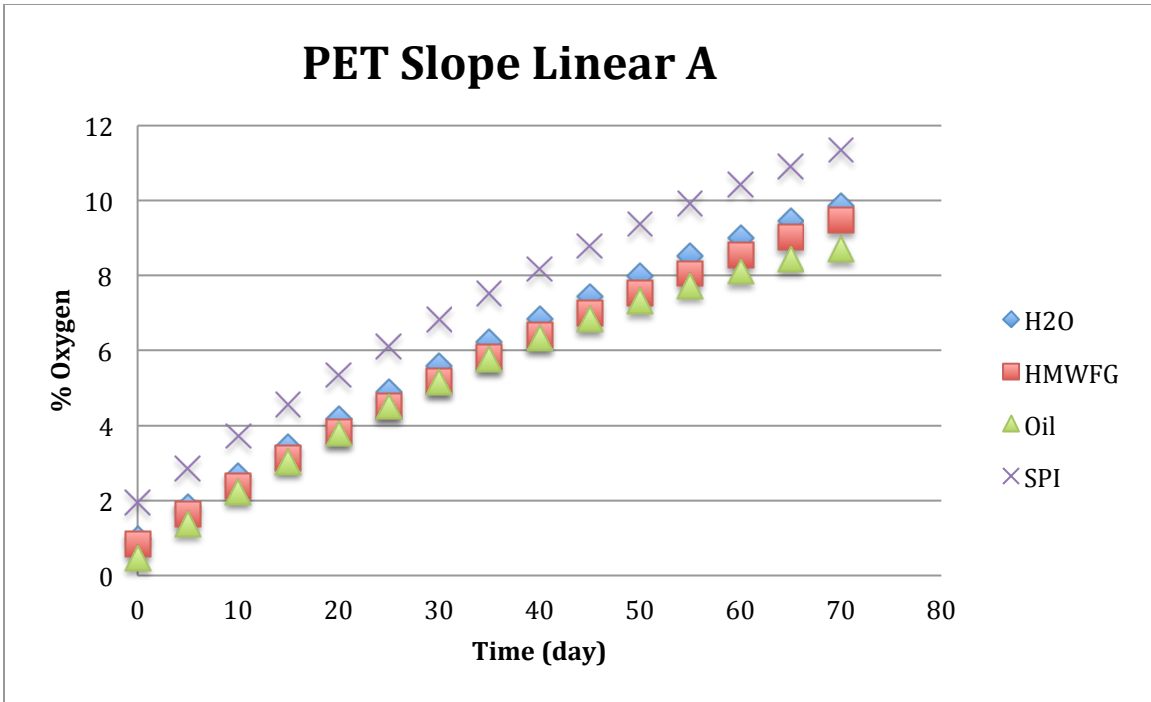


Figure 9. Linear slopes for PET treatments separated according to significant group A.

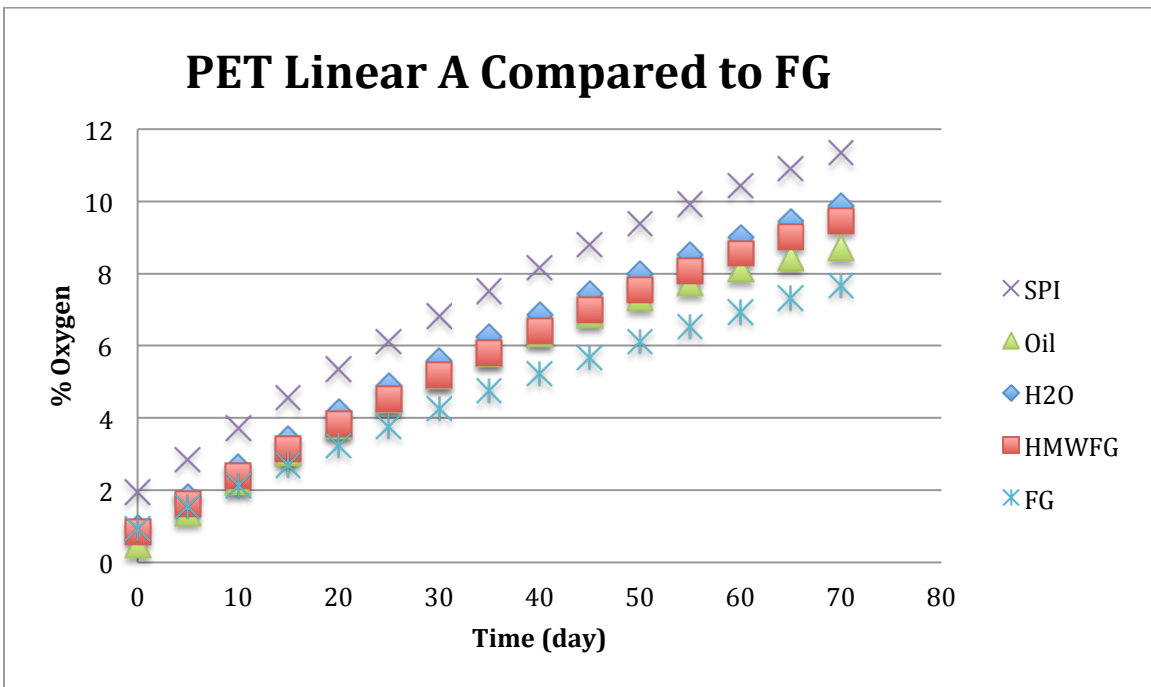


Figure 10. Graphical representation of PET statistical group A compared to FG.

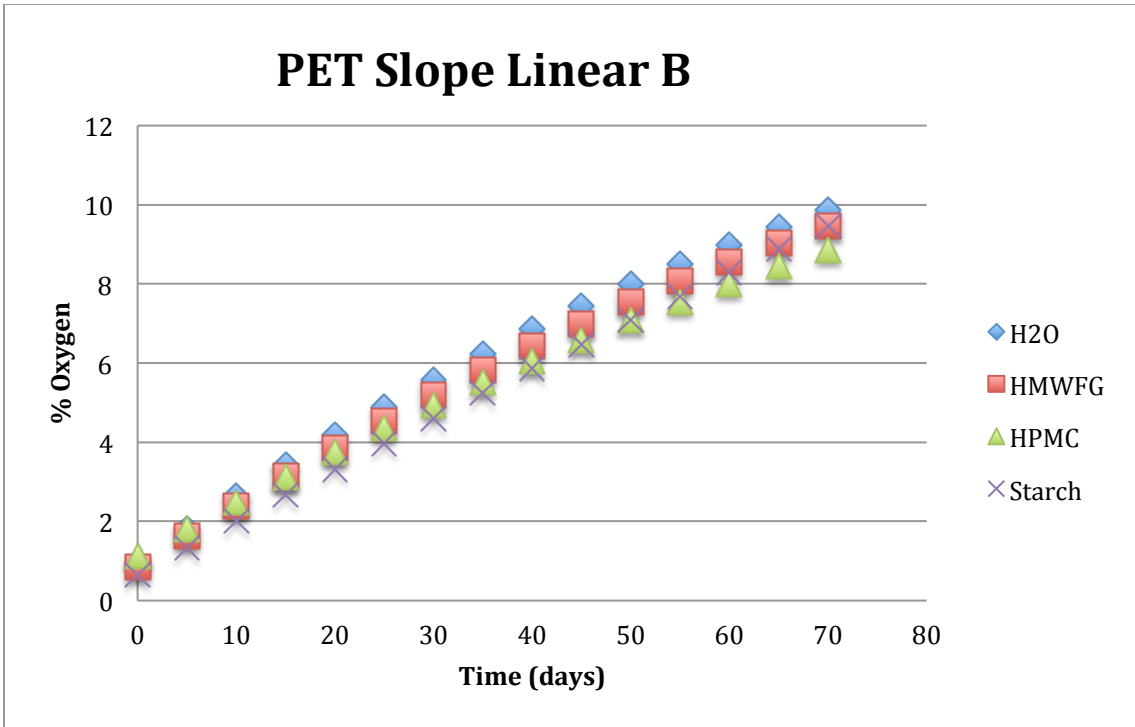


Figure 11. Linear slopes for PET treatments separated according to significant group B.

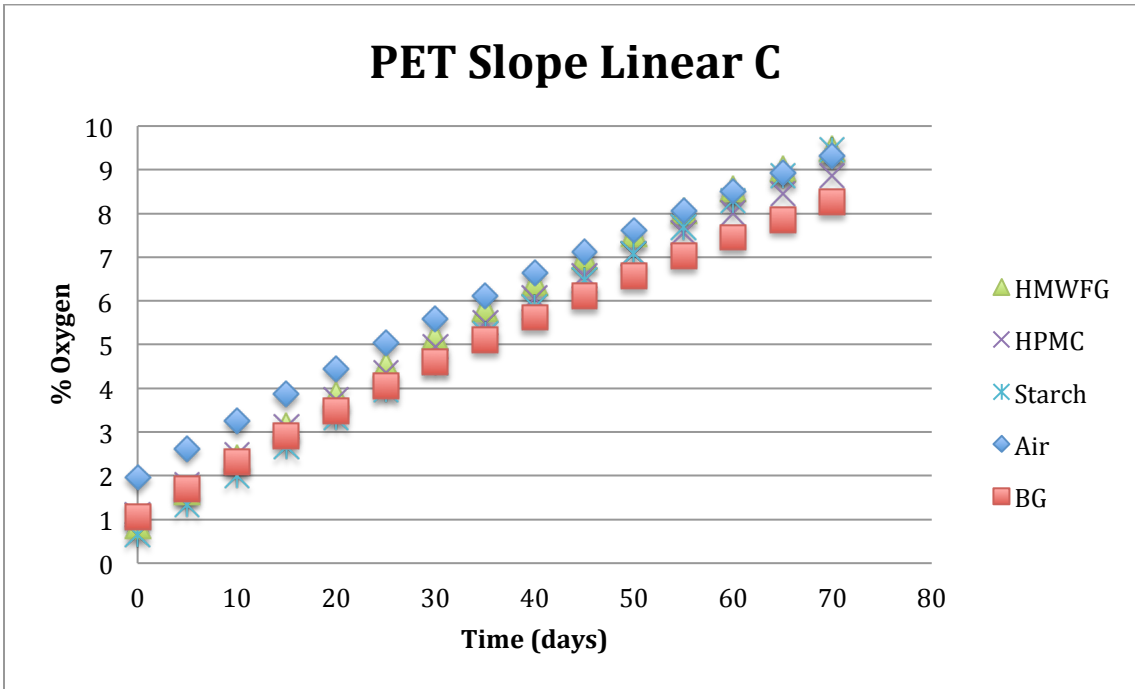


Figure 12. Linear slopes for PET treatments separated according to significant grouping C.

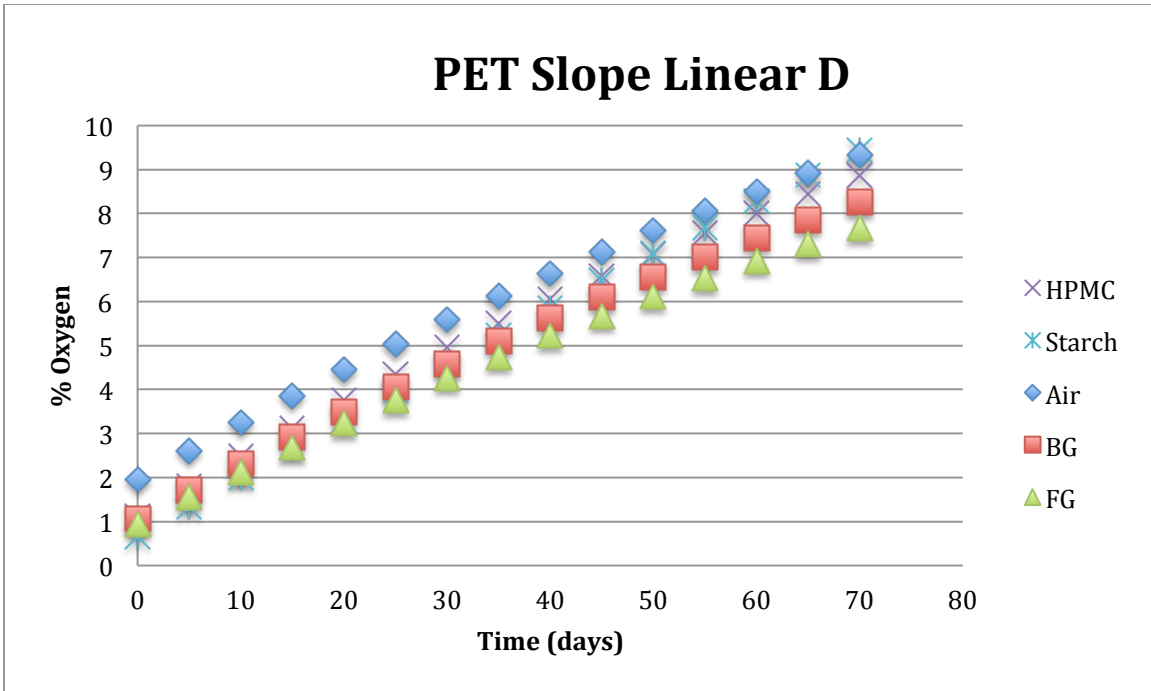


Figure 13. Linear slopes group D for PET treatments separated according to significance.

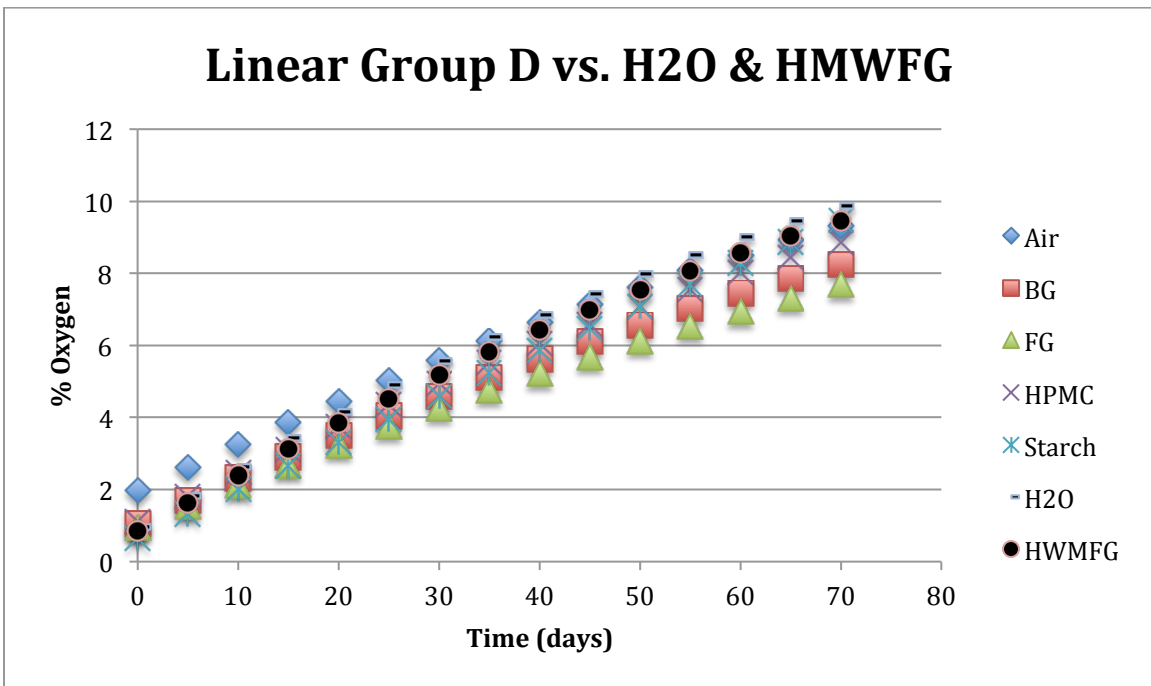


Figure 14. Linear PET grouping A compared to water and HMWFG.

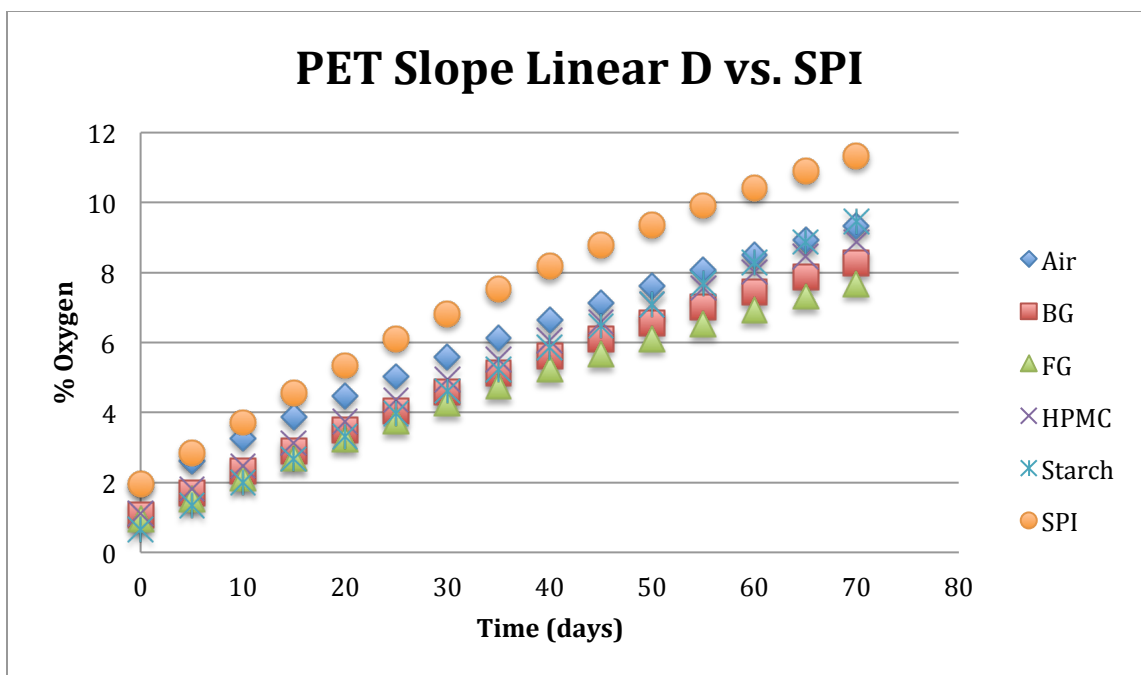


Figure 15. Linear slopes for PET treatment D with all being significantly different ($p < 0.05$) from the linear portion of the FG curve.

