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Effects of Oxygen Scavenging Package on the Quality Changes of Processed Meatball Product

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Abstract Processed meatball products were packaged in a passive package without oxygen scavenger as 1 control and 3 active packages of which have PP-based oxygen scavenger master batch materials (OSMB) of 40, 80, and 100%(w/w) in the middle layer and stored at 23 and 30°C up to 9 months. Quality changes of packaged products were evaluated by measuring the oxygen concentration of the headspace in containers, thiobarbituric acid (TBA), color, and flavor. The oxygen concentration of the package having 100% OSMB was lower than those of 40 and 80%. The color changes and TBA values of the meat ball in the package containing 100% OSMB were the least among the treatments. Using principal component analysis (PCA), the control showed more flavor change than the packages containing oxygen scavenger. As a result, all active packages could extend the shelf life of the meatball products compared with that of the passive package.

Keywords: active packaging, oxygen scavenger, thiobarbituric acid, principal component analysis

Introduction

In the past twenty years, the use of plastic has grown remarkably in packaging as its convenience for manufacturing, handling, and use compared to conventional materials such as paper, metal, and glass (1). In particular, multilayer barrier packaging has challenged metal or glass for long shelf life in food packaging because of its high gas barrier properties. One of the largest segments in the multilayer barrier packaging market is ethylene vinyl alcohol (EVOH). The demand for high gas-barrier packaging materials used in food packaging drives the growth of consumption of EVOH (2,3).

However, due to its sensitivity to moisture, EVOH has some limitations of poor gas or moisture barrier properties at high humidity conditions of the retort process. 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 in aseptic processing. 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 multilayer packaging provides excellent protection from the environment.

For this reason, in recently years, there has been a growing interest in the use of new technology using an oxygen scavenger material as active packaging for food products. The oxygen scavenger material was introduced to replace or supplement conventional multilayer barrier packaging or passive packaging because it is designed to control oxygen inside the package and provide a barrier to the environment (4). 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 (5).

As a conventional application, the use of discrete sachets containing oxygen scavengers previously mentioned has already found commercial application, but met with resistance from food packers because it is visually unappealing, especially if the sachet is broken. Also, accidental ingestion by children is another concern. Thus, a much more useful approach would be the use of multilayer plastic barrier packaging with the scavenging medium as food containers. Therefore, the objective of this study is to evaluate the effect of multilayer plastic packaging container with ferrous iron based scavengers to provide loner shelf life of processed meatball products.

Materials and Methods

Packaging container Oxygen scavenging container was manufactured by E. Saeng Co., Ltd., Seoul, Korea. The container was composed of a tray and a lid. The average weight of a tray was 14.31±0.02 g and its dimension was 180×120×30 mm. The tray was thermoformed from a sheet that has a multilayer structure produced by a feedblock system in a coextrusion sheeting line. The tray was designed as a multilayer structure, PP/adhesive/EVOH/adhesive/OSMB (Oxygen scavenger)/PP. As shown in Table 1, 3 content ratios of PP-based oxygen scavenger master batch materials (OSMB, Toyo Seikan Kaisha, Ltd., Tokyo, Japan) were used; 40, 80, and 100%(w/w). T1 was used as control. The conventional barrier material structure PP/adhesive/EVOH/adhesive/PP was produced and compared to these 3 oxygen scavenger packages (T2, T3, and T4). An amount of the oxygen scavenger was mixed with PP, and extruded to produce master-batch resins. Then, PP resins were mixed and extruded again with the expected amount of master-batch to produce the final matrix film layer. The oxygen scavenger was iron based compounds ($Fe(OH_2)$, Toyo Seikan Kaisha, Ltd., Tokyo, Japan) and the

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Table 1. Construction configuration of semi-rigid container

Code	Tray[1]	Lid
T1	PP(180)//EVOH(25)//PP(180)	PET(12)//Nylon(15)//EVOH(12)//PP(50)
T2	PP(180)//EVOH(25)//OSMB1(80)/PP(100)	PET(12)//Nylon(15)//EVOH(12)//PP(50)
T3	PP(180)//EVOH(25)//OSMB2(80)/PP(100)	PET(12)//Nylon(15)//EVOH(12)//PP(50)
T4	PP(180)//EVOH(25)//OSMB3(80)/PP(100)	PET(12)//Nylon(15)//EVOH(12)//PP(50)

[1] OSMB1, a layer extruded from 100% PP based oxygen scavenger master batch (7% iron); OSMB2, a layer extruded from 80% PP based oxygen scavenger master batch (7% iron)+20% PP; OSMB3, a layer extruded from 40% PP based oxygen scavenger master batch (7% iron)+60% PP; //: tie layer; /: non-tie layer; ( ): thickness, μm.

oxygen absorbing properties were initiated by water vapor produced in the package during the retort process. All lids for each tray were made of traditional cast films for retort process; PET/Nylon/EVOH/PP. The film was produced by triple dry lamination and slitting processes, and printed by a rotogravure printing.

