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DEVELOPMENT OF ACTIVE PACKAGING FOR RETORT FOOD; APPLICATION OF OXYGEN SCAVENGER

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Susan E. Selke
Major Professor's Signature

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DEVELOPMENT OF ACTIVE PACKAGING FOR RETORT FOOD; APPLICATION OF OXYGEN SCAVENGER

By

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ABSTRACT

DEVELOPMENT OF ACTIVE PACKAGING FOR RETORT FOOD;
APPLICATION OF OXYGEN SCAVENGER

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The technology to extend shelf life in processed food has progressed due to innovations in sterilization and barrier packaging. However, the passive packaging systems cannot completely solve the problems of oxidation, odor and discoloration due to oxygen dissolved in food, or contained in the headspace in the package. Oxygen scavenger packaging can effectively solve this problem. The packaging system interacts with inside of package, and removes headspace oxygen. In this research, three oxygen scavengers with different content of iron (%) were applied in multilayer trays with processed meat ball products, and evaluated products shelf life compared to passive barrier packaging. The oxygen concentration in the headspace, oxidation of the product, color, and flavor were evaluated periodically for samples that were stored at 23°C, 50% RH and at 30°C, 80% RH for 9 months. The results showed that all three active packages were superior to conventional passive packaging by removing headspace oxygen in the packages.

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CHAPTER 1. INTRODUCTION

1.1 Recent trends in barrier packaging

In the past twenty years, the use of plastic packaging has grown remarkably, because of its convenience for manufacturing, handling, and use [25]. In particular, multi-layer barrier packaging has challenged metal and glass for long shelf life food packaging, because of its high barrier properties, as well as its versatility and convenience. For this reason, this barrier packaging market has grown rapidly, and was projected to reach $3.8 billion in 2003 [26]. One of the largest segments of the multi-layer barrier packaging market is ethylene vinyl alcohol (EVOH) [11]. Research shows that the growth rate of EVOH was more than 10% in the barrier material market, for the years 2001 to 2005 [2]. The demand for high gas barrier packaging materials drives the growth of consumption of ethylene vinyl alcohol (EVOH). Typically, EVOH has been coextruded with moisture barrier layers because of its moisture sensitivity. Specifically, EVOH based multi-layers barrier packaging is very common in food packaging because of its excellent barrier properties.

1.2 Problem statement of passive packaging

Due to its sensitivity to moisture, EVOH has some limitations at high humidity conditions. For example, the atmosphere inside of a package cannot maintain a constant gas or moisture concentration during the retort process. EVOH based multi-layer packaging will be influenced by the atmosphere around the food because EVOH has poor moisture barrier properties. Another problem is the presence of oxygen in the food itself and within the headspace of the package. In particular, it is difficult to control or remove

headspace oxygen during packaging. Oxygen in the headspace of the packaging and in the food itself can cause off-flavor, color change, nutrient loss and increase microbial growth, even though the multi-layer packaging provides excellent protection from the environment. For this reason, new technology using an oxygen scavenger material, as one type of active packaging, was introduced to replace or supplement conventional multi-layer barrier packaging or passive packaging. The oxygen scavenger material is designed to control oxygen inside the package and provide a barrier to environmental oxygen [24].

1.3 Introduction to active packaging

Active packaging, which is often referred to as "smart packaging," is intended to sense internal or external environmental changes and modify the internal packaging environment by modifying its own properties. Therefore, the goal of active packaging is to extend the shelf life of contained food and beverage products either to remove oxygen or prevent it from entering the in-package environment, minimizing undesirable oxidative reactions [1].

The widely known commercial oxygen scavengers are ferrous compounds, catechol, ascorbic acid and analogues, ligands, oxidative enzymes such as glucose oxidase, unsaturated hydrocarbons and polyamides [10]. The most general oxygen scavengers in commercial use are ferrous iron. The primary compound is ferrous iron oxide, which oxidizes to the ferric state. The water activity in food must be above some minimum moisture requirement to oxidize the iron compounds. The level of minimum requirements varies. One of the general reaction mechanisms for iron oxidation is as follows:

$$Fe \rightarrow Fe^{+2} + 2e^-$$

$$½O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

$$Fe^{+2} + 2OH^- \rightarrow Fe(OH)_2$$

$$Fe(OH)_2 + ¼\ O_2 + ½\ H_2O \rightarrow Fe(OH)_3$$

Typically, iron-based materials have a high oxygen scavenging capacity and are relatively less expensive than the other scavenging materials previously mentioned. However, since they include iron compounds, iron based scavenging materials interfere with metal detection and the visual clarity of the package. On the other hand, organic based oxygen scavenging materials have good transparency and allow use of metal detection, which is important in food packaging. Despite these advantages, their low oxygen scavenging capacity and high cost are innate problems of these systems. When oxidation occurs, they can also generate undesirable odor compounds such as ketones or aldehydes. Thus, choice of an appropriate oxygen scavenger depends on the type of packaging used and the type of product. As a conventional application, the use of discrete sachets containing oxygen scavengers previously mentioned has already found commercial application. Inserting a sachet into the package is effective but meets with resistance from food packers, because it is visually unappealing, especially if the sachet is broken. Also, accidental ingestion of the sachet by children is a concern. Thus, a much more useful approach would be the use of multilayer plastic barrier packaging as the scavenging medium [Figure 1]. For this reason, in this research, ferrous iron based oxygen scavengers, which can be extruded and have high performance even in retort conditions, were selected to evaluate the shelf life of food.

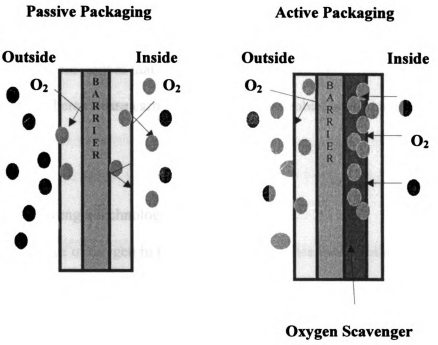


Figure 1: The mechanism of oxygen scavenging in active packaging

CHAPTER 2. LITERATURE REVIEW

2.1 Active packaging systems

Active packaging is packaging systems that interact with the internal gas environment of the package to extend the shelf life of products (mainly food). The technology modifies the internal environment and interacts with the foods, by removing gases or adding gases to the headspace of the package. Major active packaging techniques include substances that absorb oxygen, ethylene, moisture, carbon dioxide, and odors while others release carbon dioxide, anti-microbial agents, antioxidants and flavors.

2.1.1. Oxygen scavenger technology

The presence of oxygen in food packages can cause food spoilage, creating off-flavors, color changes, nutrient loss and microbial growth. Although oxygen sensitive food can be packaged using modified atmosphere packaging (MAP) or vacuum packaging, neither technique can effectively maintain 0% oxygen inside the package because they are not able to totally prevent oxygen permeating through packaging film, or oxygen contained in the food itself. Oxygen scavenger systems are one of the most promising applications of active packaging. An oxygen scavenger absorbs residual oxygen in the package and extends shelf life by preventing oxidation and aerobic microbial growth. In general, existing oxygen scavenger technologies use one or more of the following concepts: iron powder oxidation, ascorbic acid oxidation, photo sensitive dye oxidation, enzymatic oxidation, unsaturated fatty acids, or immobilized yeast on a solid material.

2.1.1.1 Iron based oxygen scavenger

The most widely used oxygen scavenging system in commercial use is iron oxidation, which is discussed in chapter 1. The sachet types of oxygen scavenger systems, like Ageless (Mitsubishi Gas Chemical CO, Japan) or Freshpax (Multisorb Technologies Inc., USA) are the most common type [10]. However, since a potential risk of accidental ingestion of a large amount of iron exists, recent trends are to incorporate the iron compound into the package. Low molecular weight iron based ingredients are dissolved or dispersed in a plastic or the plastic may be made from a polymeric scavenger, such as Oxyguard (Toyo Seikan Kaisha, Japan) [19]. The iron based absorber can be incorporated into a laminate, which can be found in packages of many foods: cured meat, cookies, pastas, and so on.

Figure 2. Sachet type and polymeric type oxygen scavenger (iron based)

2.1.1.2. Ascorbic acid oxygen scavenger

Another oxygen scavenger technique is ascorbic acid oxidation. Oxygen in the package oxidizes ascorbic acid to dehydroascorbic acid, so oxygen in the headspace of the package is removed. Since ascorbic acid is a six-carbon compound, a high weight is required to get enough oxygen absorption capacity. Its slower absorption rate compared to iron based oxygen scavengers is another drawback. Darex (Grace, Lexington, MA,

USA) is an example of this technology. It is designed to be incorporated into barrier packaging such as crown caps, plastic or metal closures. The company reports they extend the shelf life of beer by 25% [12].

2.1.1.3. Light activated oxygen scavenger

Photosensitive oxidation is the basis for an oxygen scavenger system that consists of sealing a small coil of an ethyl cellulose film containing a dissolved photosensitive dye and a singlet O_2 acceptor in a transparent package. By using lights with appropriate wavelengths, the dye molecules are excited, and then pass their excitation to oxygen as it diffuses into the film from either the package headspace or from the liquid food. The excited O_2 molecules react with the acceptor and then are consumed. While the film is illuminated, the process continues until all the oxygen reacts. The reaction scheme is the following [21]:

$$\text{Photon} + \text{dye} \rightarrow \text{dye}^*$$

$$\text{dye}^* + O_2 \rightarrow \text{dye} + O_2^*$$

$$O_2^* + \text{acceptor} \rightarrow \text{acceptor oxide}$$

$$O_2^* \rightarrow O_2$$

This photochemical process has advantages because it does not need sachets in the food package and works regardless of humidity. The first used dye was erythrosine, which is an FDA approved food color additive, plus a color sensitizer that is bleached by light. For singlet oxygen acceptors, several materials were tested: difurylidene erythrito (DEF), tetraphenyl prophine (TPP), dioctyl phthalate (DOT), and dimethyl anthracene (DMA). However, these are not approved for food contact. This type of oxygen scavenger does

not initiate in the dark. Therefore, this technique cannot be used with non-transparent film. An example of a light-activated scavenger is $Zero_2^{TM}$ (CSIRO, Australia) [10].

2.1.1.4. Enzyme based oxygen scavengers

Another oxygen scavenger technique uses enzyme reactions. The enzyme responds with a specific substance to scavenge incoming O_2. Glucose oxidase is a popular oxygen scavenging enzyme. Glucose oxidase transfers two hydrogens from the –CHOH group of glucose to oxygen with the formation of glucono-delta-lactone and hydrogen peroxide. The reaction is the following:

$$2G + 2O_2 + 2H_2O \rightarrow 2GO + 2H_2O_2$$

where G is the substrate.

However, H_2O_2 is a highly oxidizing agent and therefore objectionable, so catalase is introduced to break down the peroxide [10]:

$$2H_2O_2 + \text{catalase} \rightarrow 2H_2O + O_2 + \text{catalase}$$

From the two reactions above, the original oxygen is reduced by half, and ultimately it will become zero. The glucose plus catalase enzyme system is very sensitive to pH, water activity, temperature, and various other factors. Also, it requires water for activation, so it cannot be used for low humidity products. A commercially available sachet style oxygen scavenger of this type is the Bioka (Bioka, Finland) [22]. These oxygen scavengers can be used alone or in combination with MAP. Obviously, using them alone eliminates the MAP step and increases packaging speed. However, industry commonly removes oxygen through MAP and then uses a small amount of oxygen scavenger to remove residual oxygen in the package and maintain its concentration at less than 0.1% [20]. In addition,

to use oxygen scavenger techniques effectively, a package with a high barrier to oxygen is required.

2.1.2. Ethylene scavenging technology

Ethylene (C_2H_4) on fresh fruits accelerates ripening and softens vegetables. Therefore, to extend shelf life, the accumulation of ethylene in the packaging should be removed. The ethylene-scavenging agents incorporated into packaging film trap ethylene produced by ripening fruit or vegetables. The reaction is irreversible and only small quantities of the scavenger are required to remove ethylene at the concentrations at which it is produced. Nevertheless, these systems are not yet very successful because they do not have enough ethylene scavenging capacity. A large amount of fresh fruits and vegetables are lost due to fungal contamination and physiological damage [7]. Eventually however, this technique will contribute to an increase in ability to export fresh produce.

2.1.3. Antimicrobial packaging

To prevent or inhibit undesirable microbial growth on products, antimicrobial substances can be incorporated into or coated onto food packaging materials. The principle of antimicrobial action is based on the release of antimicrobial agents from the packaging to the product. The major potential applications are food products like meat, fish, poultry, cheese, fruits and vegetables [22]. Figure 3 shows that the blueberries in the package incorporated with an antimicrobial agent on the right side of the figure were kept fresher than those on the left. Many new antimicrobial systems have been developed [14]. Currently, nisin is the best-known coated type of antimicrobial agent.