Table 5. Quadratic slopes for PET treatments according to SAS output.

Treatment	Mean	t grouping		
Oil	-0.009625		D	
*SPI	-0.0007122		D	C
H ₂ O	-0.0006616	B	D	C
HMWFG	-0.0005395	B	D	C
HPMC	-0.0004275	B	A	C
Air	-0.0003932	B	A	
BG	-0.0003671	B	A	
FG	-0.0003602	B	A	
Starch	-0.0001464	B	A	

Data was inverted from SAS output so table would read largest to smallest slope. Significant difference at 0.05 level is indicated by different letters; *n=1, all others n>2

Quadratic group A, Figure 16, includes Starch, FG, H₂O, Air, and HPMC. These treatments have the smallest incline in slope. Quadratic group B, Figure 17, includes Air, BG, FG, H₂O, HMWFG, & HPMC. Group C in

Figure 18 includes H₂O, HMWFG, HPMC, and SPI. Group D represents treatments, H₂O, Oil, and SPI (see Figure 19).

Comparing PET Linear & Quadratic Slopes

Linear and quadratic slopes are grouped similarly, with some differences (see

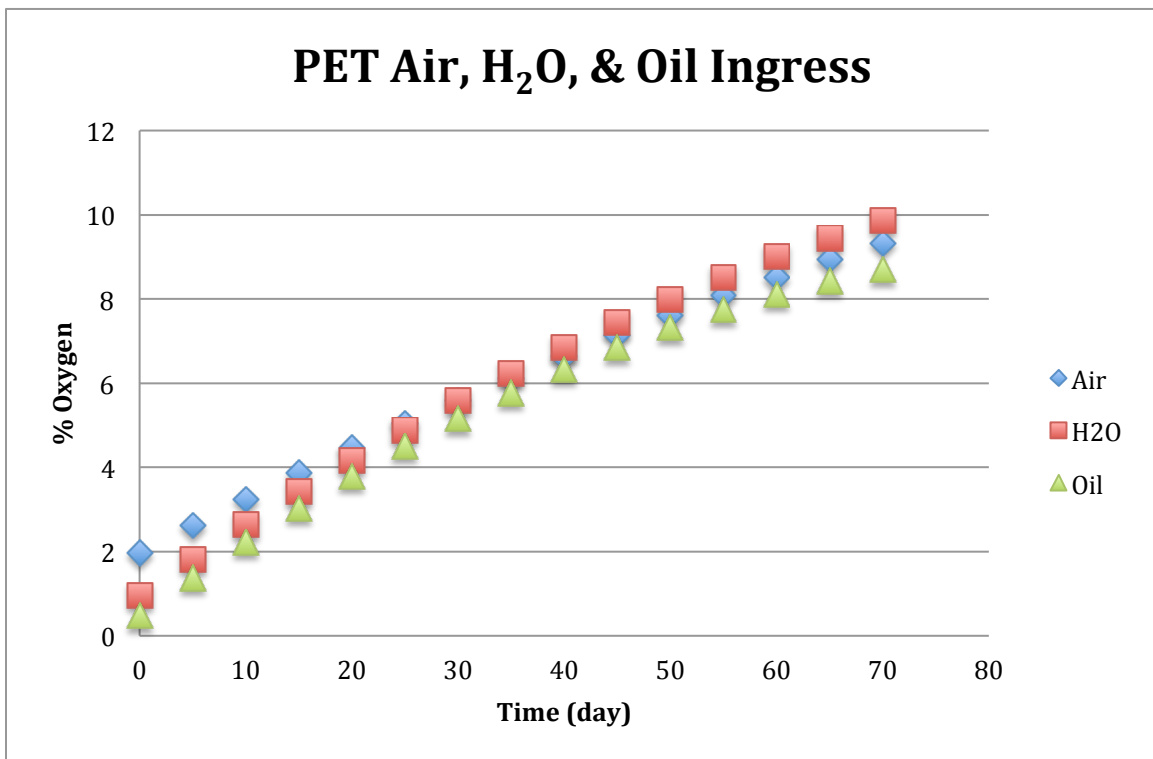


Figure 22. Graphical representation of Oil, Air and water treated PET pouches.

H₂O treated PET is also amongst the poorest oxygen barriers.

H₂O treated PET is also amongst the poorest oxygen barriers. This research suggests that water affects PET because the ingress of oxygen in H₂O treated pouches was significantly higher ($p < 0.05$) than Air treated pouches (Figure 203). Because the external retort treatments were identical, it can be assumed that the difference is related to the high internal water activity on the inside of the water treated PET pouch.

Below average barriers were grouped into linear B (Figure 11) and quadratic slope C (

Figure 18). H₂O, HMWFG, and HPMC are common to both of these linear and quadratic slopes. SPI is also included in the quadratic grouping, but excluded from the linear grouping.

Above average barriers were grouped into linear C (Figure 12) and quadratic B (Figure 17). HMWFG, HPMC, Air, and BG were common in both the linear and quadratic slopes. Starch was included in the linear section, but not the quadratic section suggesting its barrier properties increase over time. While, H₂O and FG were included in the quadratic slope section but not the linear. Water also improves its barrier properties over time. FG initially provides a good barrier, but weakens over time.

The pouches that had the best barrier are linear group D (Figure 13) and quadratic group A. (Figure 16). Treatments of Air, BG, HPMC, Starch, and FG fall into both groupings and did not have any significant difference at either part in their slopes. They have the slowest ingress of oxygen compared to all other statistical groupings. While slopes within these groups are not significantly different, changes in slope order did occur. The linear portion of the starch treatment provided the 5th best barrier, however it

). Air was used as a control, as only a paper towel was sealed into the pouch to increase headspace. Starting with the poorest barriers, treatments SPI, Oil, and H₂O are represented in linear group A (Figure 9) and quadratic group D (Figure 19).

Oil significantly decreased the barrier properties of Air treated pouches. This is important because oil is typically packaged in PET bottles. PET bottles are thicker than Pet films and have not been subjected to a high temperature and pressure process. However, Ameri Khaneghah, & Shoeibi (2012) found that the type of oil stored in PET bottles was as important as storage temperatures. Storage of all oils below 25°C was best to prevent rancidity. Many LAF's also use oil for its organoleptic qualities. Once LAF's are shelf stable, storage temperature and oil type will still affect the shelf life of the package. Packages may still need refrigeration of promote shelf life. A graphical comparison between oil, H₂O, and air can be seen in Figure .

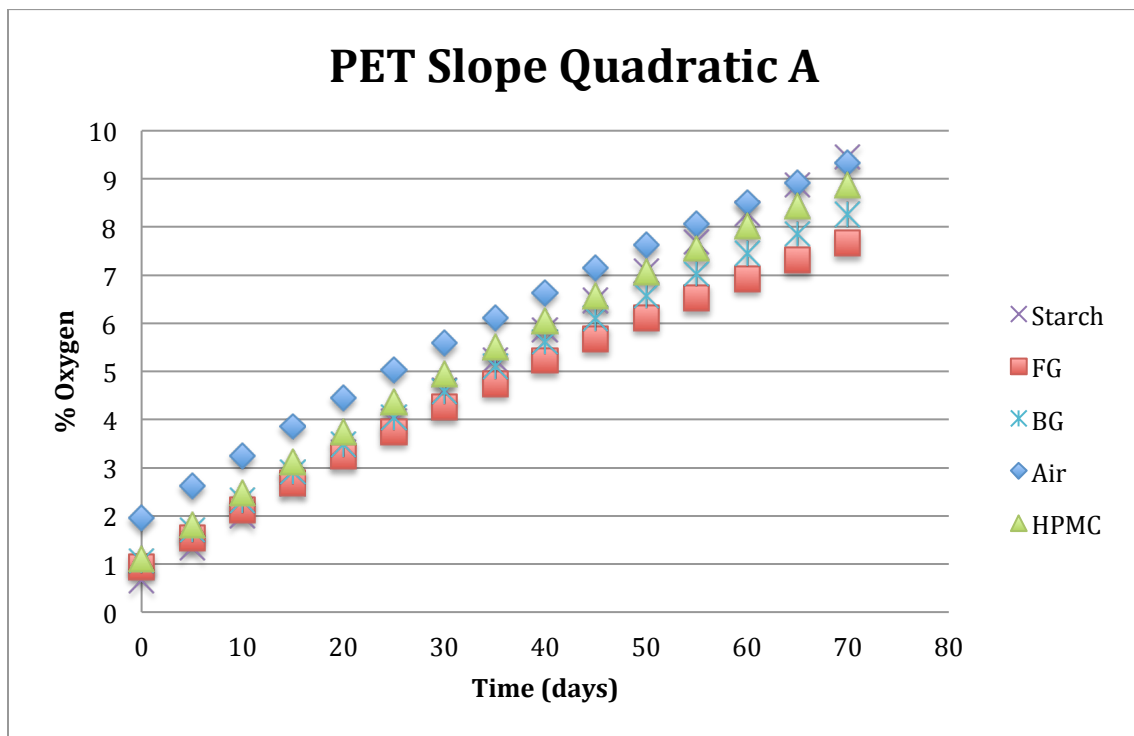


Figure 16. Quadratic slope group A for PET treatments.

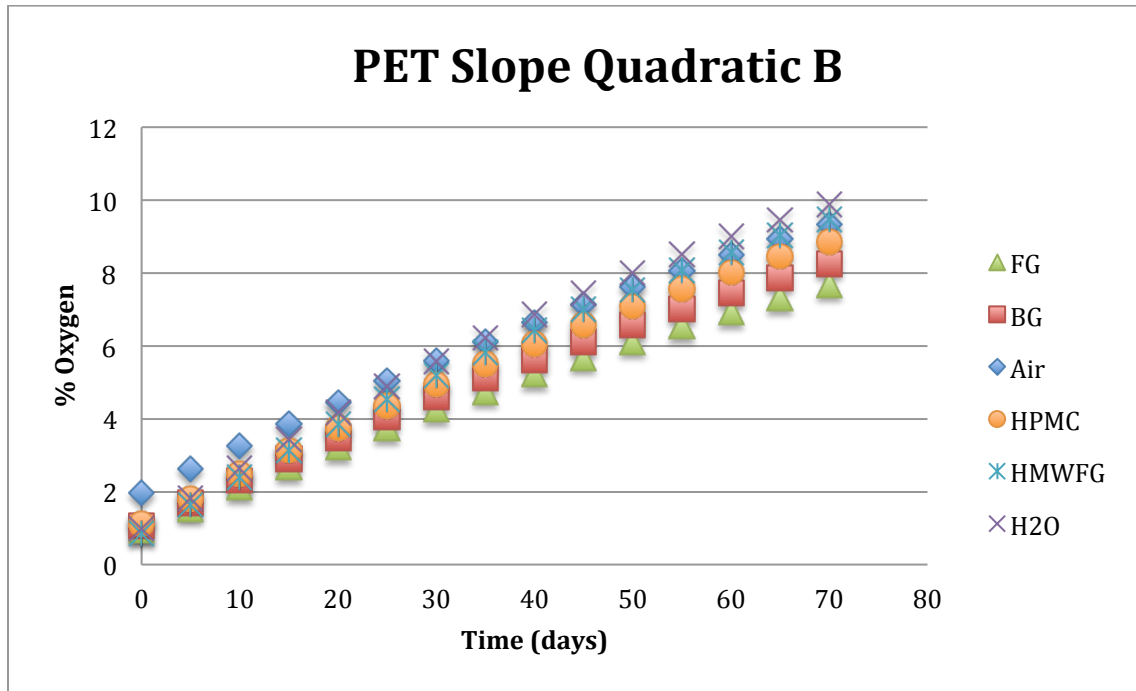


Figure 17. Quadratic slope group B for PET treatments.

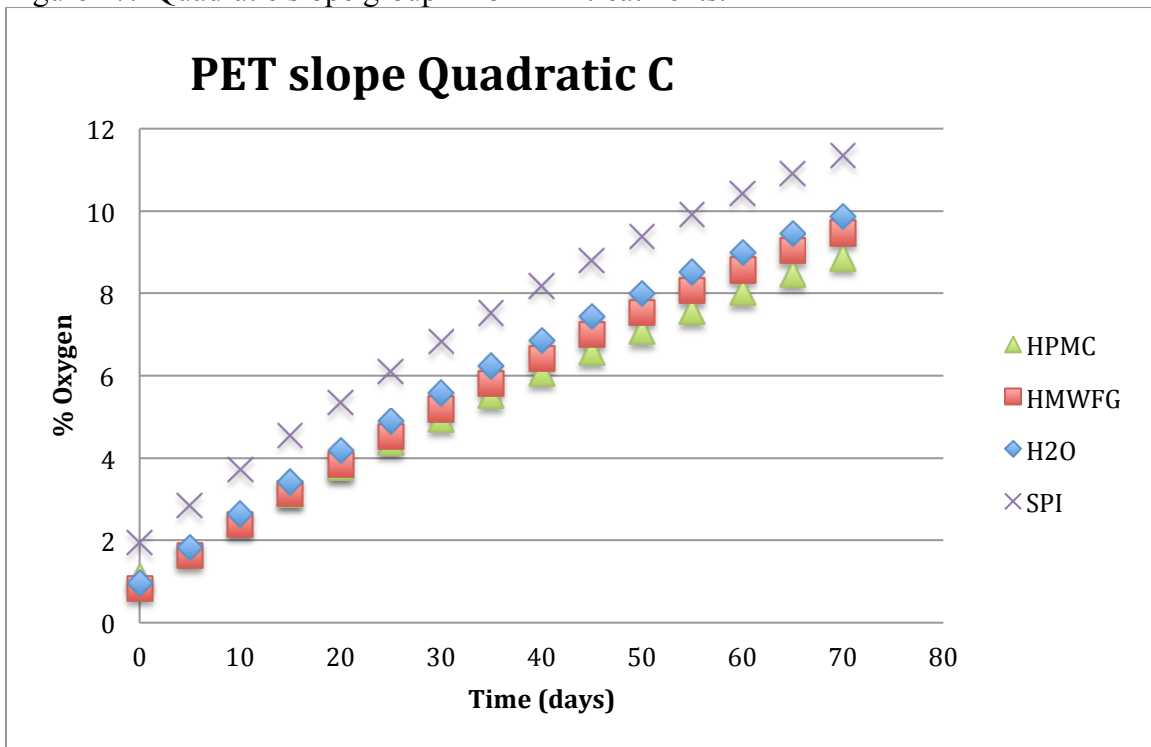


Figure 18. Quadratic slope C group for PET treatments.

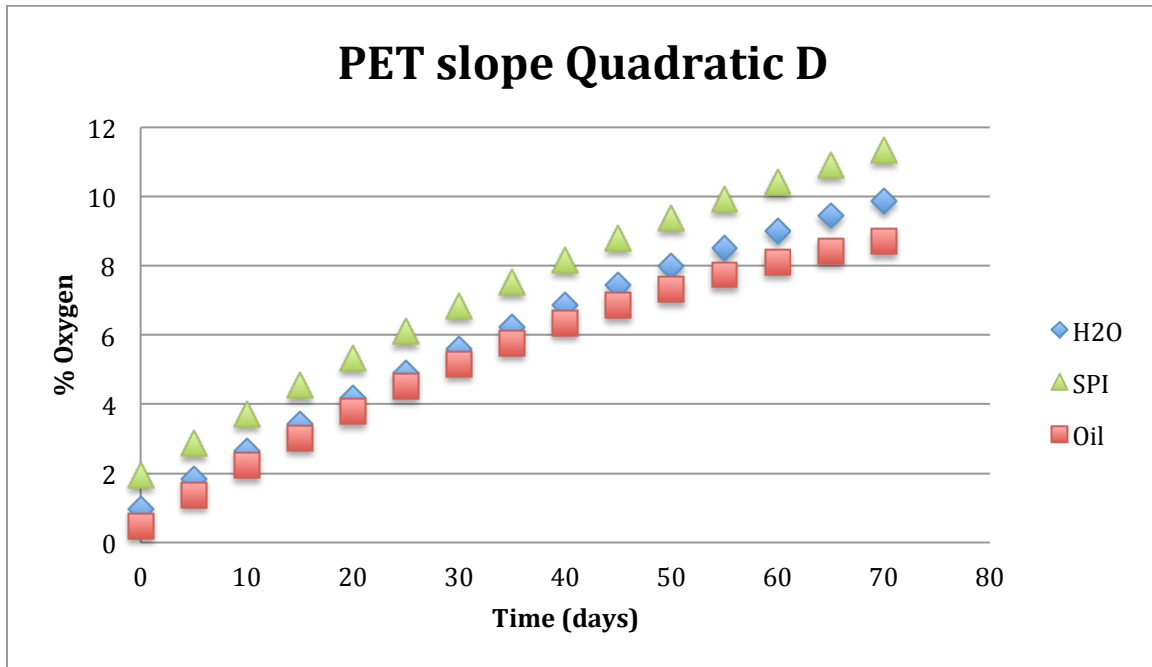


Figure 19. Quadratic slope D for PET treatments.

Table 6. Statistical analysis of the linear and quadratic slopes of PET pouches.