Food product and process conditions Commercialized meatball products were obtained from Dae Sang Co. (Seoul, Korea) for the storage stability studies. Since the meatball tray has larger headspace than other retort food packaging, the package provided enough headspace to analyze oxygen concentration in the inside of a retort packaging. The condition of retort system (Hisaka Works, Ltd., Osaka, Japan) was 1 hr at 121°C (come up time; 10 min, retort tim; 35 min, cooling time; 15 min). In order to reduce the progress of food oxidation in the package, a modified atmosphere packaging system was used. The mixed N_2 and CO_2 gas (a mixed ratio of 80% CO_2/20% N) was flushed into the headspace in the package before the lid was sealed. The heat-sealing condition was 190 to 210°C at a pressure of 2.5 kg/cm^2 for 2 sec.

Storage studies of food product Sample products were stacked in storage chambers at 2 conditions. The one condition consisted of light at a level of 800-1,000 Lux, temperature of 30°C and 80% relative humidity (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 consisted of 23°C, 50% RH and dark condition. Periodical tests were performed at day 30, 45, 60, 120, 180, 225, and 270 after filling.

Analysis of oxygen level in package The oxygen concentration was measured using an oxygen headspace analyzer (Model-3500; detection range 0.01-100%, Illinois Instruments, Johnsburg, IL, USA). Samples were withdrawn at a rate of 40 mL/min using the pump and passed by the oxygen sensor. For the first set of experiments, the efficacy of oxygen scavenger was evaluated without food. Sample trays were filled with distilled water and tested during a 6 month period, and the amount of oxygen absorbed by the oxygen scavengers were determined by the rate of decreased 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 estimate practical performance of oxygen scavenger with meatballs. Trays were filled with meatballs. The oxygen concentration in headspace was determined over a period of 9 months. The oxygen scavenger efficacy tests with distilled water were performed simultaneously from 0 to 180 days.

Color measurement The color change corresponding to the oxidation of the surface of the meatballs and the sauce was evaluated using a colorimeter (Chroma Meter Measuring Head CR-300; Minolta, Osaka, Japan), 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. For this test, samples were tested 8 times over 9 months: 7, 15, 30, 60, 90, 120, 180, and 270 days after filling.

Thiobarbituric acid (TBA) analysis Ten 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 butylated hydroxy anisole (BHA)+butylated hydroxy hydroxytoluene (BHT)]. The next experiment was conducted according to the method of Brewer *et al.* (6). The prepared 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 mg malonaldehyde/kg meat.

Flavor evaluation To measure the flavor change of the meatballs, an E-nose (FOX 3000; Alpha MOS, Belle Mead, NJ, USA) was used. The FOX 3000 contains a robotic auto sampler that takes sealed vials containing 1 g of meatball samples to an oven, syringes out a 10 mL gas sample from the headspace, and injects it into the sample injection port. The carrier gas that flows through the sensor carries the sample gas, and sensors analyze its flavor.

Statistical analysis All data are expressed as mean± standard error (SE). Statistical analysis was performed by analysis of variance (ANOVA) using the statistical analysis system (SAS Institute Inc., Cary, NC, USA). Difference in oxygen concentration in the headspace of containers between the passive and active packages was assessed by student's *t*-test at the 95% confidence level ($p<0.05$).