This natural compound has been well characterized as a food preservative and has attained GRAS status (generally recognized as safe) [22]. Sorbic acid and potassium salts are also well known food preservatives with antimicrobial activity. Many of the incorporated antimicrobials are not yet permitted for food use. Silver-substituted zeolite is the most common antimicrobial agent incorporated into plastics. However few descriptions of the effectiveness of this material have appeared and the regulatory status of the addition of antimicrobial components into foods has not been clarified in the US or Europe. Moreover, the choice of which antimicrobials to incorporate into packaging is often limited by the immiscibility of the component with the packaging material or by the heat sensitivity of the component during extrusion [10]. These types of antimicrobial agents are still being studied and developed to ensure their safety and effectiveness.

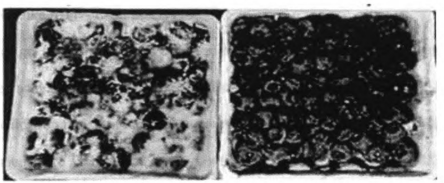


Figure 3: The effect of antimicrobial technique. The package on the left without antimicrobial agent has a significant growth of mold; the package on the right contains an antimicrobial agent.

2.1.4. Humidity scavengers

Some foods are easily damaged by moisture. In high moisture barrier packaging, moisture inside the package is trapped in the package, and then trapped moisture may condense in the package and be absorbed by the product. Therefore, food can became soft and lose consumer appeal. Conversely, excessive water evaporation through the packaging material may result in drying and hardening of foodstuffs. Some of these moisture problems can be controlled by using humidity scavengers. A certain amount of moisture can be trapped in the package, and maintain proper moisture content. Food manufacturers can use a film with the appropriate water vapor permeability or use a desiccating film or moisture controlling sachet or pad. Often, the purpose of moisture control is to lower water activity, to inhibit the growth of mold or bacteria in high water activity foods like ready-to-eat meals [10].

Silica gel is one of the most common desiccants and is used in a wide range of food, as well as non-food products such as pharmaceuticals, to maintain a low humidity. Another application type removes melting water from frozen or fresh food. Drip-absorbent sheets like Termariate (Australia) or Peaksorb (Peak Fresh Products, Australia) are examples. These applications control liquid water in high water activity foods such as meat, poultry, fruits and vegetables [22].

2.2. Future of active packaging

The technologies discussed above are only some of the commercial and non-commercial applications of active packaging. This technology is the subject of research in many countries and rapid developments may be expected. However, in the food

industry, there is still concern about introducing active components to packaging because consumers may consider the components harmful and may not accept them. To avoid such concerns and permit further development of these techniques, consumers should be more informed, using reliable information channels [23]. In addition, even if those active packaging techniques may be beneficial in extending shelf life, a holistic approach to environmental impacts needs to be considered as well as economic profits.

2.3. Factors affecting permeability of EVOH

Permeability is a measure of how easily a permeant compound transports through a solid medium. High permeability indicates that the solid material poses little resistance to the transport of the permeant. The chemical structure of the polymer and permeant are the primary factors in determining the barrier properties. The main reason for designing multilayer structures in packaging is enhancement of overall barrier properties to moisture and gas. EVOH is one of the most commonly used barrier materials. It has excellent gas and organic vapor barrier properties as long as the polymer is not exposed to high humidity conditions. Since EVOH is a polar hydrophilic polymer, moisture will act as a plasticizer that increases the free volume of the polymer, and the overall permeability will be increased greatly compared to dry conditions [17, 18]. For this reason, EVOH is always used between high moisture barrier polymer layers like PP and PE.

Another factor that can change permeability is storage temperature. The following equation shows how it affects permeability.

$$P = P_o \exp(-E_a / RT) \tag{2.1}$$

where E_a is the activation energy, R is the gas constant, P_O is a pre-exponential term and T is temperature in Kelvin. If a value of permeability, P, is given at temperature T_1, the value of the permeability P_2 at T_2, can be calculated if E_a is known [17].

$$P_2 = P_1 \cdot \exp\left[\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \tag{2.2}$$

Thus, the equation 2.2 can be written as

$$P_2 = P_1 \cdot f$$

where,

$$f = \exp\left[\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \tag{2.3}$$

CHAPTER 3. MATERIALS AND METHODS

3.1 Materials

3.1.1 Containers

The container was composed of a tray and a lid. The tray was thermoformed from a sheet that has a multilayer structure produced by a feed-block system in a coextrusion sheeting line. The tray was designed as a multilayer structure, PP/adhesive/EVOH/adhesive/OS (Oxygen Scavenger)/PP. To prepare the oxygen scavenger resin, the oxygen scavenger was mixed with PP, extruded and pelletized to produce masterbatch resins. Then, PP resins were blended with the desired amounts of masterbatch resins to produce the final matrix film layer with a homogeneous concentration of oxygen scavenger compound. For this research, the content of oxygen scavenger masterbatch in the OS layer was controlled to 100, 80, and 40%. Iron based compounds which are activated by moisture during the retort process and storage were used as the oxygen scavenger. As shown in Table 1, the concentration of oxygen scavenger in T2 was 2.5 times and that of T3 was 2 times that of T4. The oxygen scavenger of T2 was from a different company than those of T3 and T4. The gas barrier layer was 25 um of EVOH resin containing 32% ethylene. PP was selected as the moisture barrier material. A material was chosen for the tie layer that could be used in retort conditions. In this study, the details about parameters and process for the oxygen scavenger film extrusion, the names of the oxygen scavengers, and activation conditions will not be specifically reported due to a confidentiality disclosure agreement with the packaging manufacturer. T1 was used as a control, with the conventional barrier material

structure PP/adhesive/EVOH/adhesive/PP, for comparison to the three oxygen scavenger packages. (T2, T3, T4)

The lids for the trays were traditional cast film structures for retorting: PET/Nylon/EVOH/PP. The film was produced by a triple dry lamination and slitting process, and printed by roto-gravure.

The EVOH barrier layer contained 32 % ethylene. Biaxially oriented nylon was selected for its excellent pinhole resistance. For the sealing layer, cast PP film was laminated to serve as the inside of the lid. Lids containing an aluminum foil layer were compared to the lids containing EVOH. The structure compositions are described in Table 1.

Table 1. Construction configuration of meatball packaging

//: tie layer, /: non-tie layer, ( ): thickness; μm

Code	Tray	Lid
T1	PP(180)//EVOH(25)//PP(180)	PET(12)//Nylon(15)//EVOH(12)//PP(50)
T2	PP(180)//EVOH(25)//OS1(80)/PP(100)	PET(12)//Nylon(15)//EVOH(12)//PP(50)
T3	PP(180)//EVOH(25)//OS2(80)/PP(100)	PET(12)//Nylon(15)//EVOH(12)//PP(50)
T4	PP(180)//EVOH(25)//OS3(80)/PP(100)	PET(12)//Nylon(15)//EVOH(12)//PP(50)
AL-T1	PP(180)//EVOH(25)//PP(180)	PET(12)//Nylon(15)//AL(9)//PP(50)
AL-T2	PP(180)//EVOH(25)//OS1(80)/PP(100)	PET(12)//Nylon(15)//AL(9)//PP(50)
AL-T3	PP(180)//EVOH(25)//OS2(80)/PP(100)	PET(12)//Nylon(15)//AL(9)//PP(50)
AL-T4	PP(180)//EVOH(25)//OS3(80)/PP(100)	PET(12)//Nylon(15)//AL(9)//PP(50)

OS1: 100% of oxygen scavenger compound that has 7% iron

OS2: 80% of oxygen scavenger compound that has 5% iron, and 20% PP

OS3: 40% of oxygen scavenger compound that has 5% iron, and 60% PP

3.1.2 Product (food and process conditions)

As a sample product [Figure 4], meatballs were selected because they are one of the most common retort foods that are commercialized in Korea, and both the meat and the oil in the sauce are sensitive to oxidation. Since the meatball tray has a larger headspace than other retort food packaging, the package provided enough samples to analyze oxygen concentration inside of the retort packaging. The retort condition was one hr at 121°C (come up time: 10 min, retort time: 35 min, cooling time: 15 min). In order to reduce food oxidation in the package, a controlled and modified atmosphere packaging system was used. The mixed N_2 and CO_2 gas was flushed into the headspace in the package before the lid was sealed. The proportion of CO2 gas was limited to 50% because the meatball package (tray) tended to distort when the gas dissolved in the water of the food, even though the package was specially designed to resist distortion. The heat-sealing condition was 190°C to 210°C at a pressure of 2.5 kg/cm^2, for 2 seconds. The equipment is shown in Figure 5.

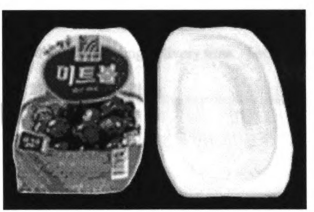


Figure 4: Description of meatball packaging

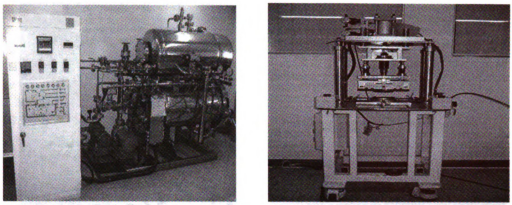


Figure 5: Retort and heat sealing machine

3.1.3 Storage conditions

Sample products were stocked in storage chambers [Figure 6] at two conditions (C1, C2). The C1 condition consisted of light at a level of 800-1,000 lux, temperature of 30°C and 80% RH, which was considered as a summer season. The high humidity condition was used to compare the barrier properties of the EVOH containing and the aluminum lid, since the permeation of oxygen through EVOH rapidly increases above 80% RH. The other condition, C2, consisted of 23°C, 50% RH and dark. C2 was set up as an annual average condition. All packaged samples were delivered from Korea to the laboratory of the MSU packaging department. Overall shipping time was 20 days and total storage period was 250 days, including delivery time. Tests were performed at 30, 45, 60, 120, 180, 225 and 270 days after filling

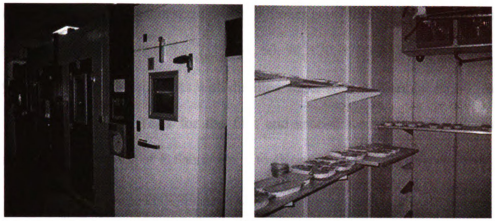


Figure 6: Environmental chamber in the School of Packaging (MSU)

3.2 Methods

3.2.1 Oxygen concentration in package

The presence of O_2 in a packaged food is often a key factor that limits the shelf life of a product. Oxidation can cause changes in flavor, color, and odor, as well as destroy nutrients and facilitate the growth of aerobic bacteria, mold and insects. Therefore, the evaluation of oxygen concentration in the headspace was considered as a major factor of this project. The oxygen concentration was measured using an Oxygen Headspace Analyzer Model-3500 (Illinois Instruments). Samples were withdrawn at a rate of 40 ml/min using the pump, and passed by the oxygen sensor. In the first set of experiments, the efficacy of the oxygen scavenger was evaluated without food. Sample trays were filled with distilled water and tested during a 6 month period, and absorption of oxygen by the oxygen scavengers was evaluated by measuring oxygen concentration. The control sample tray was compared to the oxygen scavenger packages. In the second set of experiments, the retort trays with meatballs were tested to evaluate the performance in the practice of oxygen scavenger with meatballs. Trays were filled with meatballs, and

headspace concentration was measured over a 9 month period. Oxygen concentration was measured 8 times over the 9 months: 7, 15, 30, 60, 90, 120, 180 and 270 days after filling. The oxygen scavenger efficacy tests with distilled water were performed simultaneously from 0 days to 180 days. Tests for the first and second terms (0 and 7 days) were performed at the laboratory of E.Saeng Co. Ltd (Korea), while awaiting delivery of the sample to MSU packaging department (USA).

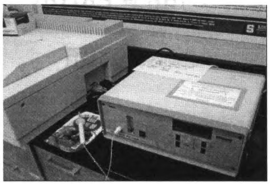


Figure 7: Oxygen headspace analyzer

3.2.2 Color

The color change corresponding to the oxidation of the surface of the meatballs and the sauce was evaluated using a colorimeter instrument (Minolta Chroma Meter Measuring Head CR-300), which was calibrated by using a reference tile, with a focus on the change of the lightness of the food by measuring the L-value, rather than on other color factors such as the a and b-values. Four packages (from T1 to T4) were stored at two conditions as described previously (3.1.3). Each sample color was measured twice, and two samples were used for each of the four package configurations for each storage condition. Then, all results for each package were averaged. For this test, samples were tested 7 times over 9 months: 30, 45, 60, 120, 180, 225 and 270 days after filling.