Treatment	Linear slope	Sig.	Quadratic slope	Sig.
Air	0.133 ± 0.009	D,C	-0.0004 ± 0.00005	A,B
BG	0.128 ± 0.013	D,C	-0.0004 ± 0.00005	A,B
FG	0.121 ± 0.008	D,C	-0.0004 ± 0.0006	A,B
H ₂ O	0.174 ± 0.046	A,B	-0.0007 ± 0.00025	B,D,C
HMWFG	0.161 ± 0.032	A,B,C	-0.0005 ± 0.00017	B,C
HPMC	0.141 ± 0.00002	B,C	-0.0004 ± 0.00002	A,B,C
Oil	0.185 ± 0.006	A	-0.0004 ± 0.00002	D
SPI	*0.184	A	-0.0007	D,C
Starch	0.136 ± 0.014	B,D,C	-0.0001 ± 0.00035	A

Significant difference (Sig.) at 0.05 level is indicated by different letters; Mean ± standard deviation. *n=1, all others n>2.

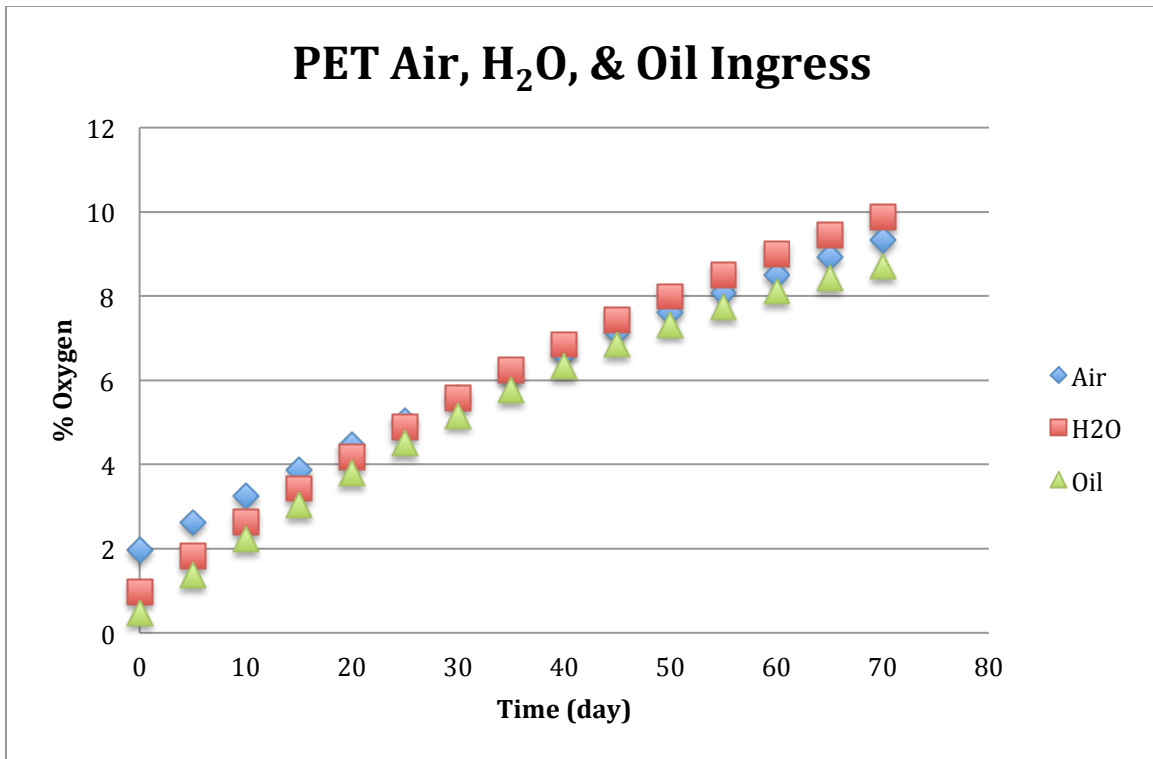


Figure 22. Graphical representation of Oil, Air and water treated PET pouches.

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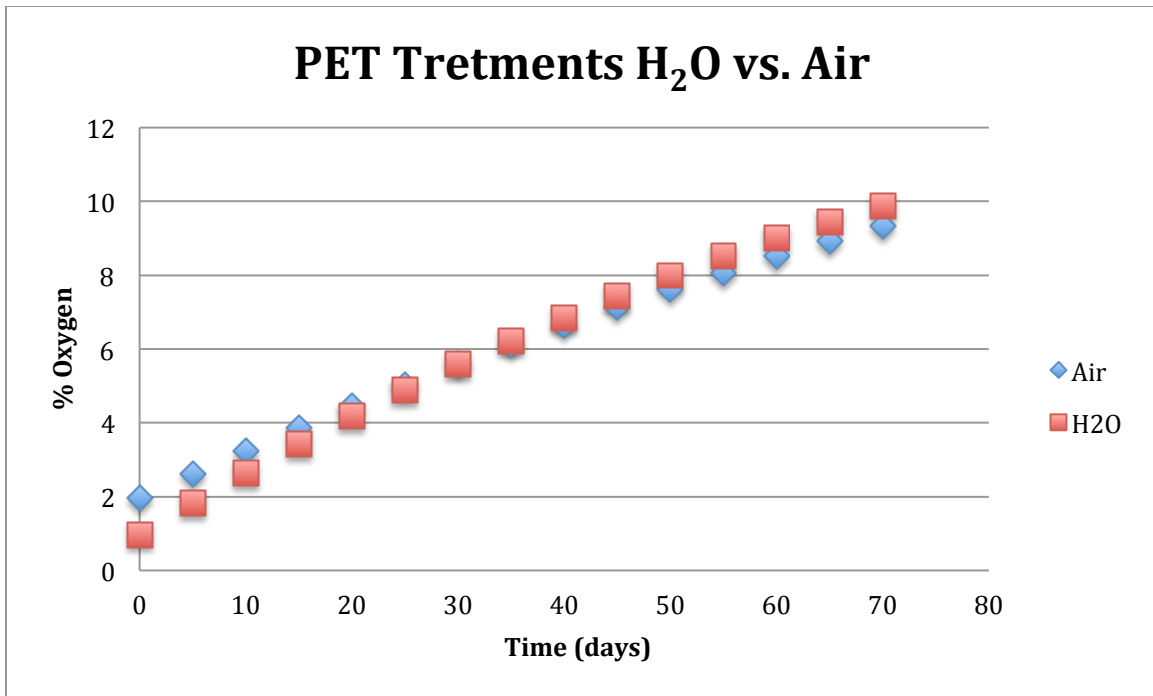


Figure 20. Graph comparing PET water vs. Air.

provided the best barrier in the quadratic portion, meaning it provides a better barrier over time.

AmPac Pouches

All treated AmPac pouches, excluding oil, did not show an oxygen ingress trend. Oil treatments showed an increase from ~0.5% oxygen to ~2% after 65 days. At the end of testing, Oil could be easily felt around the seal area of the pouches and the bulk of the pouch was slightly tackier than pouches not containing oil. This suggests that Oil is easily able to migrate through the seal area, but also able to migrate through the pouch itself.

Some of the water treated samples (See Appendix C, PET H₂O) showed an influx of oxygen from ~0.75 to ~1.75 during the first 5 days. Then the oxygen level plateaued with no additional oxygen ingress. This leveling off confirms the effectiveness of the barrier.

Ampac pouches were filled between ~0% and 2% percent oxygen. After 60 days, the oxygen had not permeated into the pouch. This suggests that when using high barrier films starting with as little oxygen as possible in the pouch is just as important as oxygen ingress over time. This is especially true for pouches treated with oil, as they were they only samples that showed any ingress.

Comparing Pouch Materials

Oil had a negative effect on all three materials studied. Some of the oxygen permeated through the films itself and some occurred through the seal area. When oil was used as a food ingredient, oxygen ingress increased at a faster rate in all the materials studied. In CPP pouches this is evident as headspace oxygen increased to ambient conditions in ~7 days whereas all other CPP treatments increased over ~25 days. This diffusion occurred mostly through the plasticized CPP. In PET pouches, the linear and quadratic slopes of oil treatments were significantly ($p < 0.05$) steeper than PET pouches treated with Air. PET needed to be melted together to create a seal, it is possible that the heat seal area allowed more oxygen ingress compared to the pouch material itself (Kraas & Darby, 2010) despite the pouches being slightly tacky with Oil at the end of sampling.

The Ampac film contained both PET and CPP layers and was the only Ampac pouch to increase in oxygen throughout the duration of the study. Oil will plasticize CPP

and decrease the oxygen barrier properties of PET. Since these materials are often used to package LAF attention should focus on food formulations high in oil. Since oil will negatively affect the shelf life of these flexible retort packaging materials on all levels of the packaging.

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CHAPTER V

CONCLUSION

Foods are classified according to their water activity and acidity. When food has a water activity above 0.85 and above a pH above 4.6, it is considered a Low Acid Canned Food (LACF). These foods have the optimum environment for the growth of bacteria due to their available water and low acidity. However, when packaged in high barrier packaging materials, the minimal amounts of oxygen allow for the growth and proliferation of anaerobic bacteria like *Clostridium botulinum*. This bacterium produces a neurotoxin that can be deadly to humans.

LACF's are required to be thermally processed to ensure sterility and protection against the growth of *C. botulinum*. This can be achieved during a high (> 212°F) temperature retort process. Historically, low acid, shelf stable foods have been packaged in metal cans, however packaging of these foods is migrating towards flexible retort pouches. Flexible retort pouches are more cost effective because of low shipping and storage costs.

However, the retort process is very stressful on packaging materials and multiple (3 or 4) laminated layers are needed to achieve the mechanical and barrier properties needed. Typical retort layers include a food contact layer, one or more barrier layers, and an outer layer. Traditionally, layers are sourced from crude oil or metal. Due to the environmental concern associated with crude oil and metal not being microwavable, recent research has focused on the use of natural materials as a possible film layer.

Many naturally occurring substances, like carbohydrates and proteins, are film formers and have excellent barrier properties in low humidity environments. However, when in contact with water, they lose their mechanical and barrier properties. Carbohydrates, proteins, and lipids are also common food ingredients in LACF's. The aim of this research was to assess how food ingredients affect the oxygen barrier properties of CPP, PET, and an Ampac trial film.

It was found that Mocon Ox-Tran data from the treated CPP films showed differences in the oxygen barrier properties. However, when compared to OxySense analysis, there was no real difference in oxygen ingress over time. Mocon analysis gives a baseline for film choice when films are clean, dry, and unprocessed. OxySense data shows how a pouch will react after processing throughout the duration of a shelf life study.

Oil negatively affected all pouch materials tested. In CPP pouches, this was due to sorption of oil and then plasticization of the film. In PET films, oil was amongst the poorest of barriers. In the Ampac trial pouches, oil treatments were the only pouches that allowed oxygen to permeate into the pouch. However, when oil was emulsified, the CPP was not plasticized. These are important conclusions as food formulation and retort pouch materials should be considered when packaging and processing shelf stable, low acid foods.

APPENDICES

Appendix A
CPP Sample Data

Graphs in Figure 21 through Figure 28 represent all samples collected for the CPP pouches treated with 10 different food ingredients. Trendline analysis was based on these individual curves. A list of trendline equations used for analysis and corresponding R^2 can be found in Table 9.

Due to the filling and sealing methods, a few samples were removed from analysis. Samples were removed base on drastic oxygen influx or dot errors. In Figure 21, the sample CPP Air-004 was removed due to rapid influx of oxygen. Inspection of this pouch on day 2 revealed an audible leak at the seal. In Figure 22, sample CPP BG-006 showed a drastic influx of Oxygen. An audible leak caused the pouch to quickly reach 21% O₂. No samples were removed from CPP FG, Figure 26, or from CPP water, Figure 27.

CPP HMWFG samples 005 & 006 did not survive the initial filling and sealing process. Redo-001 and redo-002 replaced these pouches. Figure 25 displays data for CPP HMWFG samples. CPP HMWFG redo-002 pouch was removed due to dot failure. On day 34, OxySense measurement stated the percentage of oxygen was 18.38%. When

measured with a Mocon headspace analyzer, oxygen percent was 21%. Inspection of the dot revealed discoloration and therefore sample was removed.

Figure 26 shows data for CPP HPMC pouches. HPMC presented many problems during filling and sealing. A layer of HPMC solution interfered with the resealing. In all samples, 2-3 sealing attempts were needed to properly seal the pouch. Leaked pouches resulted in eliminating samples 002, 003, 004, and 005.

Table 7. Trendline Equations for CPP Treatment.

Sample	Sample Line Equation
Air	$Y = 1.495027577 + 1.940038418*(x) - 0.075136692*(x^2) + 0.001064138*(x^3)$
BG	$Y = 1.533249296 + 1.943561234*(x) - 0.072559438*(x^2) + 0.000981844*(x^3)$
FG	$Y = 2.669545779 + 1.809934075*(x) - 0.070208331*(x^2) + 0.001058151*(x^3)$
H2O	$Y = 2.062216676 + 1.929412959*(x) - 0.077076258*(x^2) + 0.001145781*(x^3)$
HMWFG	$Y = 2.483804183 + 1.802575715*(x) - 0.067852746*(x^2) + 0.000945334*(x^3)$
HPMC	$Y = 1.893089525 + 1.847552538*(x) - 0.067300828*(x^2) + 0.000894198*(x^3)$
Oil	$Y = 3.776243766 + 5.285936987*(x) - 0.627093342*(x^2) + 0.020638673*(x^3)$
SPI	$Y = 2.110603997 + 1.83806667*(x) - 0.070010823*(x^2) + 0.000967339*(x^3)$
Starch	$Y = 1.619001198 + 1.886638057*(x) - 0.075129131*(x^2) + 0.001187542*(x^3)$
WPI	$Y = 2.035723531 + 2.003479887*(x) - 0.086383438*(x^2) + 0.001430826*(x^3)$

Leaking pouches removed included Air 004, BG-006, HPMC-002-5, SPI-004, & Starch-006. Dot failure included WPI-002 & HMWFG Redo-002. H2O-002 had no data.

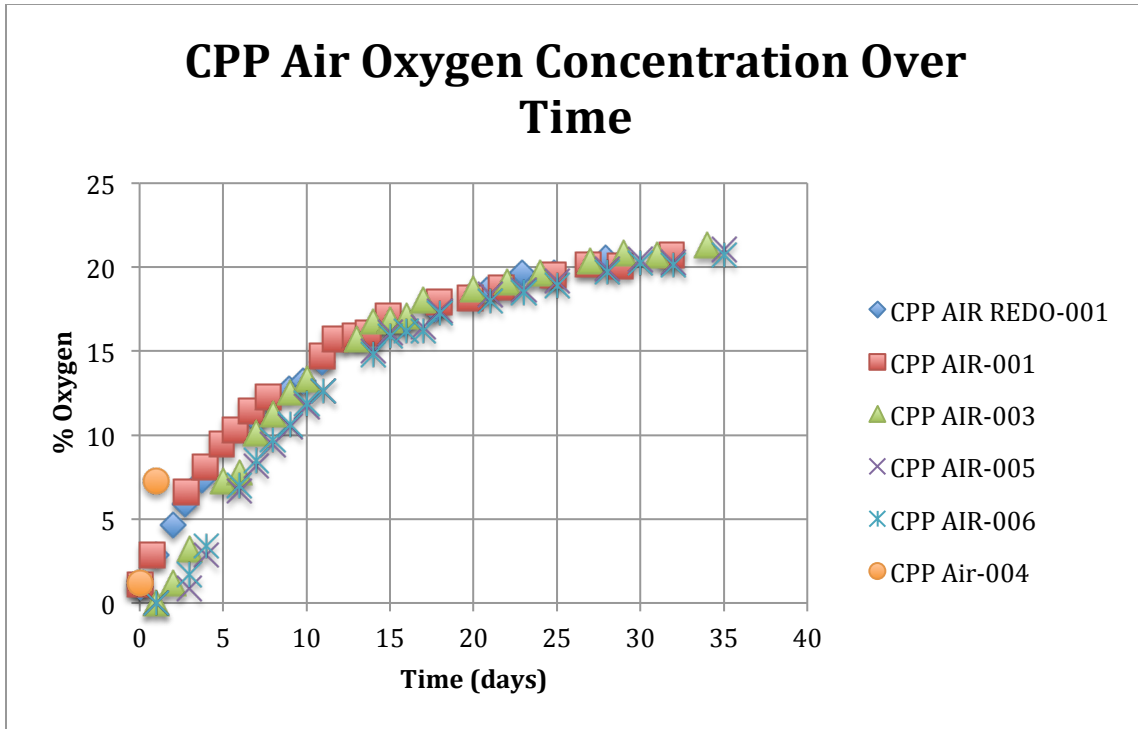


Figure 21. Oxygen Concentration over Time for CPP pouches treated with Air.