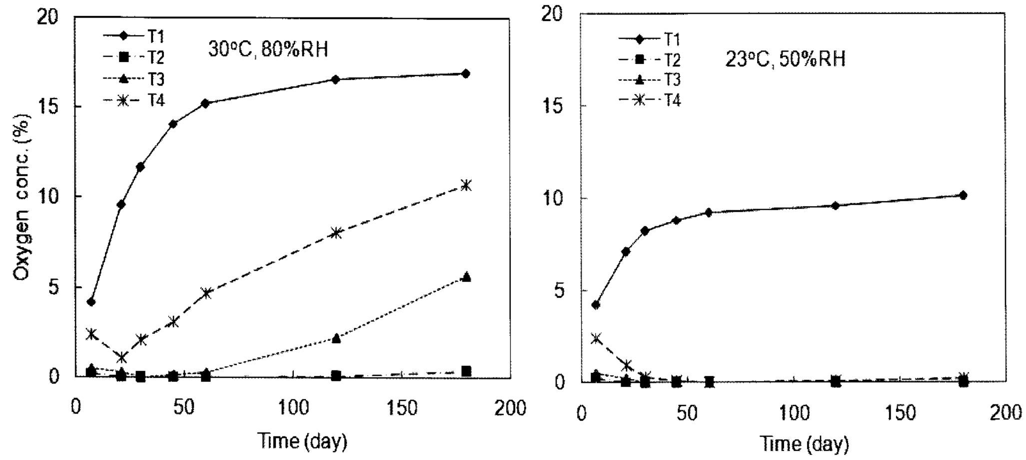

Fig. 1. Oxygen concentration of the headspace of packages filled with water as a function of storage time. Each point is the mean±SE (0.4-1.2) of 2 replicate experiments with 3 samples analyzed per replicate (n=6).

Table 2. Oxygen concentration of the headspace of packages filled with water after 180 days at 23 and 30°C

Container	Storage conditions	Percent of oxygen concentration[1]
T1	23°C, 50% RH	10.11±0.40^a
	30°C, 80% RH	16.94±0.46^A
T2	23°C, 50% RH	0.00±0.00^b
	30°C, 80% RH	0.33±0.04^D
T3	23°C, 50% RH	0.13±0.04^b
	30°C, 80% RH	5.27±0.21^C
T4	23°C, 50% RH	0.23±0.02^b
	30°C, 80% RH	10.73±0.31^B

[1] Mean±SE of each container (n=3); $^{a\text{-}b,\ A\text{-}D}$Means with different superscripts at 23 and 30°C, respectively, are significantly different (p<0.05).

Results and Discussion

Level of oxygen in the headspace of packaged container Figure 1 and Table 2 show the trend of oxygen concentration in the headspace of packages filled with distilled water during 6 months of storage. The lid was composed of aluminum laminated film in order to estimate the effect of the performance of oxygen scavenger compared to conventional passive barrier packaging. The total oxygen permeability coefficients in a multilayer structure for the tray were 2.08E-01 cc·mm/m^2·day·atm at 23°C, 75% RH and 1.74E-02 cc·mm/m^2·day·atm at 30°C, 90% RH, respectively (7). These data indicate that the oxygen permeability of moisture sensitive barrier polymers such as EVOH is influenced largely by higher humidity conditions as well as temperature.

The initial oxygen concentration in the headspace was 3% due to the amount of oxygen gas dissolved in the distilled water. Under the storage condition at 23°C, the oxygen scavenger packages (T2, T3, and T4) showed excellent passive barrier properties 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. The oxygen concentration in the oxygen scavenger packages at 23°C showed a similar value (T3=0.133%), as compared to the oxygen concentration at less than 0.1% through modified atmosphere packaging (MAP) reported by Koyama (8) from the use of a small amount of oxygen scavenger to remove residual oxygen in the package. In contrast, the oxygen concentration in T1 continuously increased. Under the storage condition at 30°C, 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, the result showed that T2 or T3 should be selected when the package needs to sustain an oxygen concentration at 3% or below the original level.

Level of oxygen in the headspace of container packaged with meatball In the evaluation of the meatball products at condition of 30°C, T1 also exhibited much higher oxygen concentration in the headspace than the active packages as shown in Fig. 2. 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 storage condition at 30°C, 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 at 30°C, the oxygen concentration in the headspace of the packages was reduced by a complicated mechanism as in those using the aluminum lid. However, 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