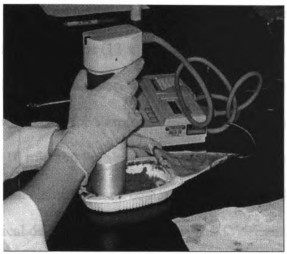


Figure 8: Colorimeter

3.2.3 TBA analysis

TBA is well known as the most widely used test method for measuring the extent of lipid oxidation in foods such as meat products. The general principle of this method is the reaction of one molecule of malonaldehyde and two molecules of TBA to form a red malonaldehyde-TBA complex, which can be quantified by spectrophotometry. The procedure and determination were as follows: 10 g of ground meatball was weighed into a 100 ml plastic bottle containing 50 ml of distilled water, and homogenized with 10 μl antioxidant solution (Tenox 5-food grade BHA+BHT). A polytron mixer (PT-35, Kinematica, AG, Switzerland) was used to homogenize the mixture on speed setting 4 for 1 min. The meat homegenate was transferred to a 500 ml extraction flask; 2.5 ml of HCl solution was added (1:2, HCl:H2O v/v), and 1 ml of sulfanilamide solution (1% W/V) was mixed in. With adding 47.5 ml of ionized distilled water, the total of the meat homogenized solution volume became 100 ml; 50 ml (meat homogenate itself) + 2.5 ml (HCl) + 47.5 ml (distilled water). The homogenized solution was placed in graduated

cylinders under spouts and 50 ml was distilled. Then 5 ml of the distilled solution was pipetted into a plastic disposable tube (13 x 100 mm), and 5 ml of thiobarbituric acid solution (0.003 g/ml,TBA/distilled water) was added. The mixture was vortex mixed and incubated in a boiling water bath for 30 min to develop color. Then the sample was cooled in ice-water for 10 min and the absorbance of the resulting supernatant solution was determined at 538 nm against a blank containing 5 ml of distilled water + 5 ml of TBA solution. The optical density was multiplied by 7.8 to determine the amount of TBA, expressed as milligrams of malonaldehyde per kilogram of meat. 10g of meatball sample was collected from each of four different areas in the container, and separately analyzed for TBA value. Two containers were tested for each treatment (T1, T2, T3, and T4). Thus the total tested samples were eight for each type of package. The test was performed 5 times over 6 months: 30, 45, 60, 120, and 180 days after filling. Figure 8 shows some of the test equipment in the TBA analysis.

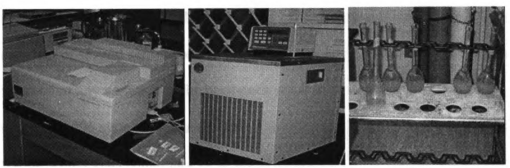


Figure 9: TBA analyzing equipment;

(a) Spectrophotometer, (b) Water Bath, (c) Condensation and Distillation

3.2.4 Flavor evaluation

Flavor, comprised of aroma and taste, is an important food quality factor. Generally, sensory analysis by panels of specially trained persons and instrumental analysis methods such as gas chromatography (GC), GC with mass spectrometry (GC-MS) or high performance liquid chromatography (HPLC) are used for flavor evaluation. For sensory testing, the most important problems include the standardization of measurements, the correctness of training, and the stability and the reproducibility of the evaluation. They affect the measurements, which are also difficult to compare between different panels. The relatively high costs for training and use of sensory panels are also a major drawback of this technique [6]. The analytical methods are time-consuming and expensive, and require skills in operating the equipment and interpreting the results. Recently, electronic nose instruments have been introduced and are increasing in use because of their success in monitoring the flavor of food [8]. To measure the flavor change of the meatballs, an E-nose (FOX 3000, Alpha MOS) was used. The FOX 3000 system with two metal oxide sensor arrays (consisting of 12 sensors) was used. Each sensor has different sensitivity and selectivity to various chemical compounds. Therefore, a combination of several sensors provides a unique fingerprint of the samples. It allows determination of any variation in the headspace volatiles of the samples. Figure 10 shows the Fox 3000 system used in this test. The robotic auto sampler of the Fox 3000 system took sealed vials containing 1g of meatball samples to an oven, syringed out a 10 ml gas sample from the headspace, and injected it into the sample injection port. The carrier gas that flowed through the sensor carried the sample gas, and sensors analyzed it. For this test, samples were tested at the end of 9 months: 270 days after filling. Six vials

which contained 1g of meatball were prepared for the E-nose test, for each package/storage condition combination. The response obtained from the sensor arrays were processed using principle component analysis (PCA).

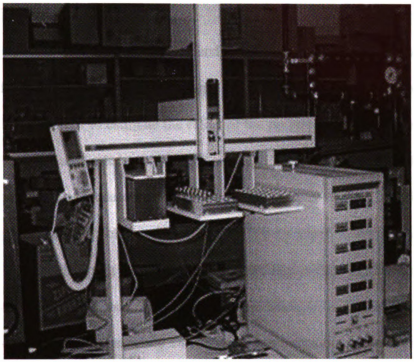


Figure 10: Electronic nose

3.2.5 Statistical analysis

Two-way analysis of variance (ANOVA) using SAS Statistical Analysis System (SAS Institute Inc, Cary, N.C.) was performed to analyze the results at the 95% confidence level (p=0.05) using the Tukey's honestly significant different multiple comparison test.

CHAPTER 4. RESULTS AND DISCUSSION

4.1 Oxygen concentration in headspace

4.1.1 Water packaging test

4.1.1.1 Results and discussion

Figure 11 and Figure 12 show the trend of oxygen concentration in the headspace of packages filled with distilled water during 6 months of storage. The lid contained an aluminum barrier in order to estimate the effect of the performance of oxygen scavenger compared to conventional passive barrier packaging (T1). The initial oxygen concentration in the headspace was 3%. Under the C2 condition (23C, 50% RH) [Figure 12], the oxygen scavenger packages (T2, T3 and T4) were superior to the passive barrier packaging (T1) in maintaining a low oxygen concentration in the package headspace. T2 and T3 reached an oxygen concentration of 0% in the headspace within 1 or 2 weeks after the filling and retorting process, while T4 reached 0% by 4 weeks. In contrast, the oxygen concentration in T1 continuously increased.

Under the C1 condition (30C, 80% RH) [Figure 11], T2 maintained the oxygen concentration below 0.5% in the headspace. Due to the increased oxygen permeation due to higher temperature and humidity, the oxygen concentration of T4 after 6 months was the same as that of T1 after 1 month. For T1, oxygen concentration rapidly increased to 12% from 3%, and passed 10% within 1 month. Therefore, if the package needs to sustain an oxygen concentration at 3% or below the original level, T2 or T3 should be selected.

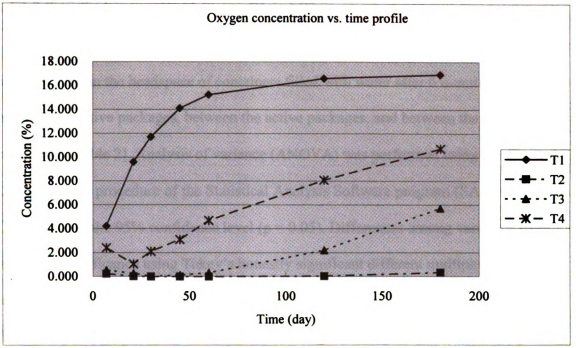


Figure 11: Oxygen concentration with water (aluminum lid, 30°C, 80% RH)

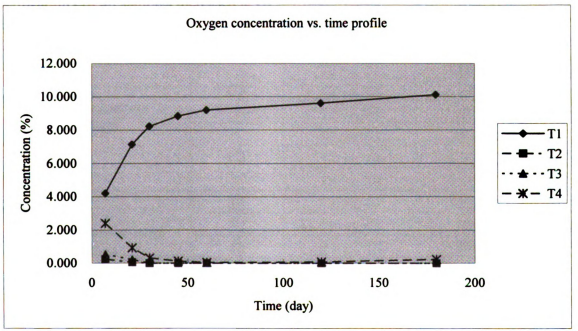


Figure 12: Oxygen concentration with water (aluminum lid, 23°C, 50% RH)

4.1.1.2 Statistical comparison between C1 and C2

Statistical analysis was done in order to see the difference in oxygen concentration in the headspace of containers filled with water after 6 months between the passive and active packages, between the active packages, and between the storage conditions [Table 2]. Analysis of variance (ANOVA) was performed using the General Linear Models procedure of the Statistical Analysis Software program (SAS Instituge Inc. Cary, N.C.) at the 95% confidence level ($p = 0.05$). Differences among variables were tested for significance using Tukey's honestly significant different multiple comparison test, and the results are shown in Table 3. T1 was significantly different ($p = 0.05$) from the active packaging (T2, T3 and T4). T2 had the greatest capacity to absorb oxygen among the active packages. T3 was better than T4 at any storage condition. Comparing C1 and C2 with the same containers, for example T1C1 vs. T1C2, the oxygen permeability of all samples increased at C2.

Table 2: Oxygen concentration of the headspace of packages filled with water after 180 days storage at C1 and C2 conditions

Container	C1 (30°C, 80% RH)	C2 (23°C, 50% RH)
T1	10.113 ± 0.400a	16.940 ± 0.455a
T2	0.000 ± 0.000b	0.328 ± 0.040b
T3	0.133 ± 0.044c	0.274 ± 0.214b
T4	0.228 ± 0.017d	10.733 ± 0.306b

Mean ± standard deviation (Unit: %, n = 3)

Table 3: T-test result for oxygen concentration in the headspace of packages filled with water after 180 days storage: Results are all significantly different at the 95% confidence level (p=0.05)

Group	Condition	Two-sample	p-value
1) Passive vs. active packages	C1	T1 vs. T2	9.26E-03*
		T1 vs. T3	1.41E-02*
		T1 vs. T4	1.94E-03*
	C2	T1 vs. T2	1.32E-02*
		T1 vs. T3	1.32E-02*
		T1 vs. T4	1.35E-02*
2) Among active packages	C1	T2 vs. T3	1.77E-04*
		T2 vs. T4	1.89E-04*
		T3 vs. T4	1.95E-02*
	C2	T2 vs. T3	2.95E-01
		T2 vs. T4	1.45E-03
		T3 vs. T4	2.46E-02
3) Between storage condition	T1	C1 vs. C2	4.07E-05*
	T2	C1 vs. C2	1.46E-02*
	T3	C1 vs. C2	1.09E-04*
	T4	C1 vs. C2	1.71E-04*

Significant differences are indicated by *

4.1.1.3 Trend / Regression line

In general, food manufacturers in Korea often ask packaging companies to provide data for the oxygen concentration as a function of storage time under the worst storage conditions such as C1 (30℃, 80% RH) in order to decide the shelf life of a new food product when they develop it. Since all packages (T1, T2, T3, and T4) were sealed with aluminum lids to prevent oxygen permeation from the lid area and filled only with water in order to avoid the reduction of oxygen concentration in the headspace of packages from oxidation by the food or sauces, the effects of active packaging using oxygen scavengers could be calculated and estimated by the equation. From the results of oxygen concentration for the C1 condition (30C, 80% RH), the trend line equation and R^2 value were determined using Micro Excel of the MS Office 2000 program. Six types of trend lines (linear, logarithmic, polynomial, power, exponential and moving average) were available. As measured by the R^2, the oxygen concentration in T2, T3 and T4 was best determined with a polynomial fit (2^{nd} order) and for T1, the best R^2 value was from a logarithmic equation. The best fit equations and corresponding R^2 values were as follows:

T1: $y = 4.0496\ln(x) - 2.5702$, $R^2 = 0.9444$

T2: $y = 4E\text{-}05x^2 - 0.0061x + 0.1992$, $R^2 = 0.8677$

T3: $y = 3E\text{-}04x^2 - 0.0195x + 0.527$, $R^2 = 0.997$

T2: $y = -9E\text{-}06x^2 + 0.0577x + 0.8473$, $R^2 = 0.9596$

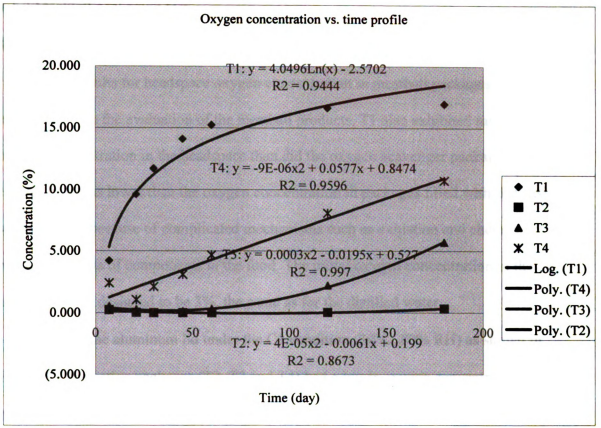


Figure 13: Trend line of oxygen concentration with water (aluminum lid, 30°C, 80% RH)

4.1.2 Meatball packaging test

4.1.2.1 Results for C1 (30°C, 80% RH)

The results for headspace oxygen concentration in meatball packages are shown in Figure 14. In the evaluation of the meatball products, T1 also exhibited much higher oxygen concentration in the headspace than did the oxygen scavenger packages. However, it was lower than the oxygen concentration in packages filled with distilled water. This is because of complicated mechanisms such as oxidation and chemical reactions by lots of components in the food. The initial oxygen concentration in the headspace was designed to be 3%, the same as for the distilled water.

Using the aluminum lid under the C1 condition (30°C, 80% RH) as shown in Figure 14, the active packages (T2, T3 and T4) had a lower oxygen concentration in the headspace than the passive barrier package (T1). The remaining oxygen in the headspace of the active packages was removed perfectly after 1 week compared with T1 which reached 0% oxygen only after 6 months.