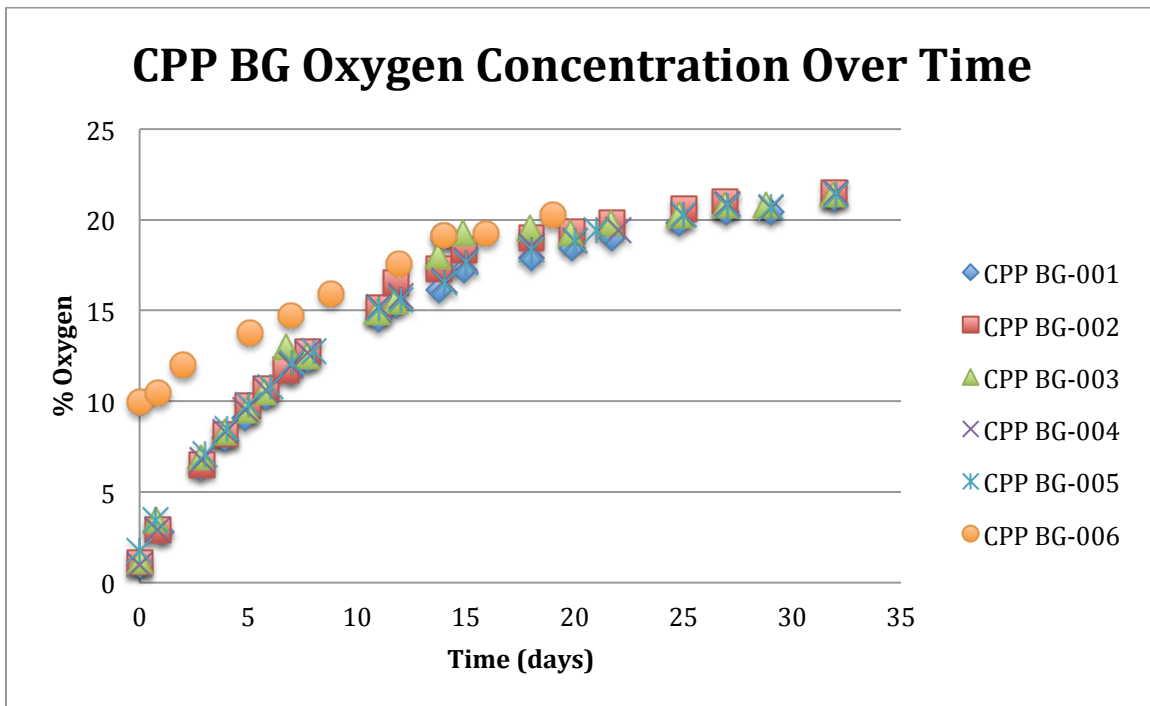


Figure 22. Oxygen Concentration over Time for CPP pouches treated with BG.

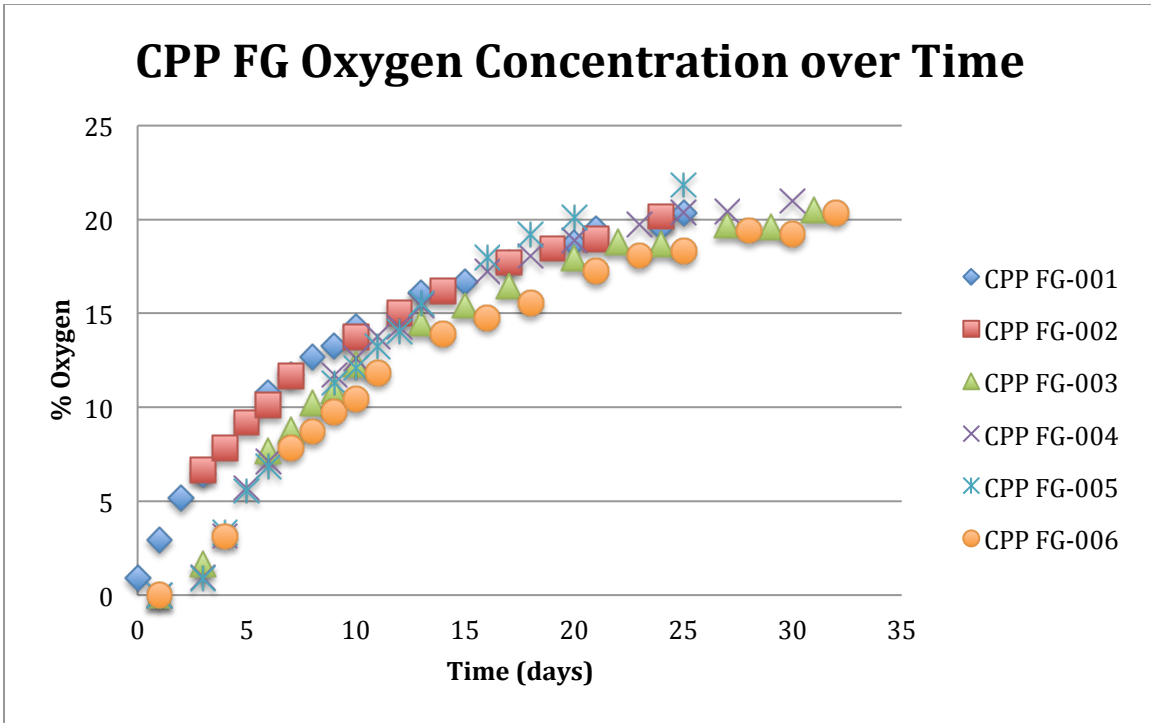


Figure 23. Oxygen Concentration over Time for CPP pouches treated with FG.

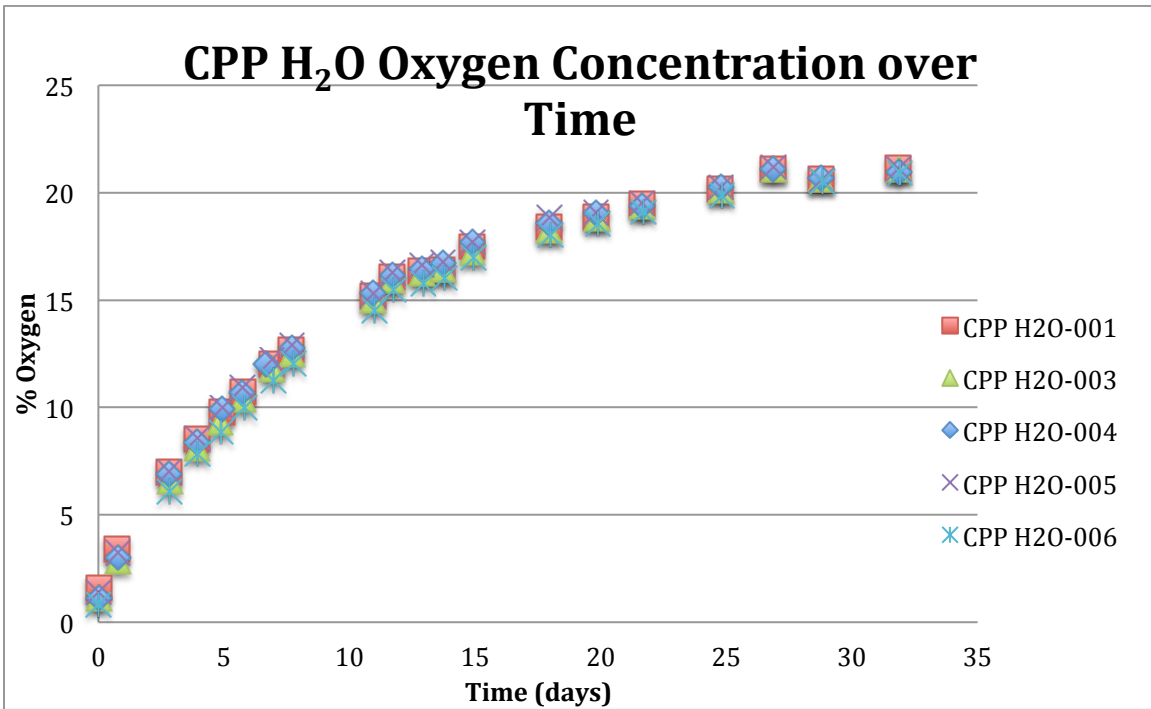


Figure 24. Oxygen Concentration over Time for CPP pouches treated with water.

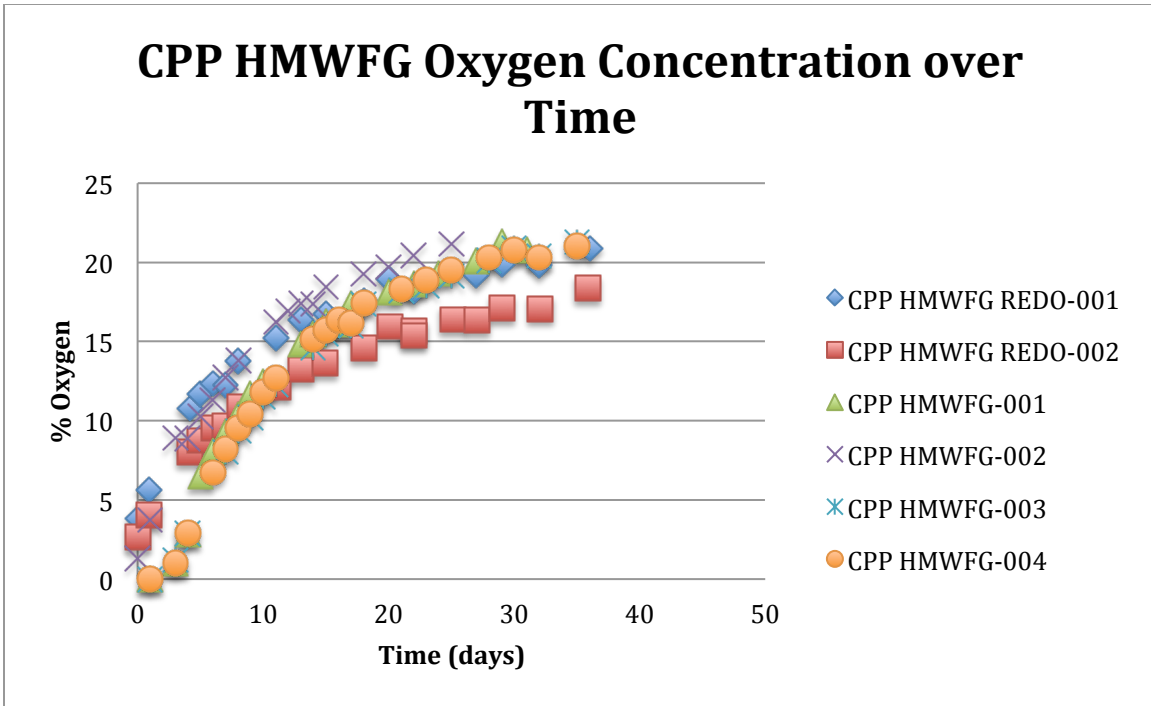


Figure 25. Oxygen Concentration over Time for CPP pouches treated with High Molecular Weight FG.

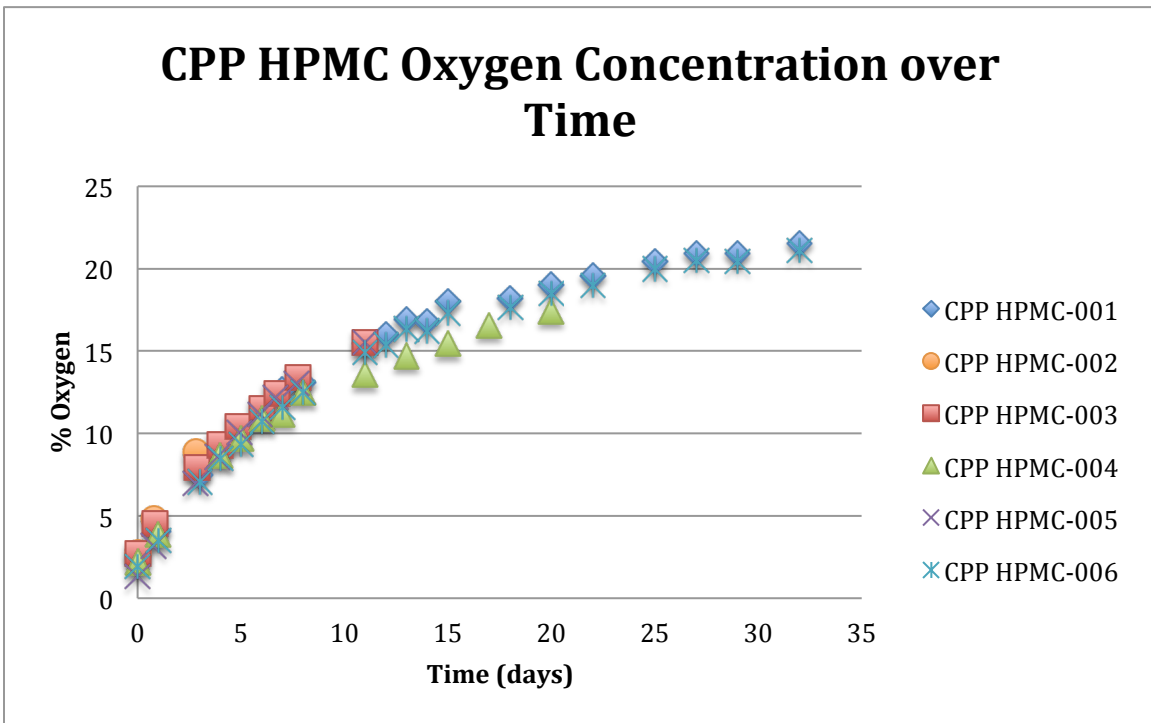


Figure 26. Oxygen Concentration over Time for CPP pouches treated with HPMC.

Two CPP Oil samples (001 & 005) did not survive the initial filling and sealing process. CPP Oil Redo 001 and 002 were used to keep sample numbers equivalent. No samples were removed for analysis. See Figure 27 for CPP Oil samples oxygen concentration over time. **InError! Reference source not found.1**, CPP WPI oxygen concentrations are graphed. Due to rapid influx of oxygen, CPP WPI 002 was removed from further analysis.

Figure 29 displays the oxygen concentration over time for CPP treated with SPI. Sample 004 was removed due to drastic influx of oxygen. Figure 30 displays the oxygen concentration over time for CPP treated with Starch. Dot failure resulted in the removal of the starch sample 006. OxySense data on 5/2/12 for sample 006 shows a percent oxygen value of 17.38%. The Mocon headspace analyzer measured 21% oxygen. Upon closer inspection of the dot, discoloration was noted.

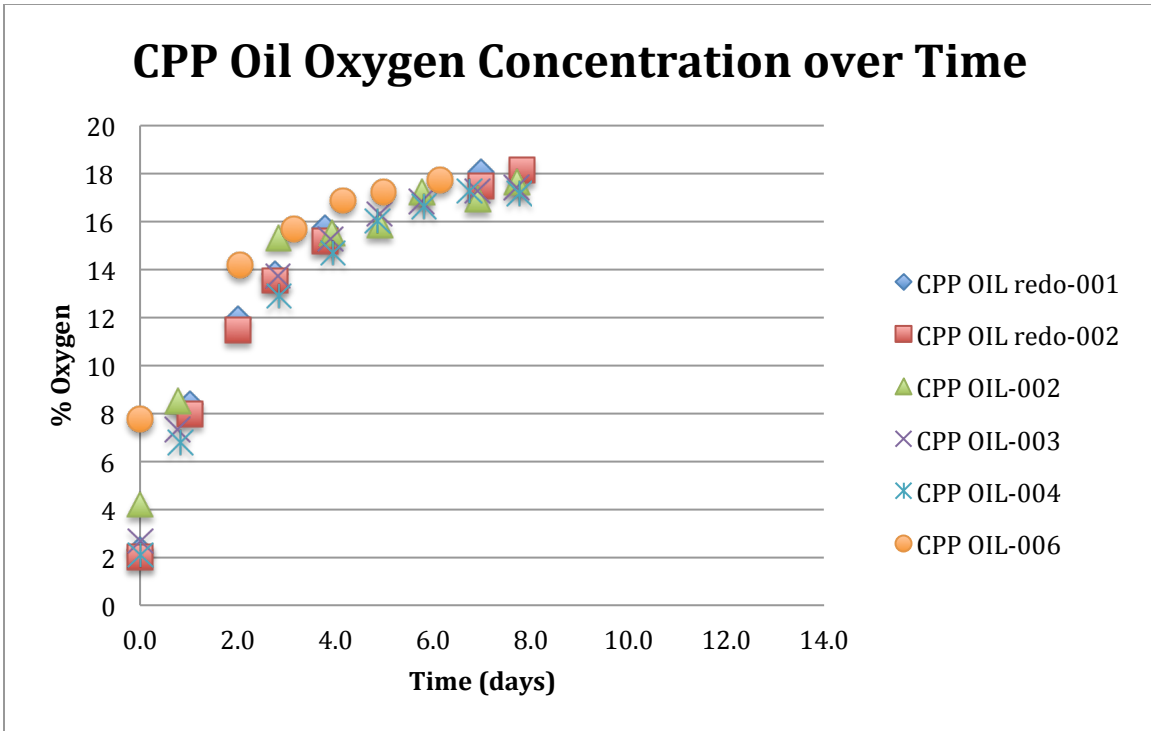


Figure 27. Oxygen Concentration over Time for CPP pouches treated with Oil.

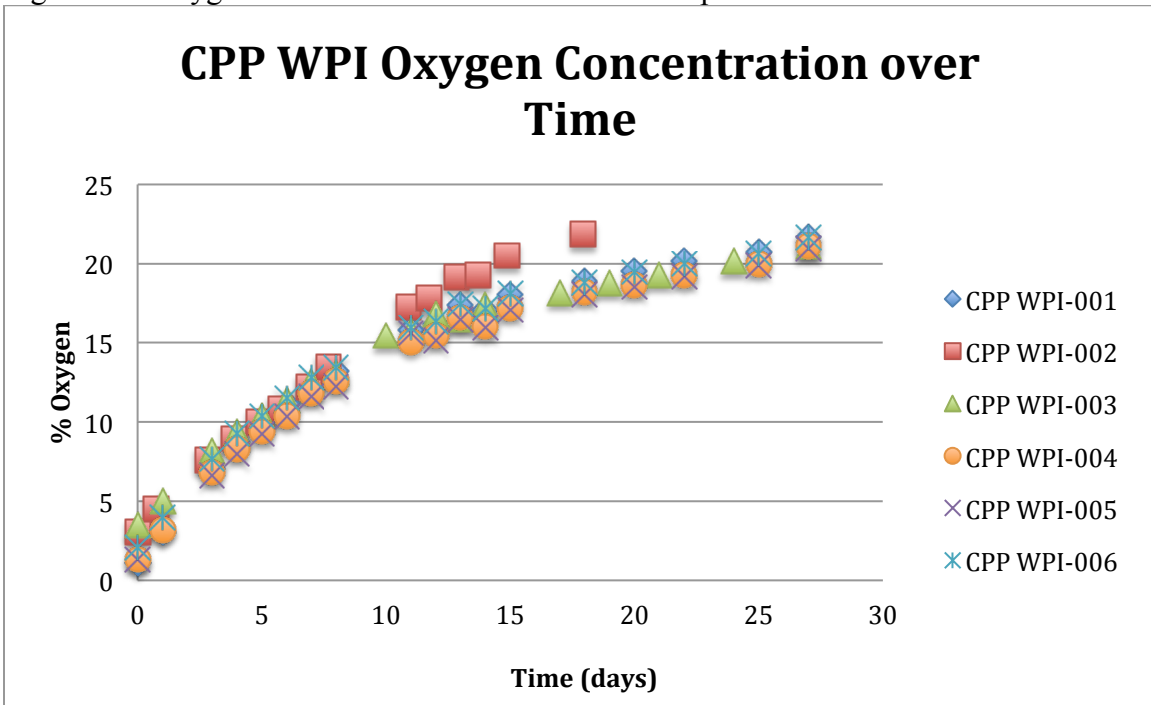


Figure 28. Oxygen Concentration over Time for CPP pouches treated with WPI.