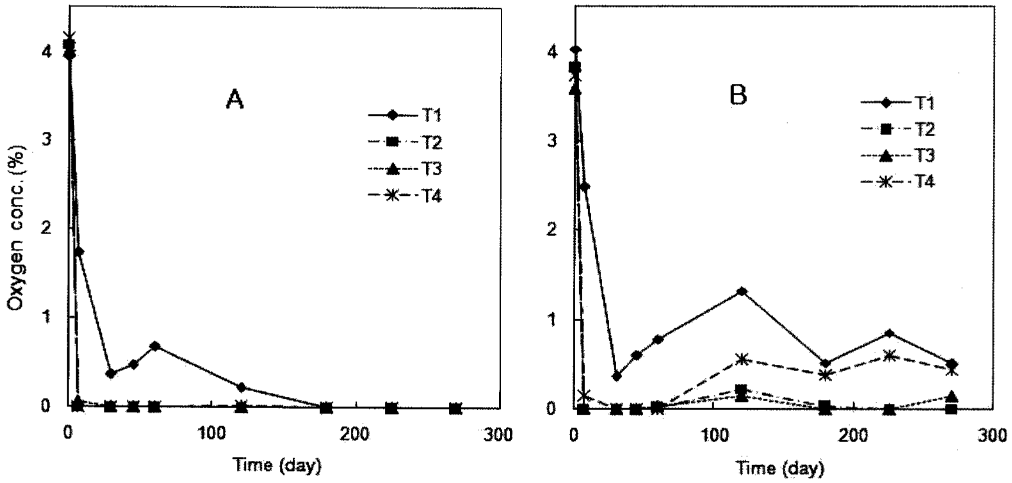

Fig. 2. Oxygen concentration in the headspace of packages containing meatballs with sealed aluminum lid (A) and plastic lid (B) as a function of storage time at 30°C, 80% RH. Each point is the mean±SE (0.2-0.4) of 2 replicate experiments with 3 samples analyzed per replicate (n=6).

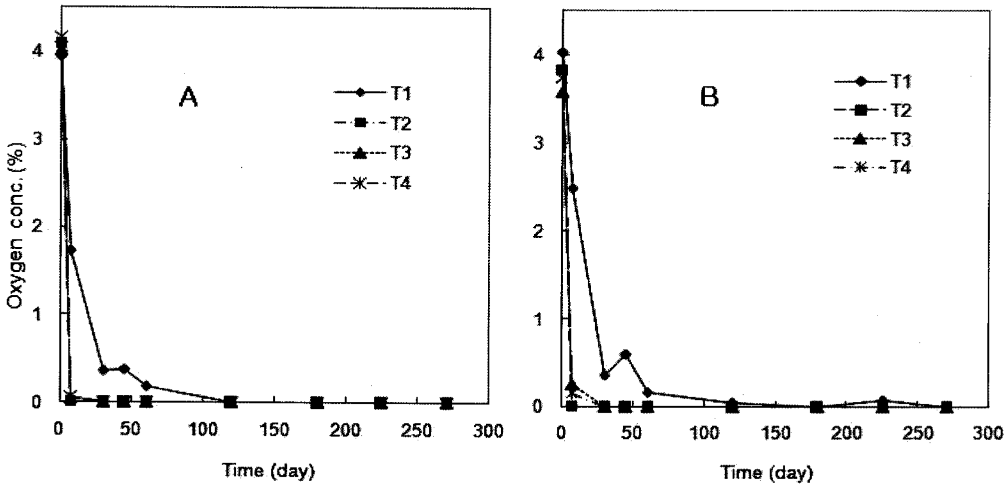

Fig. 3. Oxygen concentration in the headspace of packages containing meatballs with sealed aluminum lid (A) and plastic lid (B) as a function of storage time at 23°C, 50% RH. Each point is the mean±SE (0.1-0.3) of 2 replicate experiments with 3 samples analyzed per replicate (n=6).

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 (4). From Fig. 3 for T2, T3, and T4 at 23°C, it seems that 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 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 instead of aluminum, which cannot be used in a microwave.