Using a plastic lid laminated with EVOH film under the same condition (C1) as shown in Figure 15, the oxygen concentration in the headspace of the packages was reduced, but none of the active packages sustained 0% oxygen concentration for several months as did those using the aluminum lid. The oxygen concentration of T4 was increased compared with T2 or T3. This seemed to mainly result from the rapid increase in oxygen permeability of the EVOH film in high humidity, over 70% RH [Figure 19] [4].

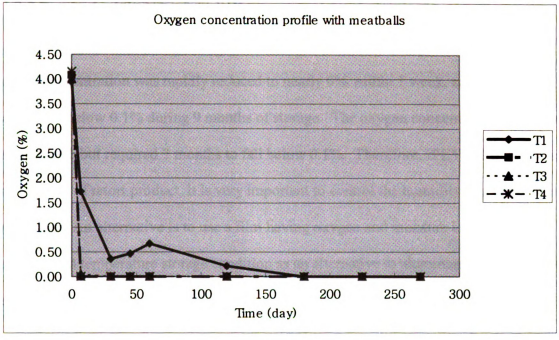


Figure 14: Oxygen concentration with meatballs (aluminum lid, 30°C, 80% RH)

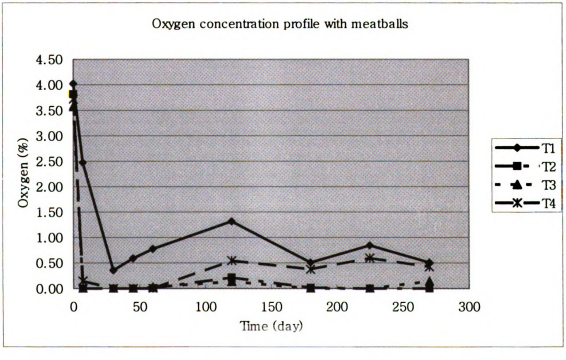


Figure 15: Oxygen concentration with meatballs (plastic lid, 30°C, 80% RH)

4.1.2.2 Results for C2 (23°C, 50% RH)

From Figure 16 and Figure 17, at C1, it can be seen that for T2, T3 and T4, the oxygen concentration was rapidly reduced to nearly 0% within 1 week, and then maintained below 0.1% during 9 months of storage. The oxygen concentration in T1 was also reduced, but required 3 months to fall below 0.1%. Therefore, if EVOH film is used for this kind of retort product, it is very important to control the humidity and temperature for storage. An alternative is to use a film having oxygen and moisture barrier at high humidity and temperature storage condition as an alternative to aluminum, which cannot be used in a microwave.

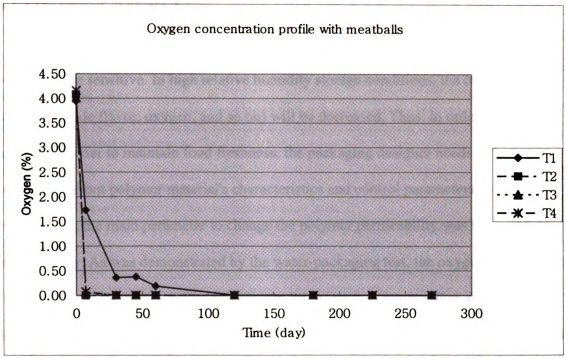


Figure 16: Oxygen concentration with meatballs (aluminum lid, 23°C, 50% RH)

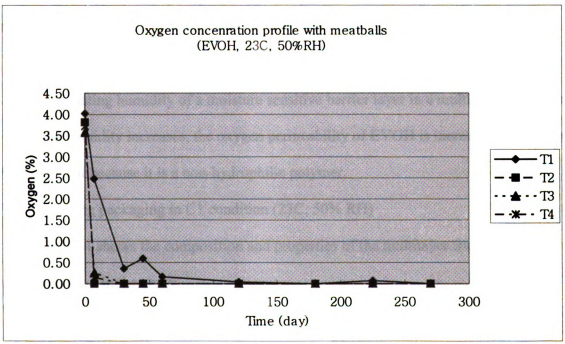


Figure 17: Oxygen concentration with meatballs (plastic lid, 23°C, 50% RH)

4.1.3 Discussion of permeability

The EVOH layer in multilayer film, the main gas barrier layer in the package, is very moisture sensitive. In high relative humidity storage conditions, the overall gas barrier (include flavor, oxygen, and so on) will be decreased. Thus, in order to achieve sufficient barrier to maintain food freshness, the packaging designer needs to have knowledge about polymer material's characteristics and control parameters.

In this study, the main parameter to change the polymer permeability was temperature and humidity. As was demonstrated by the water-packaging test, the oxygen permeability of T1 was strongly influenced by storage conditions such as temperature and humidity [Figure 11, 12]. T1 was filled with distilled water and sealed by an aluminum laminated lid stock, the same as the other packages (T2, T3 and T4), in order to be able to measure only the oxygen permeability of the trays. The barrier properties of the multilayer structure of the tray, temperature, and humidity were expected to affect permeability

4.1.3.1 Estimating humidity of a moisture sensitive barrier layer in a multilayer structure.

As humidity increases, the oxygen permeability of EVOH is increased, but that of PP is constant because it is a non-hydrophilic polymer.

1) Water filling packaging in C1 condition (23C, 50% RH)

Table 4 shows the composition and properties of the multilayer tray structure which was used in the study.

Table 4. The structure of control tray and properties

Layer	1(outside)	2	3	4	5(inside)
Material	PP	Tie	EVOH	Tie	PP
Thickness	0.18	-	0.025	-	0.18
WVTR	0.14	-	0.75	-	0.14
Humidity(%)	50	-	-	-	100
Partial pressure	P_a	-	P_2	-	P_b

- EVOH: 32 mol %
- Thickness average of thermoformed tray: mm
- WVTR: ASTM F1249 (40°C, 90% RH), unit: g.mm/m^2.day.atm [5]

In dealing with a moisture sensitive barrier, our final objective is to estimate the value of the oxygen permeability coefficient, P, of the barrier layer at its water vapor pressure p_2 at its center point. Having the data that correlates P with p, the problem becomes the estimation of p_2.

Since p_2 is the average of p_a and p_b at steady state, $p_2 = \frac{p_a + p_b}{2}$

At the steady state, the flow through the whole structure and through each layer will be the same value. As a result, the equation for p_2 will be as follows [19, 20]:

$$p_2 = \frac{p_a + p_b}{2} = \frac{p_1\left(\frac{l_2}{P_2} + 2\frac{l_3}{P_3}\right) + p_3\left(2\frac{l_1}{P_1} + \frac{l_2}{P_2}\right)}{2\left(\frac{l_1}{P_1} + \frac{l_2}{P_2} + \frac{l_3}{P_3}\right)}$$

From the upper equation, p_2 can be calculated as follows:

$$p_2 = \frac{p_a + p_b}{2} = \frac{50\cdot\left(\frac{0.025}{0.75} + 2\cdot\frac{0.18}{0.14}\right) + 100\cdot\left(2\cdot\frac{0.18}{0.14} + \frac{0.025}{0.75}\right)}{2\cdot\left(\frac{0.18}{0.14} + \frac{0.025}{0.75} + \frac{0.18}{0.14}\right)} = 75.0\%\ \text{RH}$$

2) Water filling package in C2 condition (30C, 80%RH)

Through the same method, the p of water filled package in C2 can be calculated as follows:

$$p_2 = \frac{p_a + p_b}{2} = \frac{80 \cdot \left(\frac{0.025}{0.75} + 2 \cdot \frac{0.18}{0.14}\right) + 100 \cdot \left(2 \cdot \frac{0.18}{0.14} + \frac{0.025}{0.75}\right)}{2 \cdot \left(\frac{0.18}{0.14} + \frac{0.025}{0.75} + \frac{0.18}{0.14}\right)} = 90.0\%\ \text{RH}$$

If the structure is symmetric so that the two outside layers were made of the same polymer and have the same thickness, as is the case with T1, p_2 is the average of p_1 and p_3. When the structure is not symmetric, the value of p_2 will be affected by the relative barriers of the layers.

4.1.3.2 Estimating the permeability of a multilayer structure

1) Estimation of the permeability of PP at 30°C, 90% RH [9]

From Table 4, the oxygen permeability coefficient of PP at 30°C is 1.7×10^{13} $cm^3.cm/cm^2.s.Pa$. Since PP is a non-hydrophilic polymer, PP provides a constant permeability value at any humidity conditions.

Converting the units of PP to $cc.mm/m^2.day.atm$, it can be calculated as follows [9]:

$$1.7\times10^{-13}\frac{[cm^3][cm]}{[cm^2][s][Pa]} = 1.7\times8.75\frac{[cm^3][cm]}{[m^2][day][atm]}\times\frac{10[mm]}{[cm]}$$
$$= 1.49E+02\frac{[cc][mm]}{[m^2][day][atm]}(30°C,90\%RH)$$

2) Estimation of the permeability of PP at 23°C, 75% RH [17]

As the value of E_a of PP at 30°C is 47.7 KJ/mol, the oxygen permeability of PP at 23°C can be obtained from the value at 30°C (148.75 cc.mm/m^2.day.atm).

The calculation is as follows [9, 17, 18]:

E_a of PP at 30°C = 47.7 KJ/mol ÷ 4.184 J = 11.401 Kcal/mol = 11401 cal/mol

$$\frac{E_a}{R} = \frac{11401 cal/mol}{1.987 cal/K.mol} = 5738K$$

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{1}{30+273} - \frac{1}{23+273} = -7.8E-05K^{-1}$$

$$f = \exp\frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \exp(5738 \times \text{-}7.8\text{E-}05) = 0.64$$

$$P_2 = P_1 \times f = 148.75 \times 0.64 = 9.51E+01 \text{ cc.mm/m}^2\text{.day.atm (23°C, 75\% RH)}$$

3) Estimation of the oxygen permeability of EVOH at 30°C, 90% RH

The value of non-oriented EVOH (Grade: EF-F15, EVALCA, USA) with 32 mol% ethylene between 75% to 94% RH is calculated as follows [27];

$$\ln Y = -369.15 + 9.9697RH - 0.06062RH^2 - (-119690 + 3232.1RH - 19.845RH^2)/T$$

$$= -369.15 + 9.9697(90) - 0.06062(90)^2 - [-119690 + 3232.1(90) - 19.845(90)^2] / (30 + 273)$$

$$= 2.60$$

Therefore, Y = 13.46 cc.(15μm)/m^2.day.atm

Converting the units:

$$Y = 13.46\frac{[cc][15\mu m]}{[m^2][day][atm]} \times \frac{[mm]}{10^3[\mu m]} = 1.35E-02\frac{[cc][mm]}{[m^2][day][atm]} \text{ (30°C, 90\% RH)}$$

4) Estimation of the oxygen permeability of EVOH at 23°C, 75% RH

The value of non-oriented EVOH with 32 mol% ethylene at 23°C, 75% RH is also calculated as follows [27];

$\ln Y = -369.15 + 9.9697RH - 0.06062RH^2 - (-119690 + 3232.1RH - 19.845RH^2)/T$

$= -369.15 + 9.9697(75) - 0.06062(75)^2 - [-119690 + 3232.1(75) - 19.845(75)^2] / (23+ 273) = 0.13$

Therefore, Y = 1.13 cc.(15μm)/m^2.day.atm

Converting the units:

$$Y = 1.13\frac{[cc][15\mu m]}{[m^2][day][atm]} \times \frac{[mm]}{10^3[\mu m]} = 1.13E-03\frac{[cc][mm]}{[m^2][day][atm]} \text{ (30°C, 90% RH)}$$

4.1.3.3 Total oxygen permeability of a multilayer structure

For the overall structure, the permeability coefficient P_T is given by [17, 18]

$$P_T = \frac{l_T}{\sum_{i=1}^{n} \frac{l_i}{P_i}}$$

Thus knowing the thickness of each layer and the permeability coefficient for the multilayer structure, we can calculate a total permeability coefficient, using the values in Table 5.