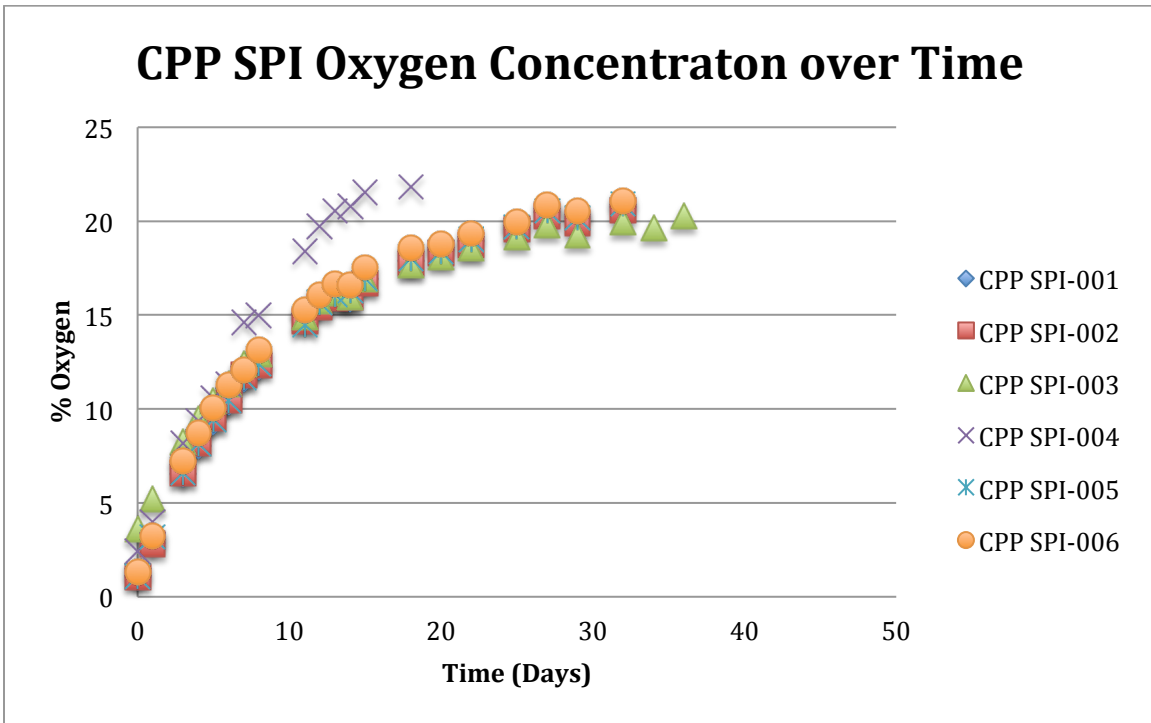


Figure 29. Oxygen Concentration over Time for CPP pouches treated with SPI.

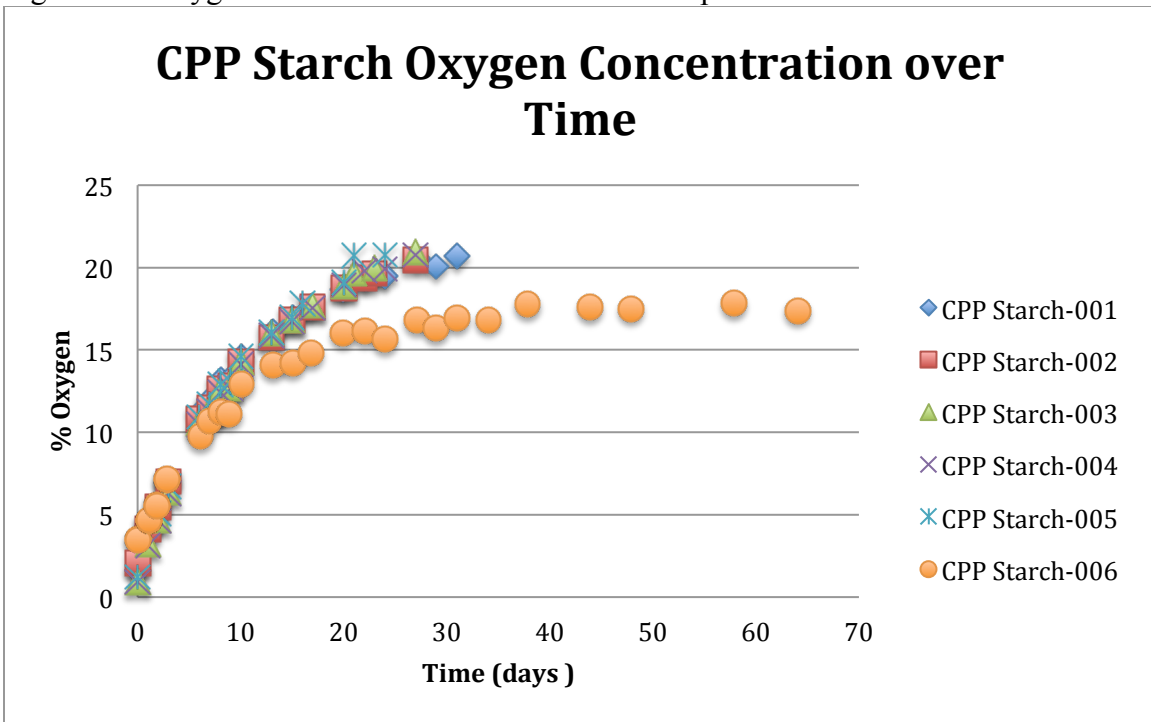


Figure 30. Oxygen Concentration over Time for CPP pouches treated with Starch.

Appendix B

PET Sample Data

Graphs in Figures 1-10 represent all samples collected for the PET pouches treated with different food ingredients. Trendline analysis was based on these individual curves. A list of these trendline equations and corresponding R^2 values are listed in Table 8.

It is a known fact that PET is a heat resistant material and it typically utilized in retort packaging for this characteristic. In this research, in order to achieve a hermetic seal, PET was melted together at 160°C. This greatly weakens the material around the seal area and created pinholes. In addition, pouches are very delicate due to the material

qualities. Some samples were popped or broken during testing due being handled with too much pressure. No samples were removed due to dot failures.

Sample number 001 was removed from PET treated with Air (Figure 31). Upon inspection of the data the pouch displayed an influx of oxygen more than double the rate of the other pouched in the series. An audible leak was not present, but a tiny pin hole or thinning of the material around the sealing area would cause this faster rate of ingress.

Figure 32 represents the data for PET pouches retorted with BG solutions. Samples 2 and 4 were removed due to leaks within in the seal area. The graph shows the ingress of Oxygen was 21% by day 15 for both samples. Other samples in the set were <10% at this same day time.

Table 8. Average trendline equations for PET treatments.

Sample	Line Equation
Air	$Y = 1.96100244 + 0.132710763x - 0.000393195x^2$
BG	$Y = 1.068566928 + 0.128417043x - 0.000367055x^2$
FG	$Y = 0.945363565 + 0.121365409x - 0.000360186x^2$
H2O	$Y = 0.968668367 + 0.173523477x - 0.000661618x^2$
HMWFG	$Y = 0.842082199 + 0.160974246x - 0.000539477x^2$
HPMC	$Y = 1.111284622 + 0.14068601x - 0.000427509x^2$
Oil	$Y = 0.478791205 + 0.184931535x - 0.000962507x^2$
SPI	$Y = 0.656913836 + 0.135914615x - 0.000146426x^2$
Starch	$Y = 1.96100244 + 0.132710763x - 0.000393195x^2$

PET pouches removed for leaking: Air-001; BG-002, 4; FG-002, 5-6; H2O-001, 4-6; HMWFG-002, 5; HPMC 001, 2, 4-5; Oil-001, 5; SPI-001-3, 5-6; Starch-002-3, 6; WPI-001-6. Pouches removed for no data PET Oil-003, 5.

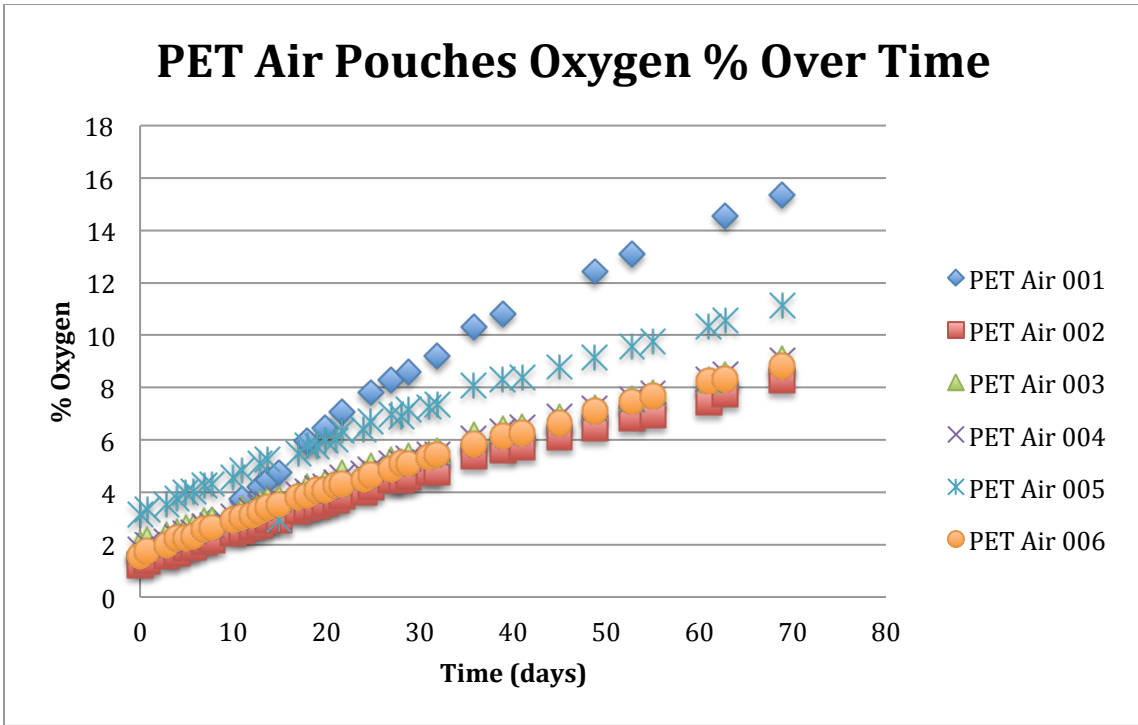


Figure 31. Oxygen concentration over time for PET pouches treated with Air.

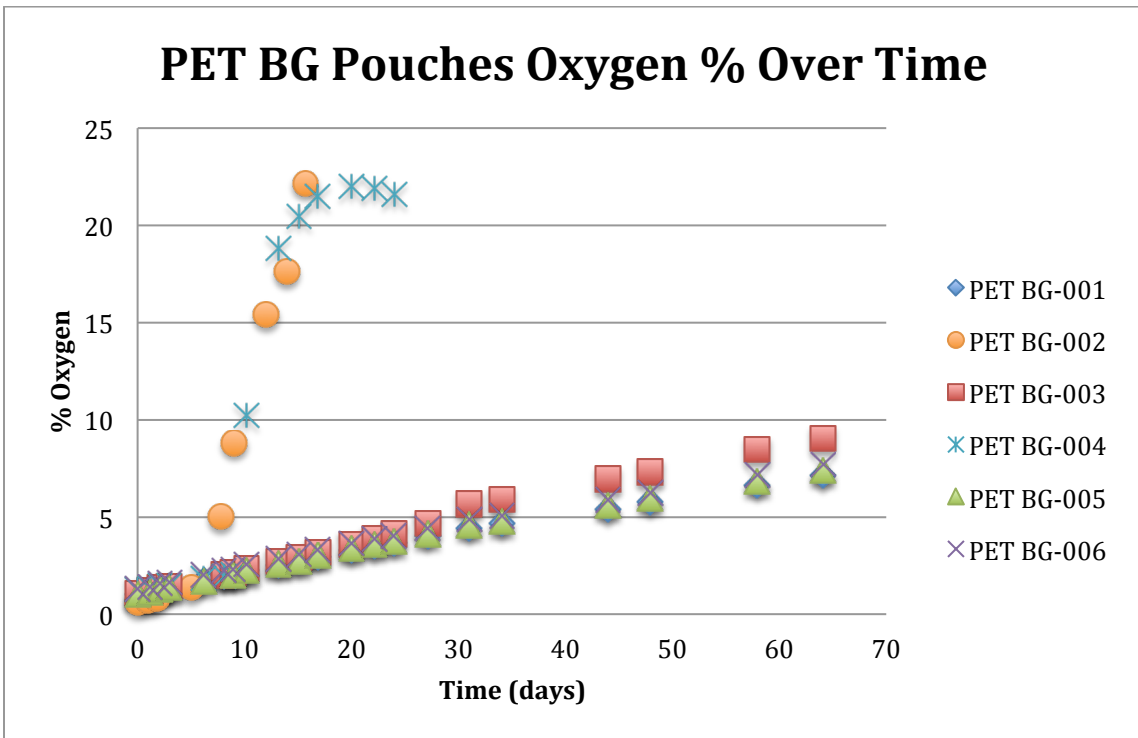


Figure 32. Oxygen Concentration over time for PET pouches treated with BG.

Samples 2, 5, and 6 were removed from the analysis for PET pouches treated with FG. In Figure 33, these graphs showed rapid leaking. Sample 6 showed rapid leaked that occurred soon after the resealing process. However, the data shows that both samples 2 and 5 began leaking a few days after sealing. The graphs follow a typical ingress similar to other pouches and then oxygen drastically moved into the pouches.

Samples 4 and 6 for PET treated with water sample 5 for PET treated with HMWFG were removed due to rapid ingress of oxygen, see Figure 34 and Figure 35 respectively. HMWFG sample 2 failed before the end of testing and therefore was removed from testing.

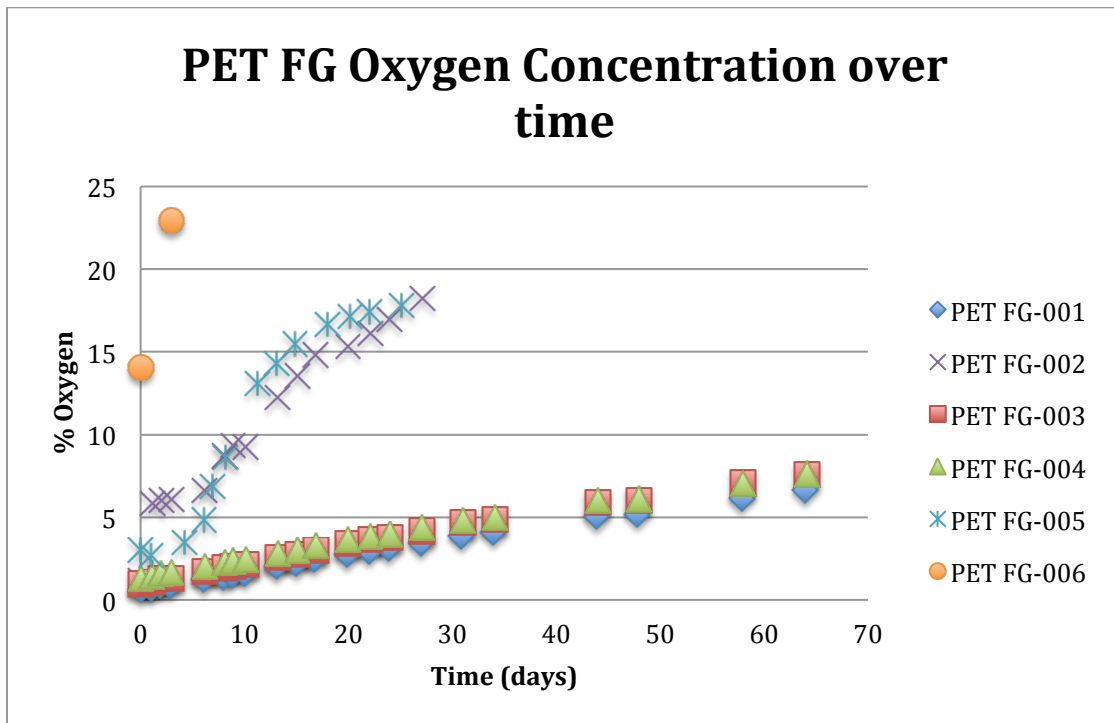


Figure 33. Oxygen concentration over time for PET pouches treated with FG.