Changes of color value As oxidation of the meatballs and sauce affects their color, the lightness was measured as one of the major indicators of the quality of the food. Figure 4 shows the change of lightness for meatballs and sauce as a function of storage time for the storage conditions of 23 and 30°C, respectively. The initial L-values for meatballs were 42.34. At the storage condition at 23°C, the L-value of the 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. A transient color change is seen at the beginning of the storage. The sharp decline in color value has also been observed in another study (9) and might be explained by oxidative processes, which stop when all the residual O_2 has been removed by reducing substances present in the product. The meatballs in all of the active packages were very lightness compared to those in the T1 container. T2 had a high degree of lightness at both storage conditions. The L-value of T2 after 270 days was similar to T1 after 45 days, T3 after 225 days, and T4 after 60 days. The results of T3 laid between T2 and T4. The result of T4 after 270 days was similar to the result of T1 after 180 days. For the storage condition at 30°C, the L-value of T1 decreased more rapidly from 45 to 120 days and reached 35.04 at 270 days after filling. The L-value of T2 after 270 days was similar to T3 after 225

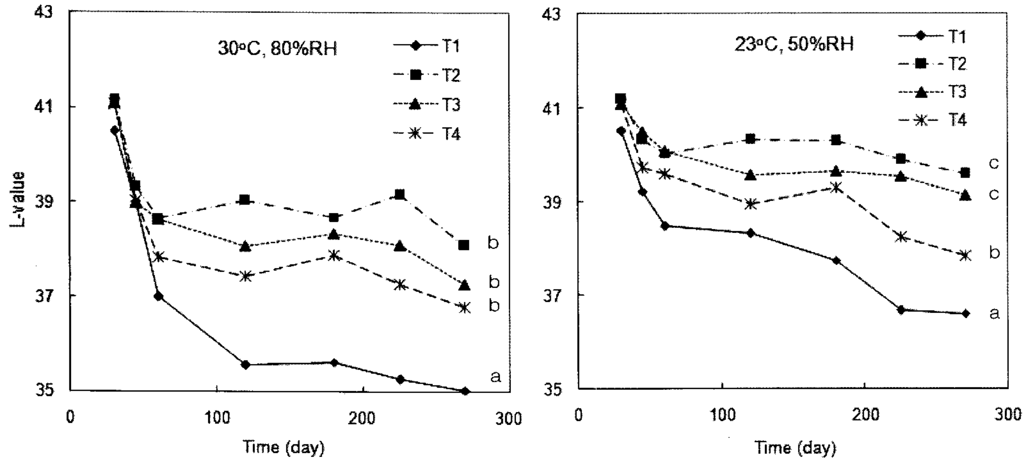

Fig. 4. Change in L-values of meatballs in the container with sealed plastic lid at each storage temperature. Each point is the mean±SE (0.4-0.8) of 2 replicate experiments with 3 samples analyzed/replicate (n=6). $^{a-c}$Means with different superscripts are significantly different (p<0.05).

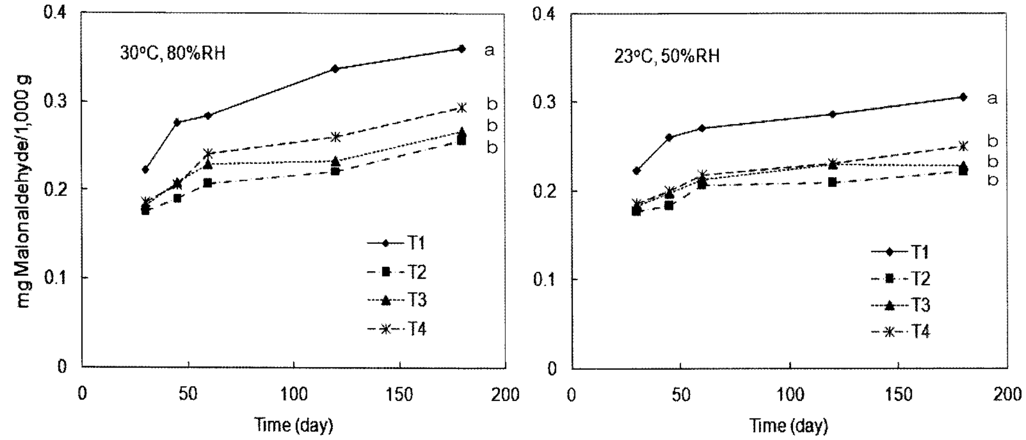

Fig. 5. Changes in thiobarbituric acid (TBA) (mg of malonaldehyde/kg) of retorted meatballs in the container with sealed plastic lid at each storage temperature. Each point is the mean±SE (0.01-0.06) of 2 replicate experiments with 3 samples analyzed per replicate (n=6). $^{a-b}$Means with different superscripts are significantly different (p<0.05).

days and close to T4 after 60 days and T1 after 45 days. The result of T1 at 120 days was close to that of T1 after 270 days at the storage condition at 23°C. This suggests that the L-value of the product was affected by the oxygen concentration as well as temperature and humidity.