Table 5. Water vapor transmission value (WVTR) of each layer in multilayer structure

Layer	Polymer	Thickness	PO_2 (23C, 75% RH)	PO_2 (30C, 90% RH)
1	PP	1.8E-01	9.51E+01	1.49E+02
2	EVOH	2.5E-02	1.13E-03	1.35E-02
3	PP	1.8E-01	9.51E+01	1.49E+02

- Thickness: mm,
- PO_1 and PO_2 : cc.mm/ m^2.day.atm

1) Total oxygen permeability coefficient at 23°C, 75% RH.

$$P_T = \frac{l_T}{\sum_{i=1}^{3} \frac{l_i}{P_i}} = \frac{(1.8E-01+2.5E-02+1.8E-01)}{\frac{1.8E-01}{9.51E+01}+\frac{2.5E-02}{1.13E-03}+\frac{1.8E-01}{9.51E+01}} = 1.74E-02 \text{ cc.mm/m}^2\text{.day.atm}$$

2) Total oxygen permeability coefficient at 30°C, 90% RH.

$$P_T = \frac{l_T}{\sum_{i=1}^{3} \frac{l_i}{P_i}} = \frac{(1.8E-01+2.5E-02+1.8E-01)}{\frac{1.8E-01}{1.49E+02}+\frac{2.5E-02}{1.35E-02}+\frac{1.8E-01}{1.49E+02}} = 2.08E-01 \text{ cc.mm/ m}^2\text{.day.atm}$$

From the upper calculation, the total oxygen permeability coefficient at 30°C, 90% RH (1.74E-02 cc.mm/m^2.day.atm) was increased about 12 times compared to that at 23°C, 75% RH (2.08E-01cc.mm/ m^2.day.atm). This mainly resulted from the increase of oxygen permeability of EVOH by increased humidity and temperature from 23°C, 75% RH to 30°C, 90% RH. Therefore, the oxygen permeability of moisture sensitive barrier polymers such as EVOH is influenced largely by higher humidity conditions as well as temperature

4.2 TBA

Figure 18 and Figure 19 show the trend of oxidation of the meatballs measured as the amount of malonaldehyde as a function of the container and storage conditions; Tables 6 and 7 show the values. For the C1 condition, one can see the meatballs in T1 were more oxidized than those in the active packages. The initial values of malonaldehyde were assumed to be identical because the same materials were cooked at the same conditions. Indeed, the values of malonaldehyde were not significantly different among packages (T1~T4). However the values of malonaldehyde in active packages were significantly lower than T1 from 45 days. In the C1 condition, the value 0.223 for T1 after 30 days, and the value 0.286 of T1 after 60 days were similar to that of the other containers (T2, 0.271; T3, 0.268; and T4, 0.293) after 180 days.

At the C2 condition, the value of malonaldehyde also had a similar trend to that of C1. After 45 days, meatballs in T1 were significantly more oxidized than in the active packages (T2, T3 and T4). After 180 days when the value of malondaldehyde in T1 was 0.300 mg/kg, it was about 20% lower than that in the C1 condition (0.361). The other containers also showed similar trends. The results showed that the temperature and humidity of the storage conditions affected the oxidation values of the retorted meatballs.

Table 6. TBA values for 6 months (plastic lid, 30°C, 80% RH)

	30 days	45 days	60 days	120 days	180 days
T1	0.223 ± 0.011^{ac}	0.276 ± 0.014^{af}	0.285 ± 0.014^{af}	0.337 ± 0.033^{ag}	0.361 ± 0.022^{ag}
T2	0.176 ± 0.047^{ac}	0.191 ± 0.013^{bef}	0.208 ± 0.017^{bef}	0.222 ± 0.024^{bfg}	0.257 ± 0.010^{bg}
T3	0.183 ± 0.077^{ac}	0.209 ± 0.033^{bef}	0.229 ± 0.010^{bf}	0.234 ± 0.014^{bcfg}	0.267 ± 0.025^{bcg}
T4	0.186 ± 0.068^{ac}	0.207 ± 0.018^{bef}	0.241 ± 0.014^{cefg}	0.260 ± 0.018^{cfg}	0.294 ± 0.014^{cg}

Mean ± standard deviation. Different letters (a through c) within a column are significantly different ($p < 0.05$). Different letters (e through g) within a row are significantly different ($p < 0.05$). N=8

Table 7. TBA values for 6 months (plastic lid, 23°C, 50% RH)

	30 days	45 days	60 days	120 days	180 days
T1	0.223 ± 0.011^{ac}	0.260 ± 0.014^{acf}	0.271 ± 0.018^{af}	0.287 ± 0.018^{af}	0.305 ± 0.026^{ag}
T2	0.176 ± 0.047^{ac}	0.183 ± 0.011^{be}	0.206 ± 0.015^{be}	0.209 ± 0.011^{be}	0.221 ± 0.017^{be}
T3	0.183 ± 0.077^{ac}	0.197 ± 0.010^{be}	0.213 ± 0.026^{be}	0.229 ± 0.047^{be}	0.228 ± 0.041^{be}
T4	0.186 ± 0.068^{ac}	0.200 ± 0.010^{bef}	0.218 ± 0.019^{bef}	0.231 ± 0.019^{bef}	0.250 ± 0.022^{bf}

Mean ± standard deviation. Different letters (a through c) within a column are significantly different ($p < 0.05$). Different letters (e through g) within a row are significantly different ($p < 0.05$). N=8

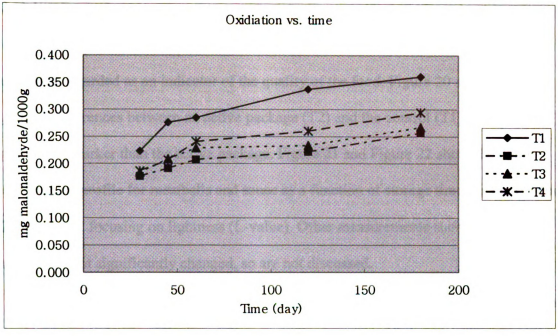


Figure 18: Trend of malonaldehyde (plastic lid, 30°C, 80% RH)

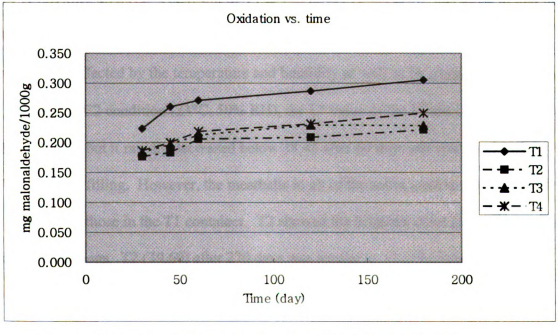


Figure 19: Trend of malonaldehyde (plastic lid, 23°C, 50% RH)

4.3 Color

As oxidation of the meatballs and sauce affects their color, the lightness (L* value) was regarded as an indicator of the quality of the food. Figure 20 shows optical lightness differences between an active package (T2) and the control (T1). T1 is significantly darker than the active package. Figure 21 and Figure 22 show the color measurement profile for meatballs and sauce as a function of storage time for the C1 and C2 conditions, focusing on lightness (L-value). Other measurements such as a* and b* values were not significantly changed, so are not discussed.

For the C1 condition (30°C, 80% RH), the L-value of T1 decreased more rapidly from 45 to 120 days and reached 35.04 at 270 days after filling. T2 (38.10) after 270 days was similar to T3 (38.11) after 225 days, and close to T4 (37.83) after 60 days and T1 (37.00) after 45 days. The result of T1 at 120 days (35.57) at C1 was close to that of T1 (36.61) after 270 days at the C2 condition. This suggests that the L-value of the product was affected by the temperature and humidity as well as by oxygen concentration.

At the C2 condition (23°C, 50% RH), the L* value of the 1st test (after 30 days) of T1 was 40.52, but it rapidly decreased below 38.48 after 60 days and reached 36.61 at 270 days after filling. However, the meatballs in all of the active packages were superior in lightness to those in the T1 container. T2 showed the brightest color (L* value) at both storage conditions. T2 (39.60) after 270 days was similar to T1 (39.23) after 45 days, T3 (39.56) after 225 days and T4 (39.61) after 60 days. The results of T3 lay between T2 and T4. The result of T4 (37.84) after 270 days was similar to the result of T1 (37.74) after 180 days. The averaged color test results are shown in Table 8 and Table 9. The

value of T1, which does not contain oxygen scavenger, at C1 and C2 was generally lower than the active packages.

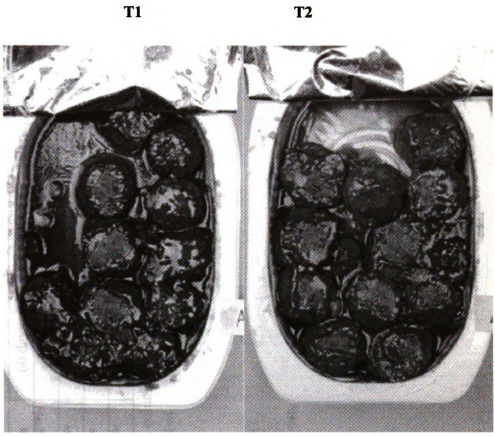


Figure 20: Difference in lightness between T1 and T2 stored at C1 (30°C, 80% RH).

Table 8. Color (lightness, L) analysis data (plastic lid, 30°C, 80% RH)

	30 days	45 days	60 days	120 days	180 days	225 days	270 days
T1	40.52 ^{ad}	39.03 ^{ae}	37.00 ^{af}	35.57 ^{af}	35.62 ^{af}	35.27 ^{af}	35.04 ^{ag}
T2	41.19 ^{ad}	39.33 ^{ade}	38.68 ^{bde}	39.04 ^{ade}	38.71 ^{be}	39.18 ^{be}	38.10 ^{ae}
T3	41.10 ^{ad}	38.99 ^{ae}	38.65 ^{bef}	38.09 ^{abef}	38.34 ^{bef}	38.11 ^{bef}	37.29 ^{abf}
T4	41.09 ^{ad}	39.05 ^{ade}	37.83 ^{abe}	37.44 ^{be}	37.88 ^{be}	37.26 ^{abe}	36.79 ^{be}

Different letters (a through b) within a column are significantly different ($p < 0.05$). Different letters (c through g) within a row are significantly different ($p < 0.05$). N=4

Table 9. Color (lightness, L) analysis data (plastic lid, 23°C, 50% RH)

	30 days	45 days	60 days	120 days	180 days	225 days	270 days
T1	40.52 [ac]	39.23 [acd]	38.48 [ade]	38.32 [ade]	37.74 [adef]	36.68 [aef]	36.61 [af]
T2	41.19 [ac]	40.32 [ac]	40.04 [bc]	40.32 [ac]	40.30 [bc]	39.89 [bc]	39.60 [bc]
T3	41.10 [ac]	40.50 [ac]	40.08 [bc]	39.56 [ac]	39.66 [abc]	39.56 [bc]	39.15 [bc]
T4	41.09 [ac]	39.72 [acd]	39.61 [abcd]	38.95 [acd]	39.30 [abcd]	38.26 [abcd]	37.84 [abd]

Different letters (a through c) within a column are significantly different ($p < 0.05$). Different letters (d through f) within a row are significantly different ($p < 0.05$). N=4

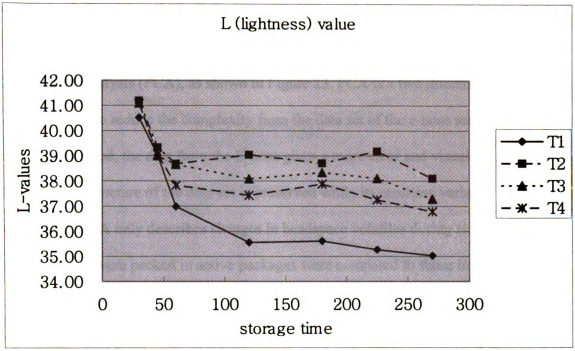


Figure 21: Trend of L value (plastic lid, 30°C, 80% RH, n=4)

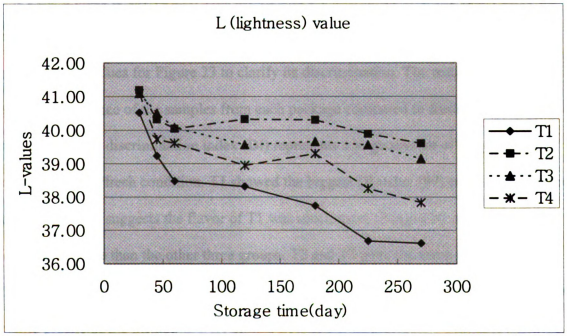


Figure 22: Trend of L value (plastic lid, 23°C, 50% RH, n = 4)

4.4 Flavor

Shelf life results based on E-nose testing have been analyzed using Principal Component Analysis (PCA), as shown in Figure 23. PCA is a two dimensional representation to reduce the complexity from the data set of the e-nose sensors. Using this analytical method, the data from the E-nose gives a more clear and visual discrimination. The inherent structure of the data-set is preserved while its resulting variance is maximized. PCA only describes changes in headspace volatiles during storage time. Meatballs that were packed in active packages were compared to those in the T1 container after 9 months of storage in the C1 condition and to fresh samples. As can be seen, the plots of T1 and those of the active packages were clearly separated. The cluster group of T1 lies on the left bottom side of the graph, and T2, T3, and T4 are separated from T1 and close to each other. This means that the headspace volatiles of the three active packages are similar or close to each other. Table 10 shows numerical discrimination values for Figure 23 to clarify its discrimination. The results indicate the degree of difference of the samples from each package compared to fresh samples. Therefore, a high discrimination index (DI) represents a large amount of flavor change from the original/fresh condition. T1 showed the biggest DI index (97) compared with the fresh group. This suggests the flavor of T1 was much more changed by oxidation after 9 months of storage than the other three groups. T2 and T3 gave the same values as each other, 51 and 52 respectively. Through the efficiency of the oxygen scavenger, changes in volatile profile of the meatballs were almost 50% lower than in T1. The DI of T4 was 68, which is a little higher value than T2 and T3, likely because the content of oxygen scavenger in T4 was lower than in the other two active packages.