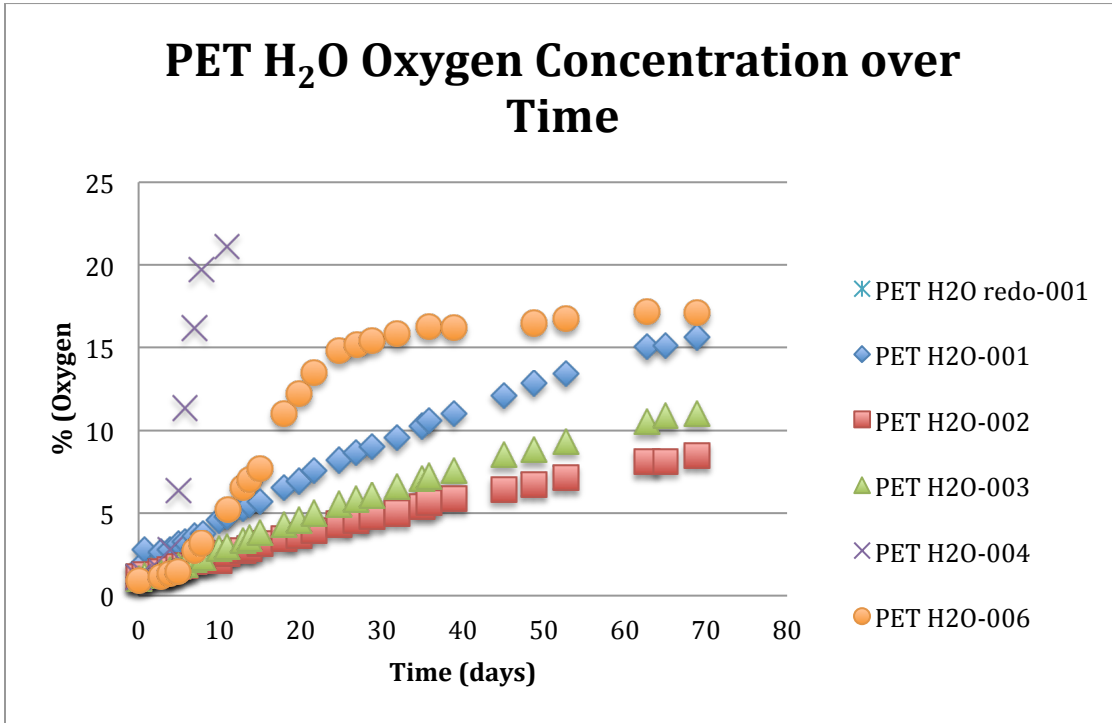


Figure 34. Oxygen Concentration over time for PET pouches treated with water.

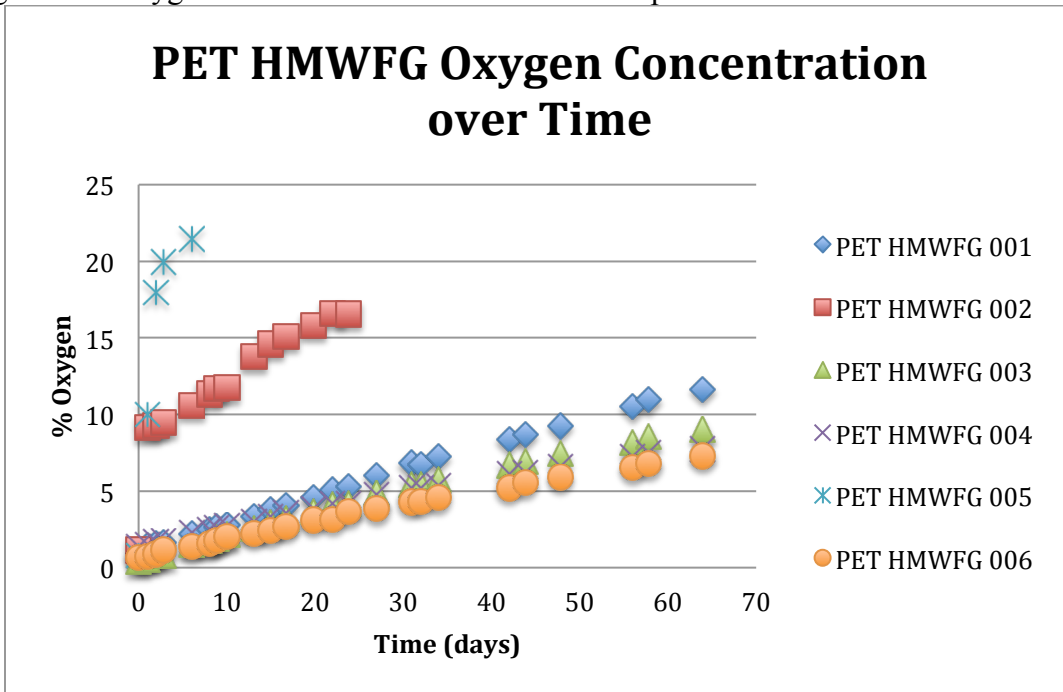


Figure 35. Oxygen concentration over time for PET ouches treated with High Molecular Weight FG.

Similar problems arose when resealing Pet HPMC pouches and CPP pouches. The HPMC layer that coated the inside of the pouch greatly interfered with resealing (melting) of the PET. Multiple attempts for sealing at 170°C were needed to effectively close the pouch below the septum. Samples 1, 2, 4, and 5 were removed due to rapid influx of oxygen. See Figure 36 for graphical interpretation of the data.

Figure 37 shows date for PET pouches treated with oil. For samples 2 and 3, no data was collected. Sample 1 was removed due to rapid influx of oxygen. Sample 5 started leaking before the end of testing. The start date of the leak was not determinable so the sample was removed. Figure 1 represents PET pouches treated with Starch.

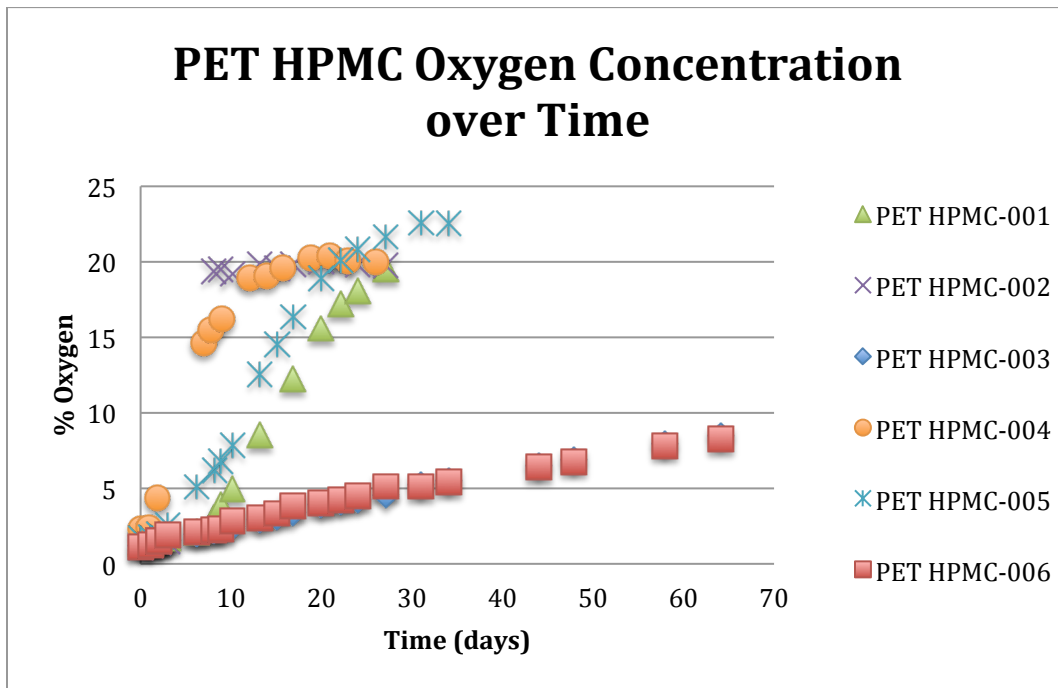


Figure 36. Oxygen concentration over time for PET pouches treated with HPMC.

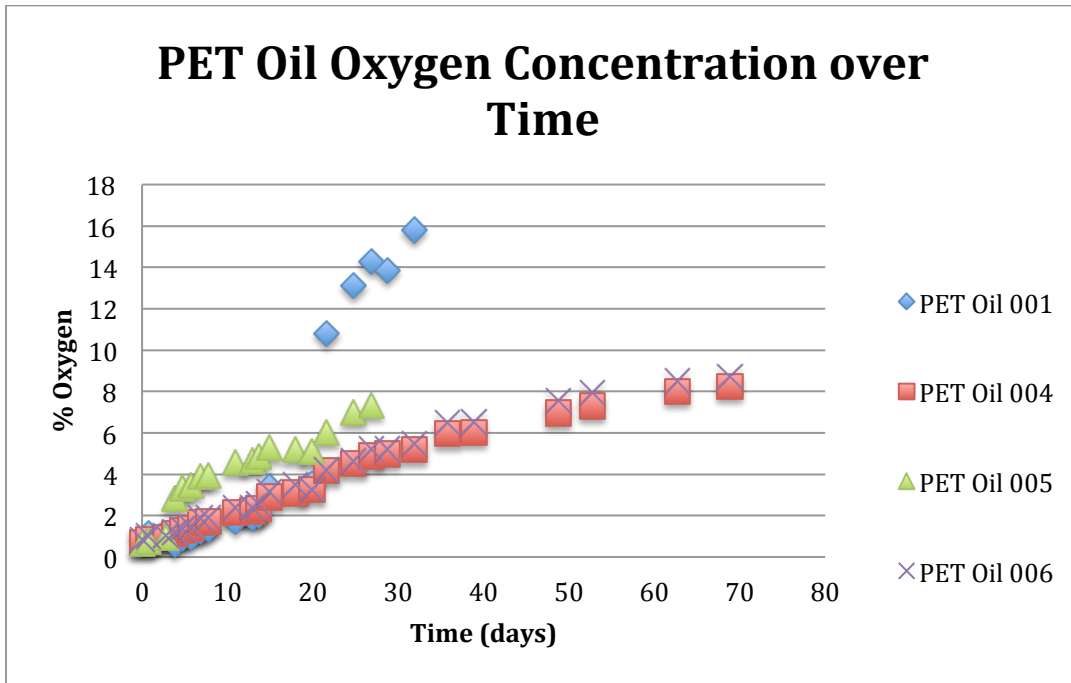


Figure 37. Oxygen concentration over time for PET pouches treated with oil.

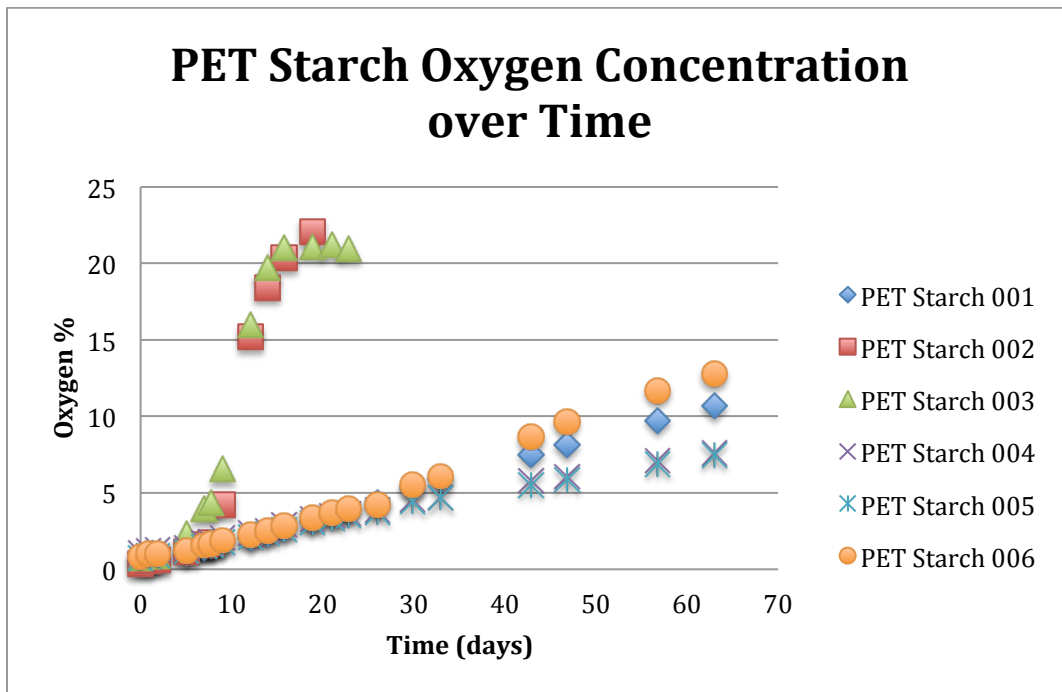


Figure 41. Oxygen concentration over time for PET pouches treated with Potato Starch.

Samples 4 and 5 were analyzed further. All others were eliminated due to gross or pinhole leaking.

Pet pouches treated with SPI and WPI, Figure and Figure 38, respectively, presented many similar problems. In SPI pouches, all but sample 004 was removed and in WPI pouches, all samples were removed due to either gross or pinhole leaks. WPI sample 3 was the only sample in that sample set that made it until the end of testing. However, upon reviewing the data, the pouch was removed due to leaking.

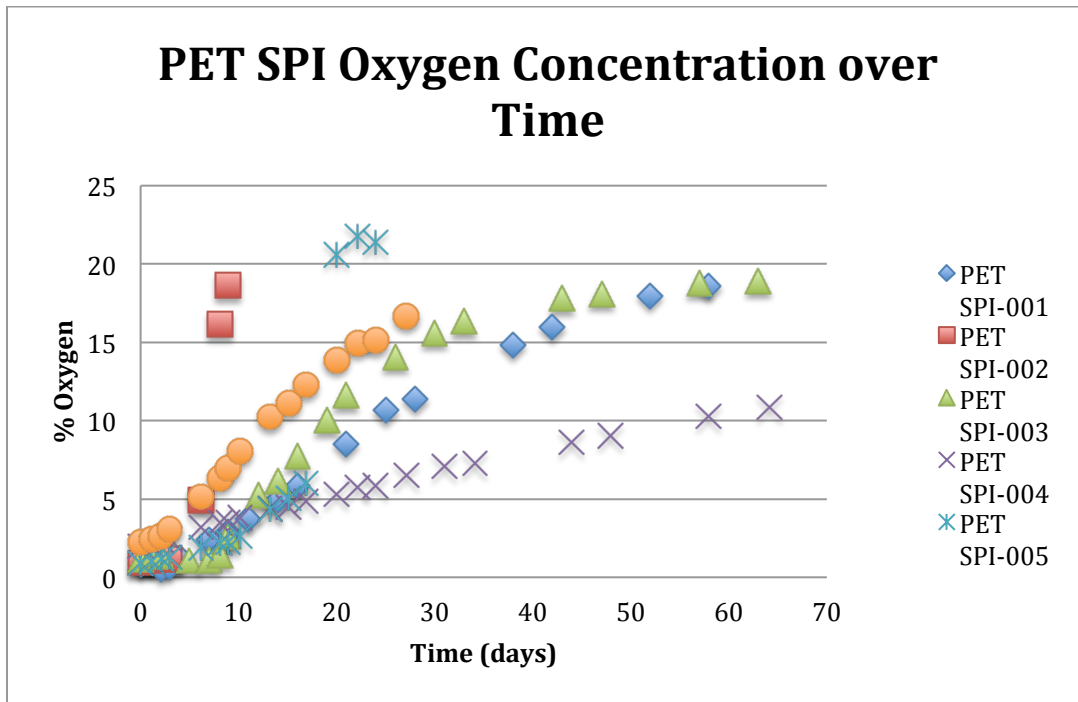


Figure 42. Oxygen Concentration for PET pouches treated with SPI.