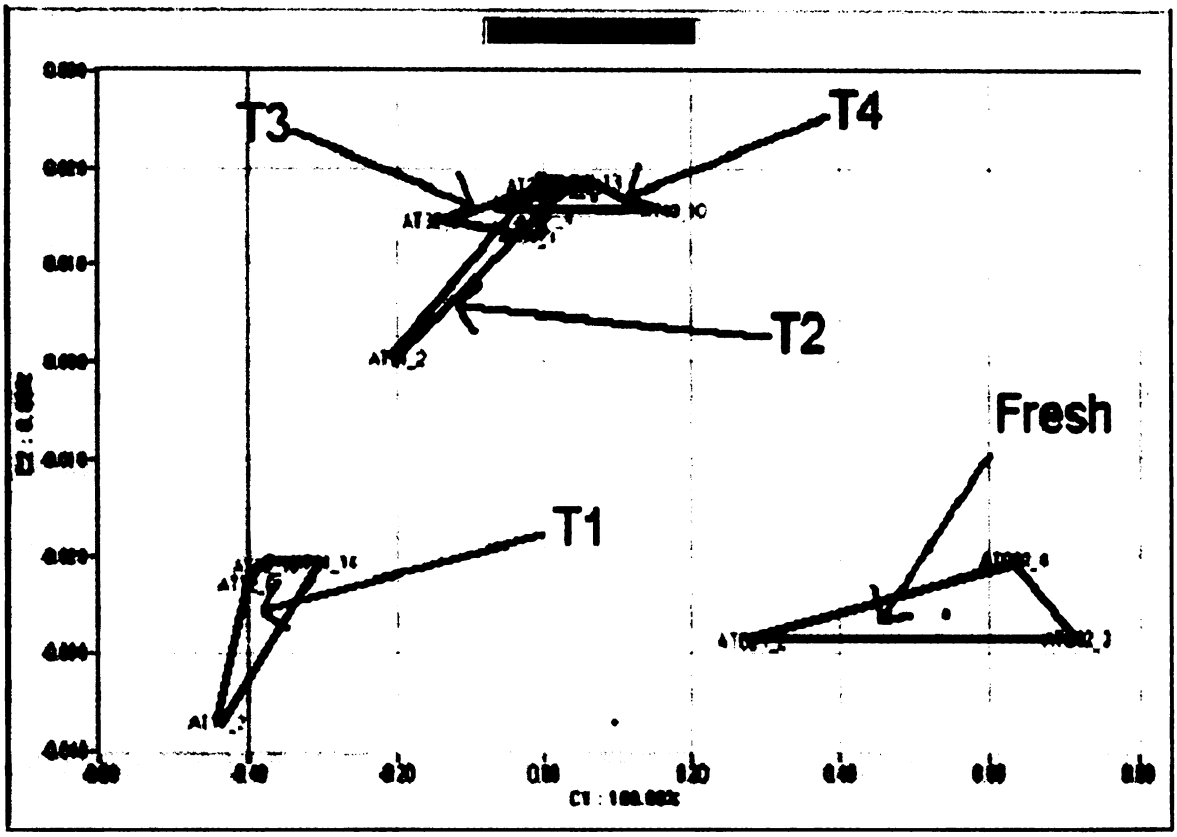


Figure 23: PCA group for meatballs after 9 month storage

Table 10: Discrimination Index (DI) for each meatball package compared to fresh samples

Group	DI
T1	97
T2	52
T3	51
T4	68

CHAPTER 5. CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

As measured by all four kinds of tests, oxygen concentration in the headspace, TBA, color and flavor, all the active packages (T2, T3 and T4) were superior to the passive package (T1) in extending the shelf life of food even though all packages incorporated an MA packaging system using a CO_2 and N_2 mixed gas-purging process on the inside of the container after filling. The results of T2 were better than the other active packages (T3 and T4). This means that the capacity of oxygen absorption increased in proportion to the increase of the quantity of oxygen scavenger in the package. Actually, the shelf life of the meatball product that was packed in a conventional passive package does not exceed 4 months in summer storage conditions, because of unpleasant odor and color change of the food. This study showed the possibility of shelf life extension by using an oxygen scavenger. The oxygen level in oxygen scavenger packages maintained a significantly lower level than that in conventional barrier packages (control). This decreased oxidation, color changes, and flavor changes during 9 months storage. The study showed a higher oxygen scavenger amount in the packages resulted in better quality maintenance. T2, which contained the highest amount of oxygen scavenger compounds, provided the best quality maintenance among the three active packages (T2, T3, and T4). The performance difference between T2 and T3 was not significant in the C2 condition (23 C, 50% RH). As temperature and humidity of the storage condition increased, the oxygen concentration in the headspace of the container increased. Therefore, in developing or designing oxygen scavenger packaging, one should consider the proper amount of compounds in order to maintain the original quality, depending on

storage conditions (temperature and humidity). Manufacturing cost is also an important consideration. The equation of Figure 13 can be used to develop this kind of new product. EVOH or oriented nylon films, which are water sensitive polymers, may not be sufficient as lid stock in high humidity and temperature storage conditions. Therefore, in order to maintain food freshness under retort conditions, other oxygen barrier materials, which have good moisture barrier, should be considered. Finally, through application of active packaging, the extension of shelf life can be expected not only for foods, but also for beverages and medical products.

5.2 Future work

The positive effects of oxygen scavenger systems were observed in this study. The iron based OS system delayed oxidative degradation, color, and flavor changes. As the next step, sensory and microbial growth evaluations are recommended to ensure the shelf life extension by the OS system. In addition, the oxygen scavenger technology required high relative humidity to trigger absorption because the reaction was promoted by moisture. It is hard to apply to a low humidity condition such as a dry product. Therefore, the first work recommended is research and development of a new OS system that is applicable to a low humidity condition. Research on an organic based OS system is also recommended, because iron based OS systems are difficult to apply to food manufacturing processes using metal detectors and transparent packages.

Appendix A

Table 11. Oxygen concentration (meatball, EVOH lid, and 23°C, 50%RH)

TRAY	FILM	1	2	3	4	5	6	7	8	9
		0 day	7 day	30 day	45 day	60 day	120 day	180 day	225 day	270 day
T1	EVOH	3.750	2.200	0.379	0.141	0.137	0.015	0.000	0.051	0.000
		4.210	2.570	0.339	0.279	0.182	0.068	0.000	0.09	0.000
		4.150	2.660	0.347	x	x	x	x	x	0.000
		3.980	x	x	x	x	x	x	x	x
	Avg	4.023	2.477	0.355	0.210	0.160	0.042	0.000	0.071	0.000
T2	EVOH	4.010	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		3.410	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		3.470	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		4.370	0.000	x	x	x	x	x	x	x
	Avg	3.815	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
T3	EVOH	2.990	0.327	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		3.560	0.146	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		3.820	0.317	0.000	x	x	x	x	x	x
		3.930	x	x	x	x	x	x	x	x
	Avg	3.575	0.263	0.000	0.000	0.000	0.000	0.000	0.000	0.000
T4	EVOH	3.260	0.193	0.000	0.000	0.000	0.001	0.000	0.000	0.000
		3.430	0.118	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		4.210	0.127	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		3.980	x	x	x	x	x	x	x	x
	Avg	3.720	0.146	0.000	0.000	0.000	0.001	0.000	0.000	0.000

Appendix A (Continued)

Table 12. Oxygen concentration (meatball, aluminum lid, and 23°C, 50%RH)

TRAY	FILM	1	2	3	4	5	6	7	8	9
		0 day	7 day	30 day	45 day	60 day	120 day	180 day	225 day	270 day
T1	AL	4.390	1.750	0.192	0.470	0.125	0.000	0.000	0.000	0.000
		3.610	1.970	0.408	0.280	0.244	0.003	0.000	0.000	0.000
		3.570	1.460	0.439	x	x	x	0.000	0.000	0.000
		4.200	x	0.405	x	x	x	0.000	0.000	0.000
	Avg	3.943	1.727	0.361	0.375	0.185	0.002	0.000	0.000	0.000
T2	AL	4.160	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		4.030	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		3.770	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		4.370	0.000	x	x	x	x	x	x	x
	Avg	4.083	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
T3	AL	3.850	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		4.410	0.065	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		3.800	0.087	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		3.960	x	x	x	x	x	x	x	x
	Avg	4.005	0.052	0.000	0.000	0.000	0.000	0.000	0.000	0.000
T4	AL	4.580	0.074	0.002	0.000	0.000	0.000	0.000	0.000	0.000
		4.150	0.094	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		4.140	0.044	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		3.750	x	x	x	x	x	x	x	x
	Avg	4.155	0.071	0.001	0.000	0.000	0.000	0.000	0.000	0.000

Appendix A (Continued)

Table 13. Oxygen concentration (meatball, EVOH lid, and 30°C, 80%RH)

TRAY	FILM	1	2	3	4	5	6	7	8	9
		0 day	7 day	30 day	45 day	60 day	120 day	180 day	225 day	270 day
T1	EVOH	3.750	2.200	0.701	0.586	1.432	2.050	0.245	0.589	0.377
		4.210	2.570	0.722	0.597	1.345	2.800	0.680	1.100	0.438
		4.150	2.660	0.680	x	x	x	x	0.800	x
		3.980	x	x	x	x	x	x	x	x
	Avg	4.023	2.477	0.701	0.592	1.389	2.425	0.463	0.845	0.408
T2	EVOH	4.010	0.000	0.000	0.000	0.014	0.010	0.022	0.000	0.000
		3.410	0.000	0.000	0.000	0.000	0.111	0.009	0.000	0.000
		3.470	0.000	0.000	0.000	x	x	x	x	x
		4.370	0.000	0.000	x	x	x	x	x	x
	Avg	3.815	0.000	0.000	0.000	0.007	0.061	0.015	0.000	0.000
T3	EVOH	2.990	0.327	0.000	0.000	0.023	0.077	0.000	0.000	0.266
		3.560	0.146	0.000	0.000	0.028	0.195	0.000	0.000	0.020
		3.820	0.317	0.000	0.000	x	x	x	x	x
		3.930	x	0.000	x	x	x	x	x	x
	Avg	3.575	0.263	0.000	0.000	0.026	0.136	0.000	0.000	0.143
T4	EVOH	3.260	0.193	0.000	0.000	0.476	0.820	0.570	0.829	0.519
		3.430	0.118	0.000	0.000	0.693	0.492	0.313	0.637	0.855
		4.210	0.127	0.000	0.000	x	x	x	x	x
		3.980	x	0.000	x	x	x	x	x	x
	Avg	3.720	0.146	0.000	0.000	0.585	0.656	0.442	0.733	0.687

Appendix A (Continued)

Table 14. Oxygen concentration (meatball, aluminum lid, and 30°C, 80%RH)

TRAY	FILM	1	2	3	4	5	6	7	8	9
		0 day	7 day	30 day	45 day	60 day	120 day	180 day	225 day	270 day
T1	EVOH	4.390	1.750	0.701	0.360	0.570	0.242	0.0001	0.000	0.000
		3.610	1.970	0.722	0.571	0.760	0.192	0.000	0.000	0.000
		3.570	1.460	0.680	0.466	0.680	0.212	0.000	0.000	0.000
		4.200	x	x	x	x	x	x	x	x
	Avg	3.943	1.295	0.526	0.349	0.503	0.162	0.000	0.000	0.000
T2	EVOH	4.160	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		4.030	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		3.770	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		4.370	0.000	x	x	x	x	x	x	x
	Avg	4.083	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
T3	EVOH	3.850	0.004	0.000	0.000	0.000	0.001	0.000	0.000	0.000
		4.410	0.065	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		3.800	0.087	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		3.960	x	x	x	x	x	x	x	x
	Avg	4.005	0.052	0.000	0.000	0.000	0.000	0.000	0.000	0.000
T4	EVOH	4.580	0.074	0.000	0.000	0.000	0.004	0.000	0.000	0.000
		4.150	0.094	0.000	0.000	0.000	0.006	0.000	0.000	0.000
		4.140	0.044	0.000	0.000	0.000	0.000	0.000	0.000	0.000
		3.750	x	x	x	x	x	x	x	x
	Avg	4.155	0.071	0.000	0.000	0.000	0.005	0.000	0.000	0.000

Appendix B (continued)

Table 15. Oxygen concentration (water, aluminum lid, and 23°C, 50%RH)

TRAY	FILM	7 Day	15 Day	30 Day	45 Day	60 day	120 day	180 day
T1	AL	4.020	8.160	9.340	10.290	8.730	8.49	10.51
		4.420	7.730	8.770	9.070	9.600	8.51	9.71
	Avg	4.220	7.945	9.055	9.680	9.165	8.500	10.110
T2	AL	0.269	0.021	0.000	0.000	0.000	0	0
		0.455	0.100	0.000	0.000	0.000	0	0
	Avg	0.362	0.061	0.000	0.000	0.000	0.000	0.000
T3	AL	0.204	0.440	0.000	0.000	0.000	0	0
		0.339	0.004	0.000	0.000	0.000	0	0
		0.272	0.222	0.000	0.000	0.000	0.000	0.000
	Avg	2.820	0.911	0.263	0.130	0.030	0.06	0.212
T4	AL	1.984	0.943	0.360	0.123	0.050	0.1	0.245
		2.402	0.927	0.312	0.127	0.040	0.080	0.229
	Avg	0.269	0.021	0.000	0.000	0.000	0	0

Appendix B (continued)

Table 16. Oxygen concentration (water, aluminum lid, and 30°C, 80%RH)

TRAY	FILM	7 Day	15 Day	30 Day	45 Day	60 day	120 day	180 day
T1	AL	4.020	9.070	10.780	14.020	13.280	16.39	17.39
		4.420	9.730	12.630	14.190	13.190	16.83	16.48
		x	10.000	x	x	x	x	x
	Avg	4.220	9.600	11.705	14.105	13.235	16.610	16.935
T2	AL	0.269	0.044	0.000	0.000	0.002	0.0071	0.368
		0.455	0.001	0.000	0.000	0.000	0.07	0.288
	Avg	0.362	0.022	0.000	0.000	0.001	0.039	0.328
T3	AL	0.204	0.080	0.000	0.120	0.271	2.31	5.61
		0.339	1.345	0.009	0.132	0.355	2.11	5.8
		x	1.355	x	x	x	x	x
	Avg	0.272	0.927	0.005	0.126	0.313	2.210	5.705
T4	AL	2.820	1.123	1.571	3.070	4.570	8.7	11.02
		1.984	0.985	2.640	3.100	4.780	7.46	10.44
	Avg	2.402	1.054	2.106	3.085	4.675	8.080	10.730

Appendix C

Table 17. TBA value (meatball, EVOH lid, 23°C, 50% RH)

TRAY	Sample NO.	1st	2nd	3rd	4th	5th
C2		30 Day	45 Day	60 Day	120 Day	180 Day
T1	1A1	0.218	0.257	0.250	0.273	0.265
	1A2	0.211	0.281	0.265	0.312	0.296
	1B1	0.211	0.250	0.250	0.304	0.328
	1B2	0.226	0.257	0.265	0.273	0.273
	2A1	0.218	0.265	0.281	0.304	0.320
	2A2	0.242	0.281	0.296	0.265	0.335
	2B1	0.234	0.250	0.265	0.273	0.296
	2B2	0.226	0.242	0.296	0.289	0.328
	Average	0.223	0.260	0.271	0.287	0.305
T2	1A1	0.218	0.179	0.187	0.218	0.218
	1A2	0.211	0.195	0.211	0.203	0.250
	1B1	0.164	0.179	0.226	0.211	0.203
	1B2	0.148	0.172	0.203	0.226	0.226
	2A1	0.218	0.172	0.187	0.195	0.218
	2A2	0.078	0.187	0.226	0.218	0.203
	2B1	0.179	0.203	0.211	0.195	0.242
	2B2	0.195	0.179	0.195	0.203	0.211
	Average	0.176	0.183	0.206	0.209	0.221
T3	1A1	0.179	0.203	0.203	0.195	0.226
	1A2	0.195	0.179	0.242	0.179	0.281
	1B1	0.195	0.195	0.164	0.172	0.203
	1B2	0.148	0.211	0.195	0.234	0.172
	2A1	0.195	0.203	0.218	0.312	0.257
	2A2	0.172	0.195	0.211	0.250	0.273
	2B1	0.179	0.203	0.218	0.265	0.179
	2B2	0.203	0.187	0.250	0.226	0.234
	Average	0.183	0.197	0.213	0.229	0.228
T4	1A1	0.023	0.179	0.211	0.242	0.211
	1A2	0.226	0.203	0.218	0.218	0.234
	1B1	0.211	0.195	0.187	0.250	0.265
	1B2	0.218	0.211	0.211	0.226	0.273
	2A1	0.195	0.203	0.211	0.203	0.242
	2A2	0.172	0.211	0.218	0.211	0.242
	2B1	0.218	0.203	0.242	0.242	0.250
	2B2	0.226	0.195	0.250	0.257	0.281
	Average	0.186	0.200	0.218	0.231	0.250

Table 18. TBA value (meatball, EVOH lid, 30°C, 80% RH)

TRAY	Sample NO.	1st	2nd	3rd	4th	5th
C2		30 Day	45 Day	60 Day	120 Day	180 Day
T1	1A1	0.218	0.281	0.289	0.343	0.328
	1A2	0.211	0.265	0.273	0.328	0.351
	1B1	0.211	0.273	0.304	0.351	0.382
	1B2	0.226	0.281	0.296	0.335	0.343
	2A1	0.218	0.304	0.265	0.359	0.367
	2A2	0.242	0.257	0.273	0.335	0.390
	2B1	0.234	0.265	0.281	0.265	0.343
	2B2	0.226	0.281	0.296	0.382	0.382
	Average	0.223	0.276	0.285	0.337	0.361
T2	1A1	0.218	0.195	0.234	0.203	0.257
	1A2	0.211	0.211	0.211	0.242	0.242
	1B1	0.164	0.195	0.195	0.211	0.265
	1B2	0.148	0.172	0.218	0.179	0.273
	2A1	0.218	0.195	0.195	0.242	0.250
	2A2	0.078	0.172	0.187	0.250	0.265
	2B1	0.179	0.203	0.226	0.218	0.250
	2B2	0.195	0.187	0.195	0.234	0.257
	Average	0.176	0.191	0.208	0.222	0.257
T3	1A1	0.179	0.172	0.218	0.226	0.234
	1A2	0.195	0.187	0.242	0.250	0.242
	1B1	0.195	0.179	0.242	0.226	0.265
	1B2	0.148	0.234	0.218	0.257	0.296
	2A1	0.195	0.179	0.234	0.242	0.304
	2A2	0.172	0.218	0.226	0.211	0.265
	2B1	0.179	0.242	0.234	0.226	0.281
	2B2	0.203	0.257	0.218	0.234	0.250
	Average	0.183	0.209	0.229	0.234	0.267
T4	1A1	0.023	0.218	0.265	0.250	0.281
	1A2	0.226	0.234	0.234	0.273	0.296
	1B1	0.211	0.211	0.226	0.289	0.312
	1B2	0.218	0.195	0.242	0.273	0.304
	2A1	0.195	0.179	0.226	0.257	0.281
	2A2	0.172	0.218	0.242	0.242	0.273
	2B1	0.218	0.211	0.234	0.234	0.312
	2B2	0.226	0.187	0.257	0.265	0.296
	Average	0.186	0.207	0.241	0.260	0.294

Appendix D

Table 19. Color analysis data of meatball packages (EVOH lid, 23°C, 50%RH)

TRAY	No	30 Day			45 Day			60 Day			120 Day			180 Day			225 Day			270 Day		
		L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*
T1	1-1	40.3	15.0	26.9	39.3	14.8	30.5	38.5	14.9	29.5	38.2	14.1	27.0	37.3	12.4	26.8	35.5	13.0	25.1	36.0	12.8	25.2
	1-2	40.5	14.1	27.3	39.2	15.4	31.2	38.5	15.0	27.7	38.3	15.3	29.7	37.5	13.6	26.6	36.2	13.1	30.5	37.8	14.9	29.3
	2-1	40.2	13.5	27.1	38.5	13.5	27.1	39.0	13.4	29.1	38.2	14.0	25.3	38.4	13.0	26.5	37.2	12.6	23.4	36.0	12.6	25.6
	2-2	41.0	13.6	27.9	39.9	13.1	26.5	38.0	14.4	25.9	38.5	14.3	26.9	37.9	13.3	26.6	37.8	13.9	27.1	36.6	12.1	23.7
	AVE	40.5	14.1	27.3	39.2	14.2	28.9	38.5	14.5	28.0	38.3	14.4	27.2	37.7	13.1	26.6	36.7	13.1	26.5	36.6	13.1	25.9
T2	1-1	40.2	15.9	26.0	39.4	15.0	28.3	40.3	13.8	25.7	41.1	15.9	25.5	40.1	12.9	24.9	39.9	12.9	25.5	40.0	14.4	26.6
	1-2	41.9	16.7	32.9	40.3	15.8	31.9	39.4	15.1	28.1	41.2	13.3	27.1	40.5	14.4	26.8	40.5	12.4	26.7	38.9	13.1	26.3
	2-1	42.6	14.2	29.6	41.3	14.8	30.3	40.4	14.0	25.6	39.6	12.9	26.1	39.5	14.1	29.0	39.1	13.1	25.9	40.0	12.6	24.5
	2-2	40.1	15.9	30.8	40.3	15.4	29.2	40.0	13.7	29.6	39.4	14.1	25.9	41.1	13.4	25.9	40.0	14.0	24.3	39.6	13.6	27.2
	AVE	41.2	15.7	29.8	40.3	15.2	29.9	40.0	14.2	27.3	40.3	14.0	26.1	40.3	13.7	26.7	39.9	13.1	25.6	39.6	13.4	26.2
T3	1-1	41.3	16.2	31.8	40.0	14.7	26.1	40.9	13.6	25.4	37.1	14.3	27.1	39.2	13.4	25.4	39.0	11.9	23.9	40.1	11.6	24.2
	1-2	42.0	15.9	32.2	40.7	15.8	29.2	39.3	15.5	31.7	39.9	14.8	26.2	38.4	12.9	25.3	40.7	12.3	26.2	38.0	12.7	25.1
	2-1	39.8	15.0	27.6	40.3	13.3	24.7	40.7	15.7	30.5	41.1	15.4	27.2	41.0	13.6	26.4	39.5	13.2	26.6	39.6	13.1	24.9
	2-2	41.2	14.9	27.0	41.0	14.2	27.0	39.4	17.2	32.9	40.2	15.8	26.9	40.1	14.3	28.8	39.0	13.1	25.5	38.9	12.9	26.3
	AVE	41.1	15.5	29.7	40.5	14.5	26.8	40.1	15.5	30.1	39.6	15.1	26.8	39.7	13.5	26.5	39.6	12.6	25.5	39.2	12.6	25.1
T4	1-1	39.8	17.1	29.5	39.7	15.3	28.0	40.3	12.6	26.0	37.3	13.6	26.5	39.0	13.4	25.5	38.2	12.2	25.8	37.9	12.6	25.7
	1-2	41.1	14.4	28.6	39.3	15.9	29.8	39.6	15.4	28.8	39.5	14.0	27.0	38.1	11.8	24.0	38.1	12.5	28.3	36.7	12.9	26.0
	2-1	42.9	14.2	26.8	40.2	14.8	26.8	39.8	13.9	26.1	40.0	13.7	25.4	39.9	12.9	25.5	39.1	14.0	26.5	38.2	11.6	23.9
	2-2	40.6	14.3	23.8	39.6	13.5	27.5	38.7	15.0	27.7	38.9	14.6	26.2	40.2	11.3	25.9	37.7	13.5	27.6	38.6	12.3	23.6
	AVE	41.1	15.0	27.2	39.7	14.9	28.0	39.6	14.2	27.2	39.0	14.0	26.3	39.3	12.4	25.2	38.3	13.1	27.1	37.8	12.3	24.8

Table 20. Color analysis data of meatball packages (EVOH lid, 30°C, 80%RH)