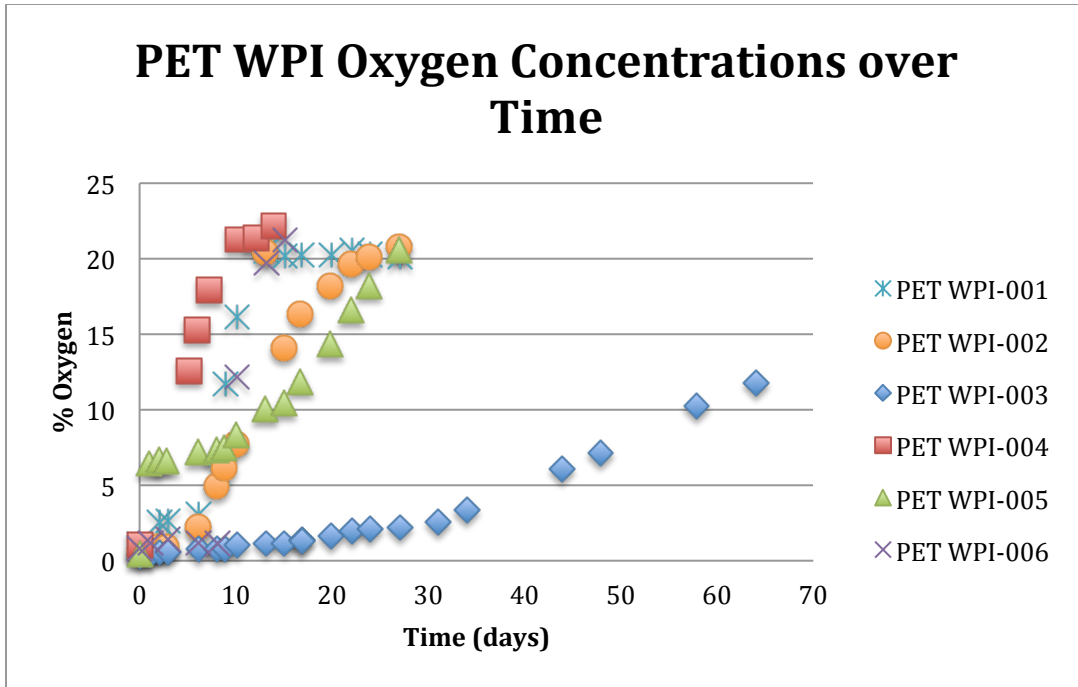


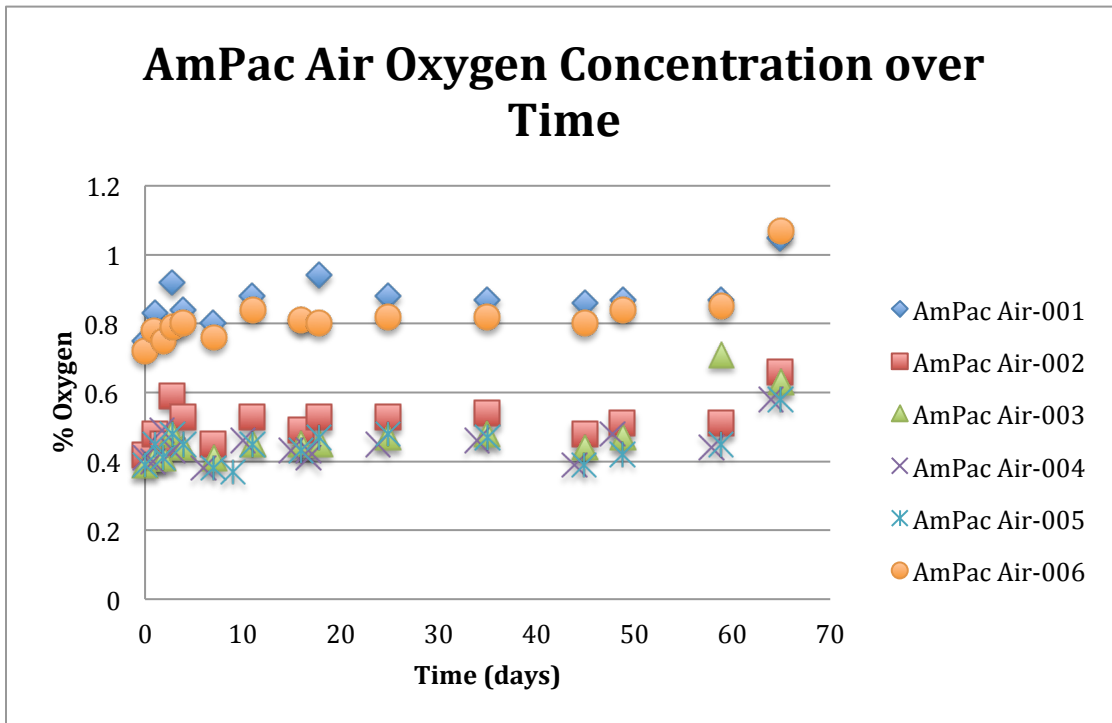
Figure 38. Oxygen Concentration over time for PET pouches treated with WPI.

Appendix C

AmPac Sample Data

Figures 44 through 53 display the sample data for AmPac films treated with ten different food ingredients. Trendline analysis was based on the individual sample data.

A list of trendline equations and corresponding R^2 values are represented in



. All treatments, excluding oil, had R^2 values <0.67 . Due to the low R^2 correlation values, trendline equations could not be used for further analysis as horizontal lines have no trend.

AmPac pouches treated with oil had trendlines with R^2 values between 0.88-0.97. No samples were removed from analysis.

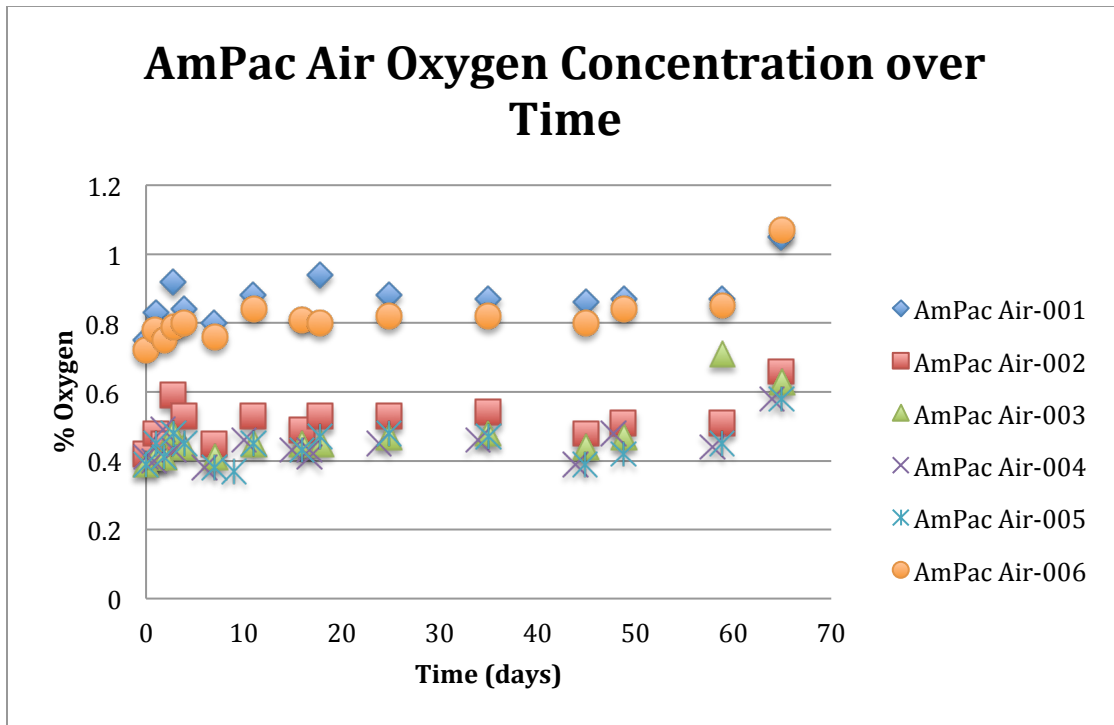


Figure 39. Oxygen concentration over time for Ampac films treated with Air.

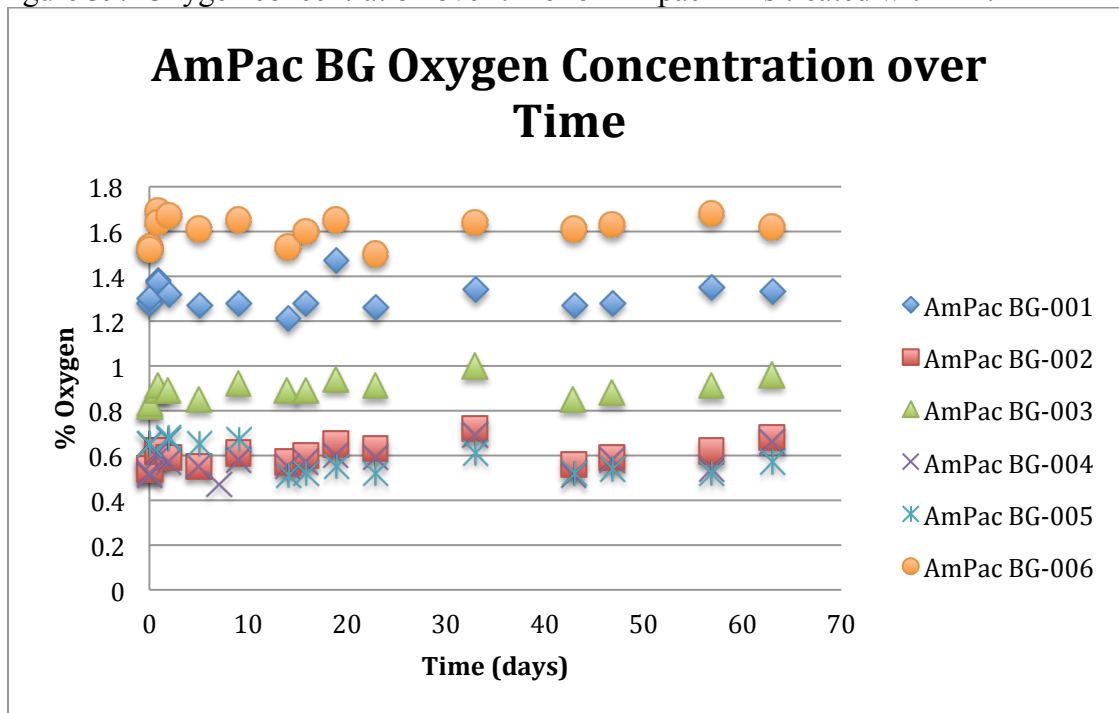


Figure 40. Oxygen concentration over time for Ampac films treated with BG.

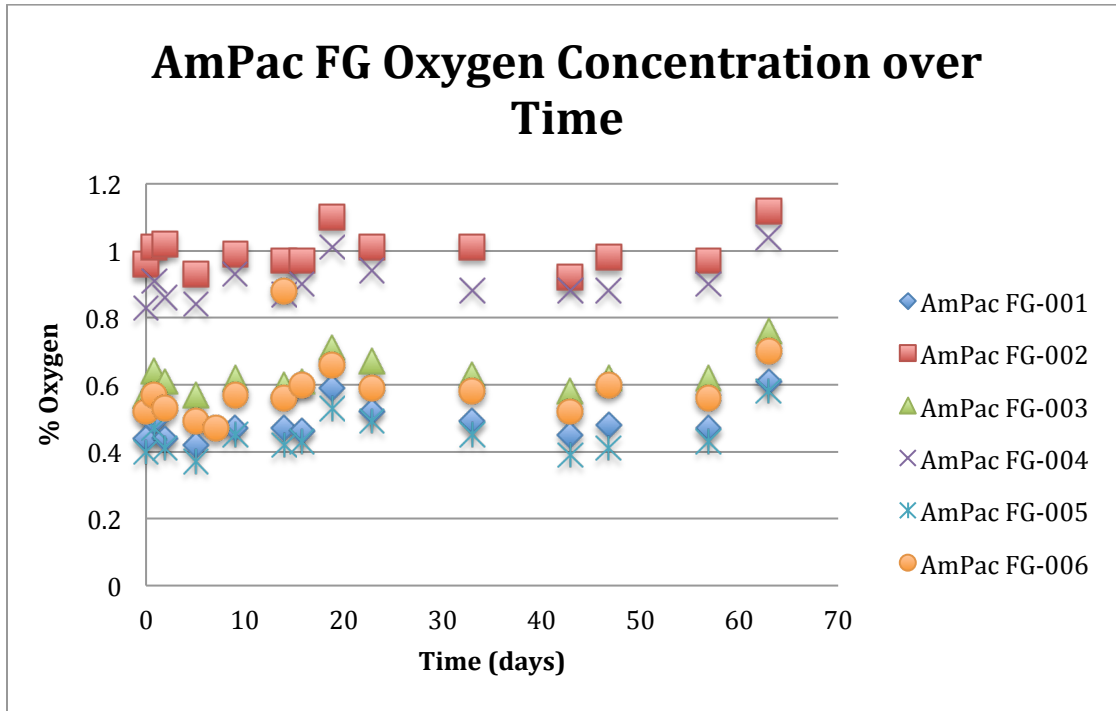


Figure 41. Oxygen concentration over time for Ampac films treated with FG.

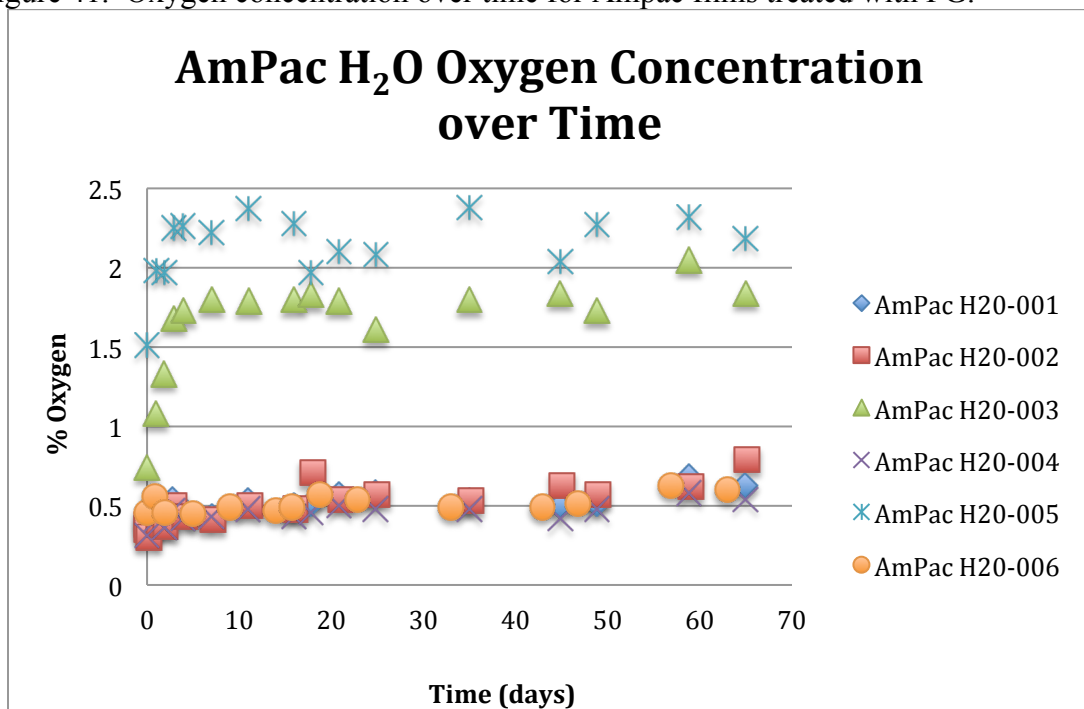


Figure 42. Oxygen concentration over time for Ampac films treated with water.

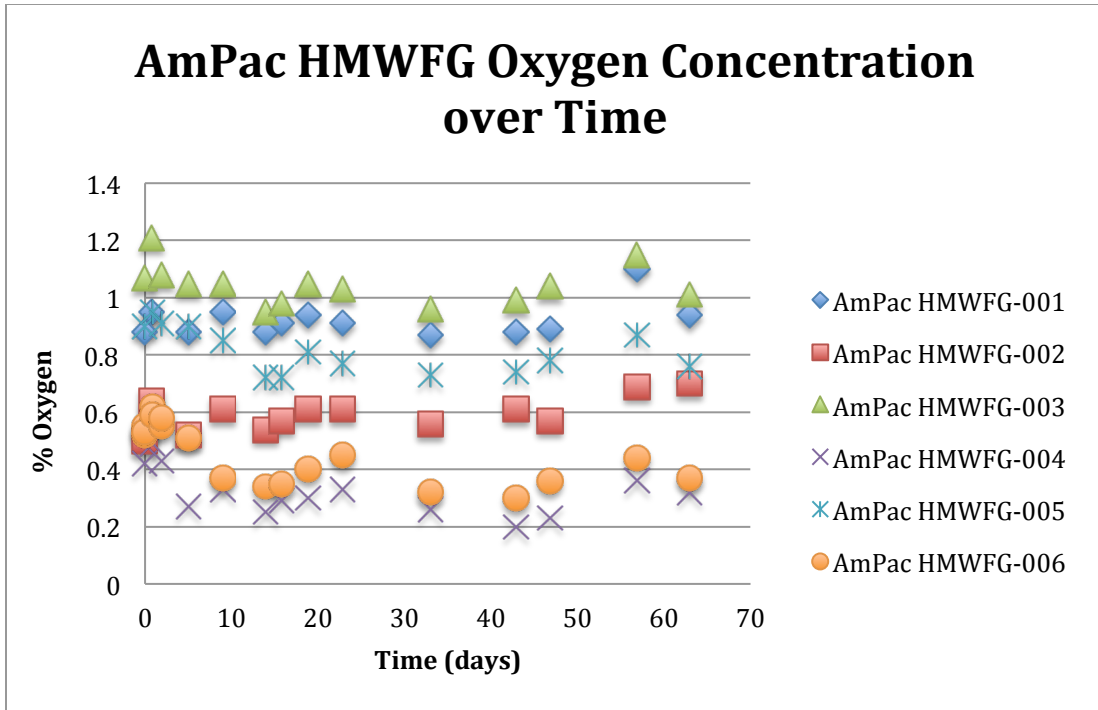


Figure 43. Oxygen concentration over time for Ampac films treated with High Molecular Weight FG.