TRAY	No	30 Day			45 Day			60 Day			120 Day			180 Day			225 Day			270 Day		
		L*	a*	b*	L*	a*	b*	L*	a*	B*	L*	a*	b*	L*	a*	b*	L*	a*	b*	L*	a*	b*
T1	1-1	40.3	15.0	26.9	38.9	16.3	30.0	37.4	15.3	27.1	35.2	12.2	23.1	35.8	11.1	21.8	35.8	10.5	22.0	35.2	10.7	24.1
	1-2	40.5	14.1	27.3	38.9	19.0	34.9	36.7	13.5	26.4	35.7	13.0	24.3	35.9	11.6	23.3	35.1	11.4	22.4	34.9	10.7	22.5
	2-1	40.2	13.5	27.1	38.6	14.3	26.7	36.8	12.9	25.5	35.3	12.5	23.9	35.1	10.8	22.5	35.4	10.8	21.2	35.3	10.6	21.7
	2-2	41.0	13.6	27.9	39.7	13.8	26.7	37.0	13.2	28.2	36.0	14.6	28.5	35.6	10.9	21.3	34.8	11.7	22.8	34.8	12.6	23.4
	AVE	40.5	14.1	27.3	39.0	15.8	29.6	37.0	13.7	26.8	35.6	13.1	25.0	35.6	11.1	22.2	35.3	11.1	22.1	35.0	11.1	22.9
T2	1-1	40.2	15.9	26.0	39.4	13.5	25.0	38.1	14.0	24.8	38.8	11.8	21.2	37.9	10.6	20.7	39.2	11.4	25.7	38.3	11.1	21.3
	1-2	41.9	16.7	32.9	38.8	14.6	27.3	38.5	13.7	25.3	39.2	12.5	23.8	39.9	10.8	22.3	39.6	11.9	23.3	38.0	10.3	18.6
	2-1	42.6	14.2	29.6	41.0	13.0	23.7	39.3	13.3	25.9	39.5	11.1	22.0	39.6	10.9	21.3	39.2	10.4	20.4	38.8	12.0	23.4
	2-2	40.1	15.9	30.8	38.1	13.1	26.2	38.9	13.1	26.2	38.7	11.7	21.5	37.4	11.1	21.8	38.7	12.8	24.2	37.3	11.3	23.0
	AVE	41.2	15.7	29.8	39.3	13.6	25.6	38.7	13.5	25.5	39.0	11.8	22.1	38.7	10.9	21.5	39.2	11.6	23.4	38.1	11.2	21.6
T3	1-1	41.3	16.2	31.8	39.0	14.3	24.8	38.9	15.1	27.3	37.4	12.4	23.1	38.8	10.6	21.1	37.4	10.2	21.5	37.3	10.8	21.4
	1-2	42.0	15.9	32.2	38.2	14.7	25.5	37.9	13.0	25.9	37.9	13.3	24.0	38.3	9.5	20.3	38.5	11.1	22.9	37.5	10.4	20.8
	2-1	39.8	15.0	27.6	39.5	13.7	26.7	38.9	14.0	27.1	38.1	10.6	19.0	37.8	11.2	23.7	38.1	10.1	21.0	37.0	10.7	21.2
	2-2	41.2	14.9	27.0	39.2	13.3	29.6	39.0	12.8	25.9	39.0	12.1	22.5	38.4	13.0	23.3	38.5	9.3	20.2	37.4	9.7	19.2
	AVE	41.1	15.5	29.7	39.0	14.0	26.7	38.7	13.7	26.5	38.1	12.1	22.2	38.3	11.1	22.1	38.1	10.2	21.4	37.3	10.4	20.7
T4	1-1	39.8	17.1	29.5	38.8	13.8	25.1	37.7	13.4	26.6	37.6	11.6	22.6	38.9	11.8	22.4	36.6	10.7	20.8	36.9	10.0	20.5
	1-2	41.1	14.4	28.6	37.2	14.8	28.2	37.3	11.9	23.0	36.8	10.0	19.9	38.0	9.3	21.5	38.5	10.4	21.1	36.4	8.7	20.7
	2-1	42.9	14.2	26.8	40.5	14.3	26.9	38.0	11.4	22.4	37.8	11.8	20.7	37.3	10.4	21.1	38.9	9.5	21.2	37.3	9.5	20.5
	2-2	40.6	14.3	23.8	39.7	14.1	24.9	38.5	12.6	22.3	37.6	13.4	24.3	37.4	10.4	21.1	35.0	10.6	20.7	36.6	9.1	20.6
	AVE	41.1	15.0	27.2	39.1	14.3	26.3	37.8	12.3	23.6	37.4	11.7	21.9	37.9	10.5	21.5	37.3	10.3	20.9	36.8	9.3	20.6

Appendix E

Figure 24. Discrimination Index (DI) for T1 and fresh samples

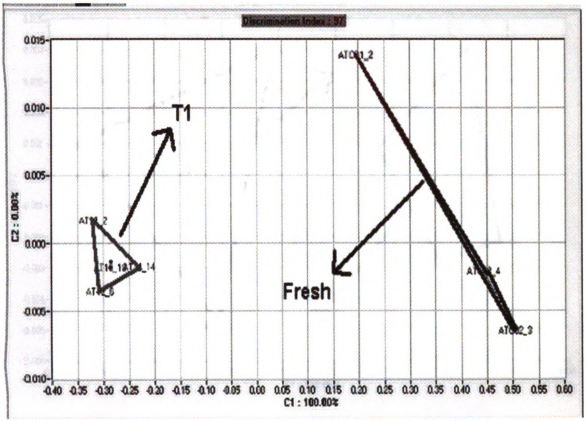


Figure 25. Discrimination Index (DI) for T2 and fresh samples

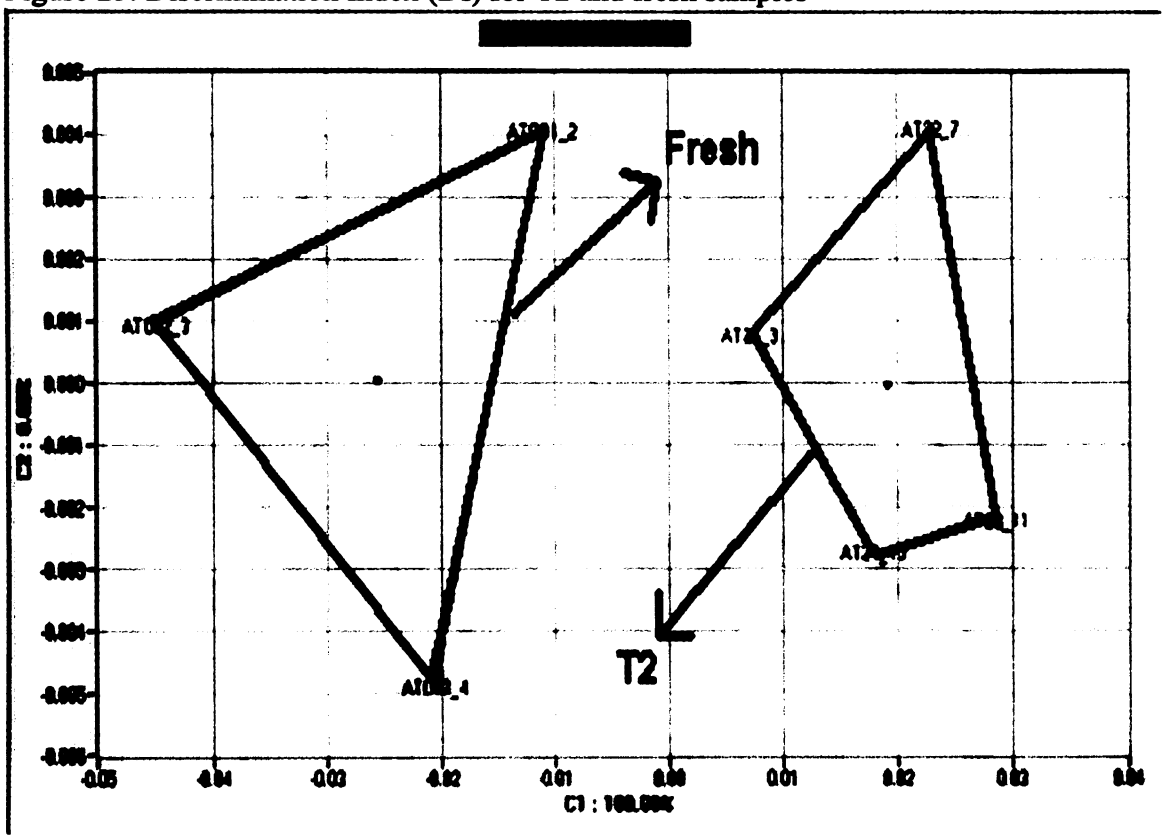


Figure 26. Discrimination Index (DI) for T3 and fresh samples

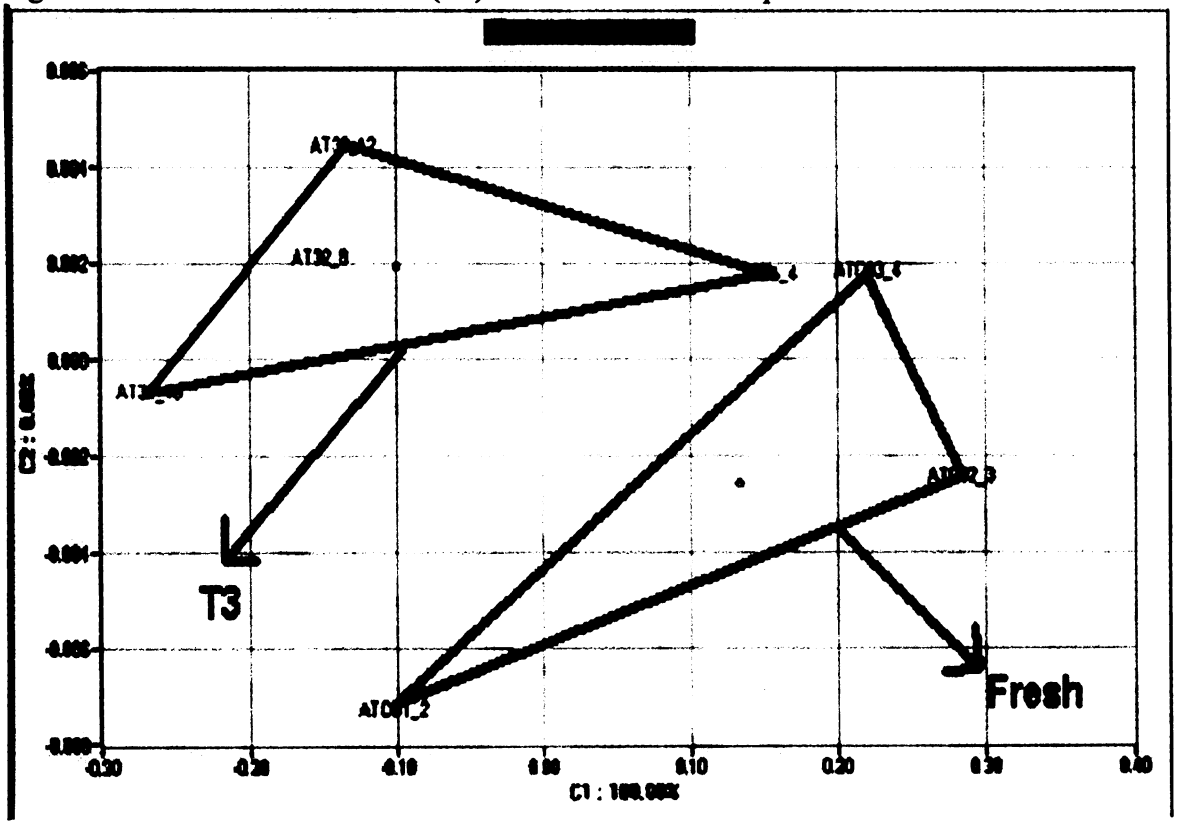
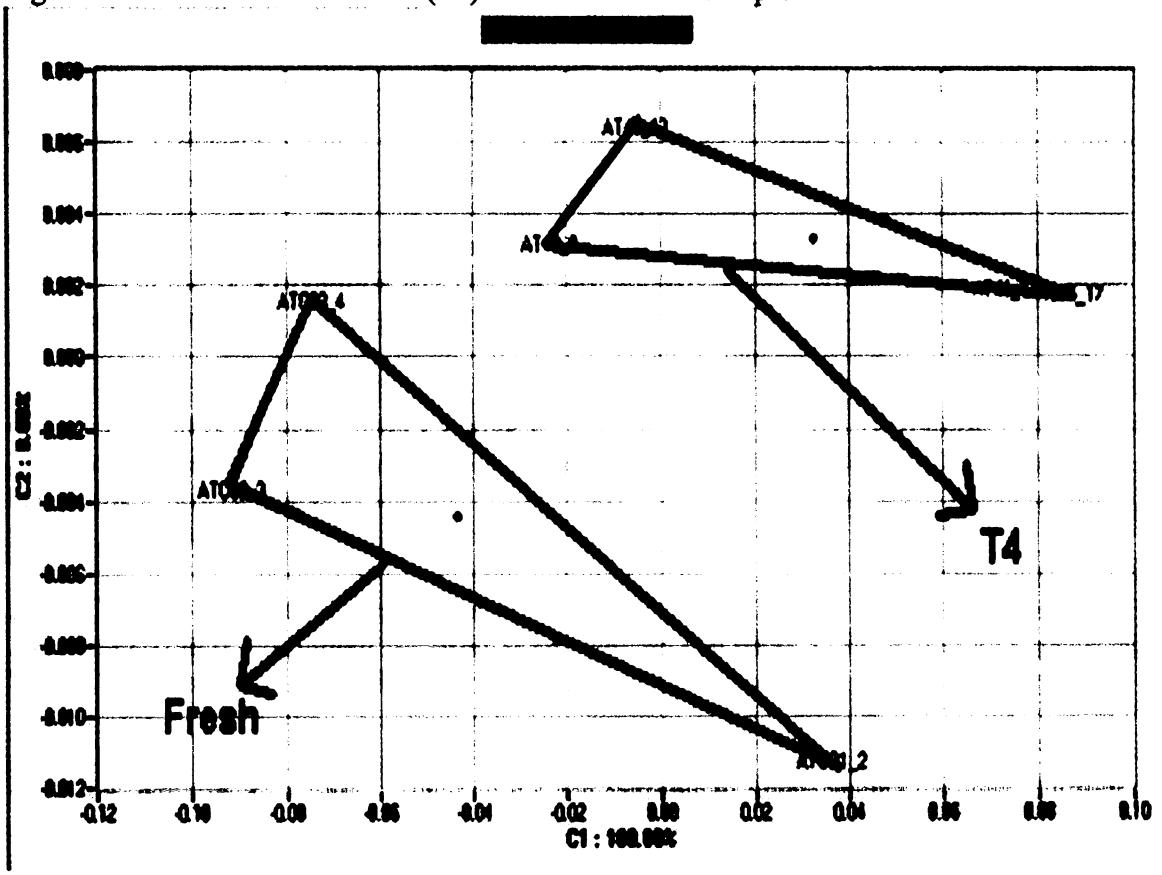


Figure 27. Discrimination Index (DI) for T4 and fresh samples



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