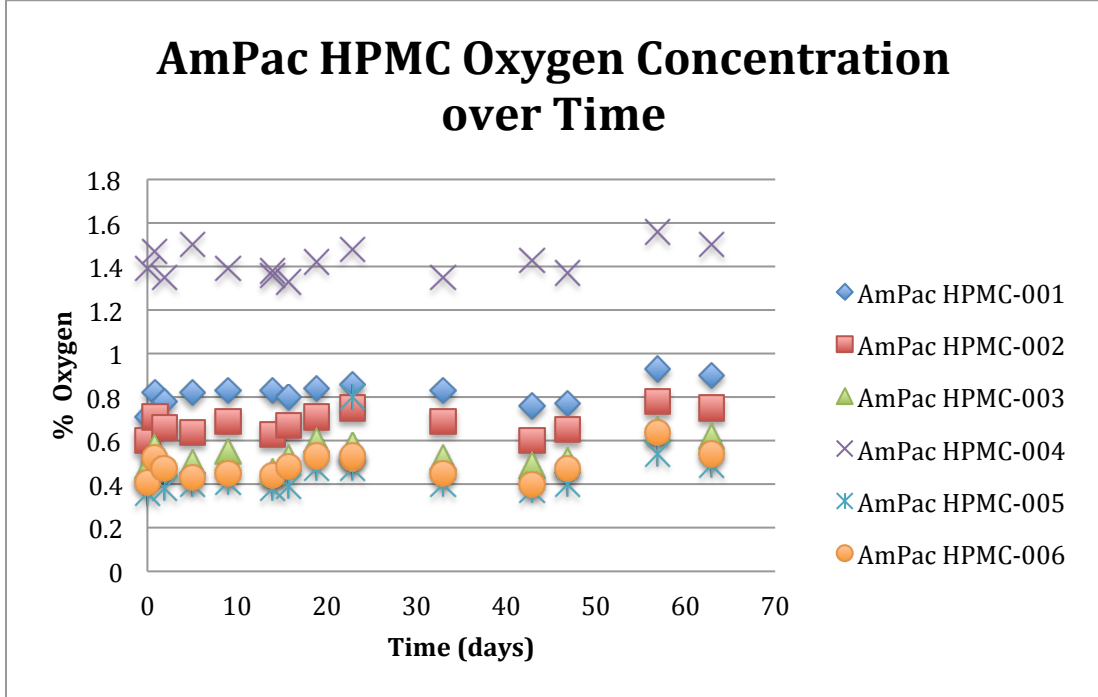


Figure 44. Oxygen concentration over time for Ampac films treated with HPMC.

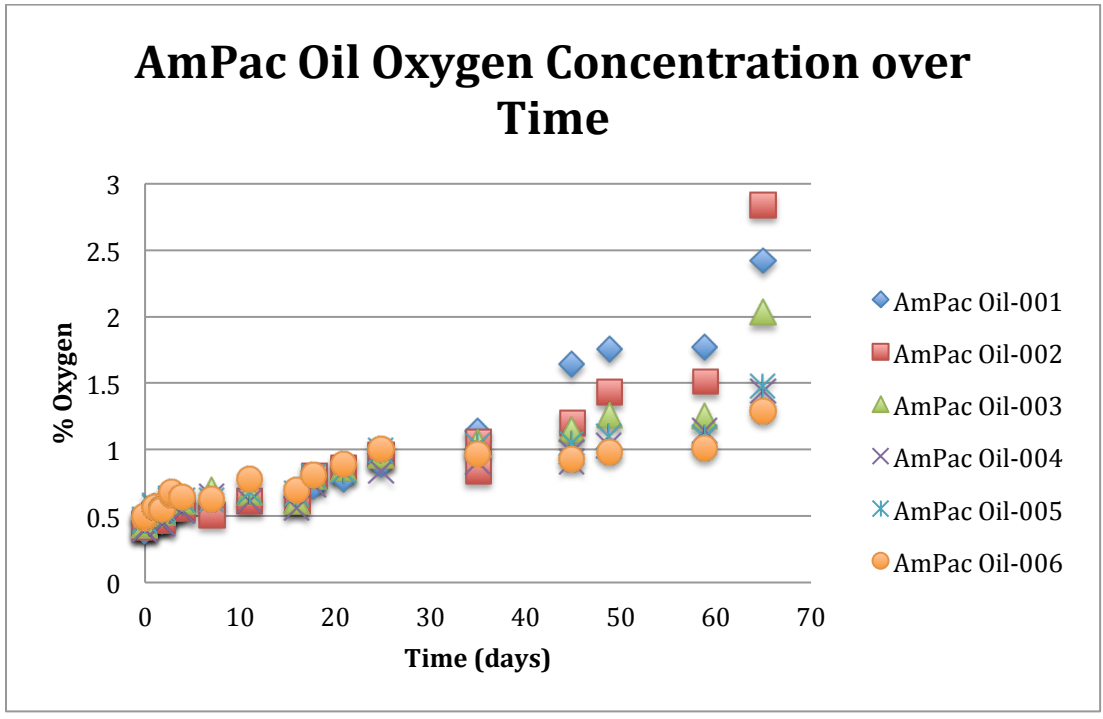


Figure 45. Oxygen concentration over time for Ampac films treated with Oil.

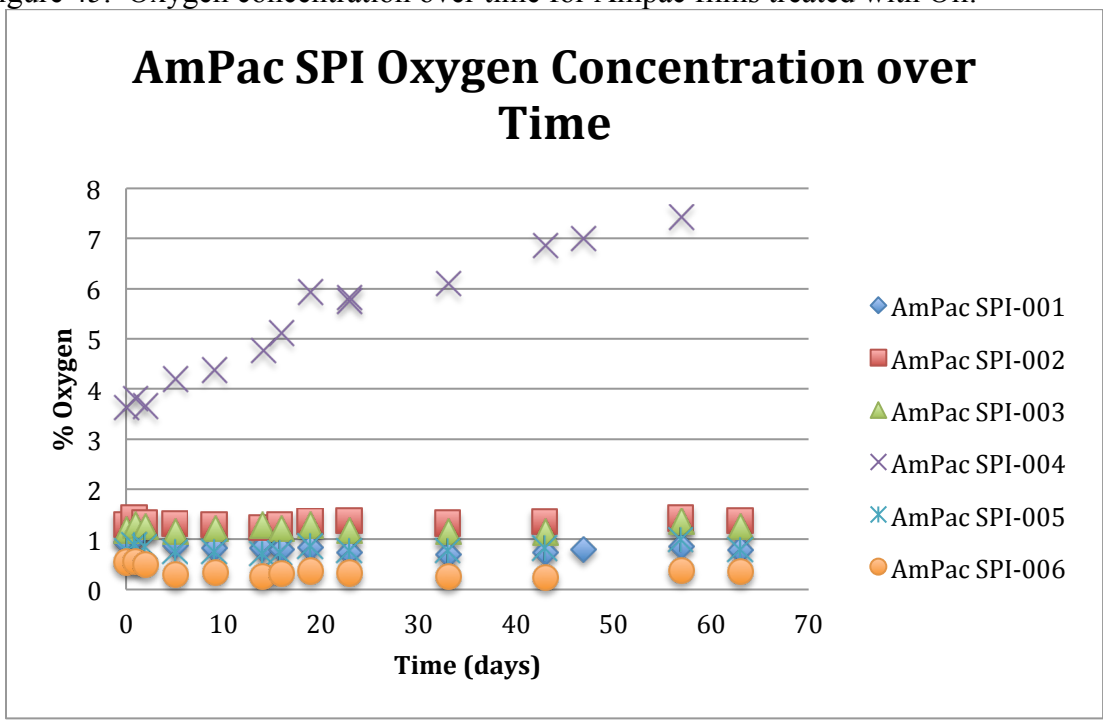


Figure 46. Oxygen concentration over time for Ampac films treated with SPI.

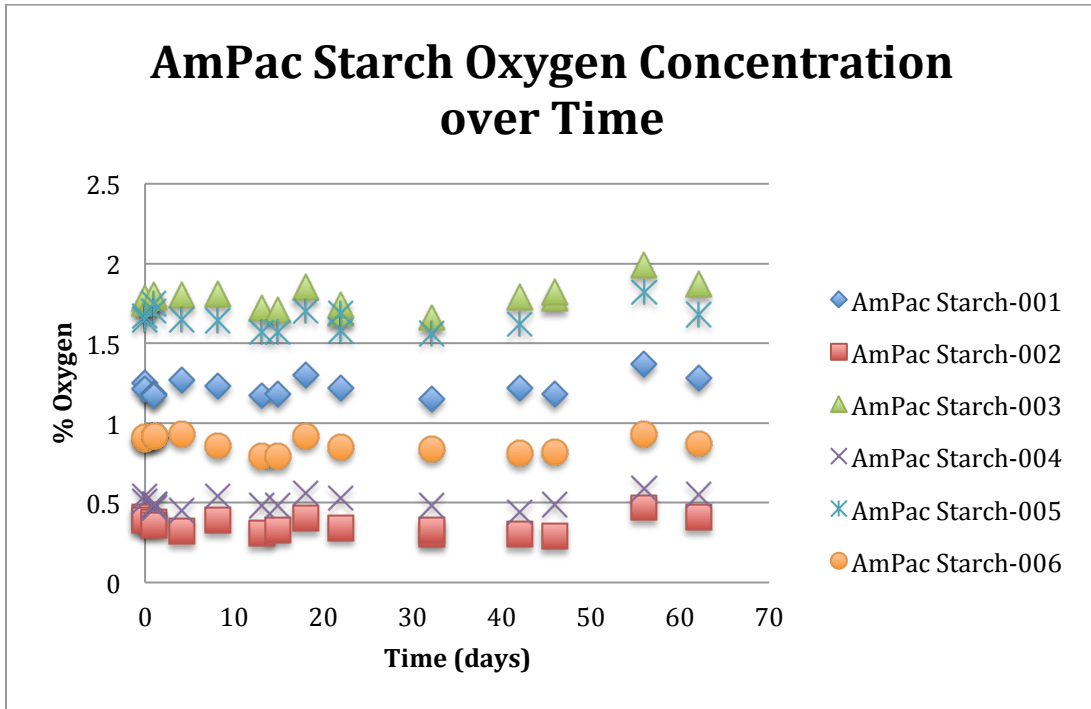


Figure 47. Oxygen concentration over time for Ampac films treated with Potato Starch.

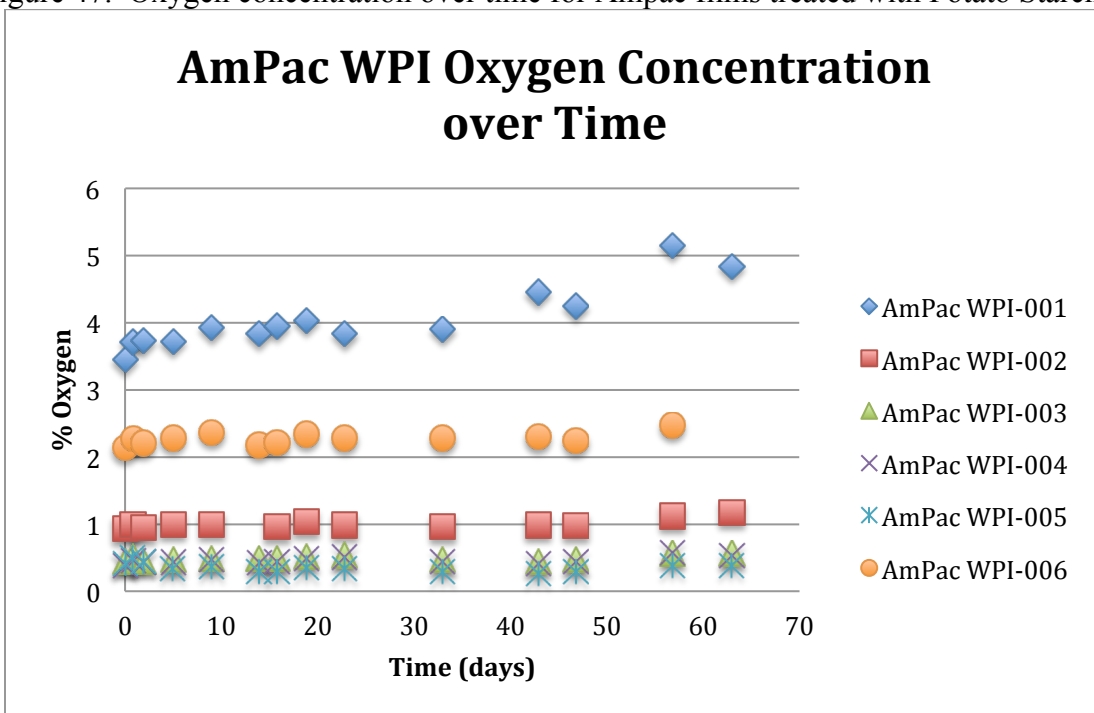


Figure 48. Oxygen concentration over time for Ampac films treated with WPI.

Table 9. Line Equations and R² values for Ampac pouches used for analysis.

Treatment	Line equation	R²
AmPac Air-001	$y = 0.0019x + 0.8202$	R ² = 0.35325
AmPac Air-002	$y = 0.0013x + 0.4851$	R ² = 0.22607
AmPac Air-003	$y = 0.003x + 0.4052$	R ² = 0.60741
AmPac Air-004	$y = 0.0012x + 0.4158$	R ² = 0.2661
AmPac Air-005	$y = 0.001x + 0.4196$	R ² = 0.19008
AmPac Air-006	$y = 0.0026x + 0.7585$	R ² = 0.54236
AmPac BG-001	$y = 6E-05x + 1.3105$	R ² = 0.00051
AmPac BG-002	$y = 0.001x + 0.5841$	R ² = 0.1986
AmPac BG-003	$y = 0.0009x + 0.877$	R ² = 0.18174
AmPac BG-004	$y = 0.0008x + 0.5534$	R ² = 0.10392
AmPac BG-005	$y = -0.002x + 0.6326$	R ² = 0.40298
AmPac BG-006	$y = 0.0006x + 1.599$	R ² = 0.04049
AmPac FG-001	$y = 0.0012x + 0.4585$	R ² = 0.20345
AmPac FG-002	$y = 0.0006x + 0.9829$	R ² = 0.05259
AmPac FG-003	$y = 0.0011x + 0.6034$	R ² = 0.19432
AmPac FG-004	$y = 0.0012x + 0.8764$	R ² = 0.188
AmPac FG-005	$y = 0.0009x + 0.4232$	R ² = 0.11946

Table 10. Line Equations and R² values for Ampac pouches used for analysis.
(continued)

Treatment	Line equation	R²
AmPac FG-006	$y = 0.0011x + 0.564$	R ² = 0.05036
AmPac H2O-001	$y = 0.0024x + 0.4639$	R ² = 0.52937
AmPac H2O-002	$y = 0.005x + 0.4028$	R ² = 0.67784
AmPac H2O-003	$y = 0.0088x + 1.4547$	R ² = 0.33274
AmPac H2O-004	$y = 0.0021x + 0.405$	R ² = 0.5113
AmPac H2O-005	$y = 0.0036x + 2.0563$	R ² = 0.12586
AmPac H2O-006	$y = 0.0016x + 0.4763$	R ² = 0.38898
AmPac HMWFG-001	$y = 0.0011x + 0.8948$	R ² = 0.1352
AmPac HMWFG-002	$y = 0.0018x + 0.5494$	R ² = 0.40338
AmPac HMWFG-003	$y = -0.0006x + 1.0591$	R ² = 0.03583
AmPac HMWFG-004	$y = -0.0018x + 0.3617$	R ² = 0.21087
AmPac HMWFG-005	$y = -0.0018x + 0.8584$	R ² = 0.24103
AmPac HMWFG-006	$y = -0.0033x + 0.5145$	R ² = 0.45443
AmPac HPMC-001	$y = 0.0013x + 0.7888$	R ² = 0.25226
AmPac HPMC-002	$y = 0.0011x + 0.6547$	R ² = 0.17965
AmPac HPMC-003	$y = 0.0013x + 0.5068$	R ² = 0.25003

AmPac HPMC-004	$y = 0.0013x + 1.3888$	$R^2 = 0.15408$
AmPac HPMC-005	$y = 0.0012x + 0.4199$	$R^2 = 0.04967$
AmPac HPMC-006	$y = 0.0014x + 0.4535$	$R^2 = 0.19985$
AmPac Oil-001	$y = 0.0003x^2 + 0.0108x + 0.4702$	$R^2 = 0.97231$
AmPac Oil-002	$y = 0.0005x^2 - 0.0018x + 0.5216$	$R^2 = 0.88899$
AmPac Oil-003	$y = 0.0001x^2 + 0.0095x + 0.5324$	$R^2 = 0.90501$
AmPac Oil-004	$y = 5E-05x^2 + 0.0093x + 0.4863$	$R^2 = 0.93419$
AmPac Oil-005	$y = 5E-06x^3 - 0.0005x^2 + 0.0249x + 0.5098$	$R^2 = 0.94004$
AmPac Oil-006	$y = 8E-06x^3 - 0.0008x^2 + 0.0309x + 0.5199$	$R^2 = 0.92935$
AmPac SPI-001	$y = -0.0023x + 0.8887$	$R^2 = 0.29831$
AmPac SPI-002	$y = 0.0012x + 1.3151$	$R^2 = 0.20561$
AmPac SPI-003	$y = 0.0006x + 1.2147$	$R^2 = 0.04022$
AmPac SPI-004	$y = 0.0689x + 3.8814$	$R^2 = 0.94499$
AmPac SPI-005	$y = 0.0013x + 0.7814$	$R^2 = 0.13009$
AmPac SPI-006	$y = -0.0022x + 0.412$	$R^2 = 0.19439$
AmPac Starch-001	$y = 0.0011x + 1.2027$	$R^2 = 0.14108$
AmPac Starch-002	$y = 9E-05x + 0.3562$	$R^2 = 0.0013$
AmPac Starch-003	$y = 0.0015x + 1.7502$	$R^2 = 0.17454$
AmPac Starch-004	$y = 0.0006x + 0.4938$	$R^2 = 0.0882$
AmPac Starch-005	$y = 0.0006x + 1.6451$	$R^2 = 0.02657$
AmPac Starch-006	$y = -0.0007x + 0.8846$	$R^2 = 0.07241$
AmPac WPI-001	$y = 0.02x + 3.585$	$R^2 = 0.82815$

Table 11. Line Equations and R2 values for Ampac pouches used for analysis.
(continued)

Treatment	Line equation	R²
AmPac WPI-002	$y = 0.0022x + 0.9531$	$R^2 = 0.48842$
AmPac WPI-003	$y = 0.001x + 0.4695$	$R^2 = 0.23905$
AmPac WPI-004	$y = 0.0014x + 0.4264$	$R^2 = 0.33468$
AmPac WPI-005	$y = -0.0011x + 0.3799$	$R^2 = 0.12253$
AmPac WPI-006	$y = 0.0025x + 2.2248$	$R^2 = 0.29342$