Changes in TBA value As shown in Fig. 5, the trend of oxidation of the meatballs was measured by the amount of malonaldehyde as functions of the containers and storage conditions. For the storage condition at 30°C, one can see the meatballs in T1 were more oxidized than those in the active packages. The initial values of malonaldehyde (0.18±0.02 mg malonaldehyde/kg) were assumed to be identical because the same materials were cooked under the same conditions, but the values of malonaldehyde differed between T1 and other containers in the first evaluation after 30 days. Actually, in the storage condition at 30°C, 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 storage condition at 23°C, the value of malonaldehyde also had a similar trend to that of the storage condition at 30°C. Meatballs in T1 were more oxidized than in the active packages (T2, T3, and T4). After 180 days when the value of malondaldehyde in T1 at 23°C was 0.300 mg/kg, it was about 20% lower than that in the storage condition at 30°C (0.361 mg/kg). The other containers also showed similar trends and represented that the temperature and humidity of the storage conditions affected the oxidation values of the retorted meatballs. These results agree with the statements of Seydim *et al.* (10). They stated that the concentration of O_2 in the package atmosphere is the determining factor for the rate of lipid oxidation. Vacuum packaging and N_2 gas flushing had lower TBA values during the storage, as compared to meat in O_2 packages. Minimal control of the oxygen content in the N_2 and vacuum packaging atmospheres limited oxidation and thus resulted in lower TBA values for meat products.

Changes of flavor The dataset plot obtained from the samples by using meatballs in active packages and in the T1 container after 9 months of storage at 30°C were analyzed by principal component analysis (PCA). The

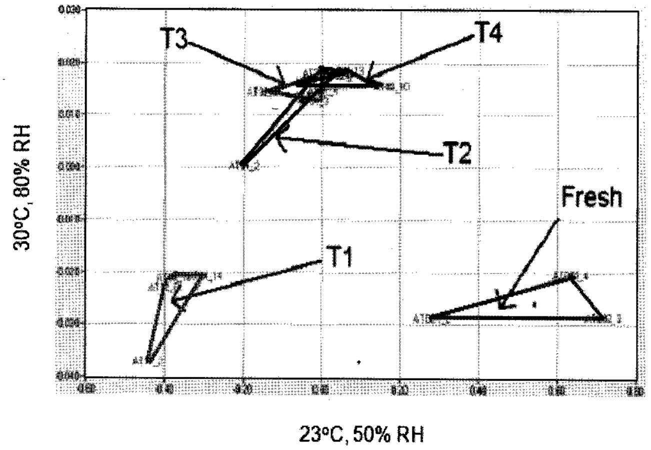

Fig. 6. PCA group for the flavor of meatballs in each container after 9 month storage.

Table 3. Discrimination index for the difference of the samples from each package

Group for each container	Discrimination index (DI)
T1	97
T2	52
T3	51
T4	68

PCA plot is shown in Fig. 6. As shown the results, 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 flavors of the 3 active packages are similar or close to each other. Table 3 shows numerical discrimination values to clarify its discrimination in Fig. 6. The results indicate the degree of difference of the samples from each package compared to fresh samples. A discrimination index (DI) with a range of 1-100 is reported from the PCA plot. The higher index number represents a large amount of flavor change from the original/fresh flavor. T1 showed the biggest DI of 97 compared with the fresh group. It shows that the flavor of T1 was much more changed by the oxidation after 9 months of storage than other 3 groups. T2 and T3 gave the same values as each other 51 and 52, respectively. Through the efficiency of the oxygen scavenger, flavor changes 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, since the content of oxygen scavenger in T4 was lower than in the other 2 active packages.

From these results, it was proven the ferrous oxygen scavenger compound is adaptable to a thermoformed tray that is made by a multilayer co-extrusion process, which is useful for a retorted product that has a large volume of headspace in the package. Meanwhile, EVOH or oriented nylon films, which are water sensitive polymers (11), may be not sufficient as lid stock in high humidity and temperature storage conditions. In order to improve food freshness under retort conditions, other oxygen barrier materials, which have a moisture barrier, should be considered. Sensory and microbial growth evaluations for the future studies will be helpful to monitoring the shelf life extension of the meatball products by the oxygen scavenger system. Research on an organic based oxygen scavenger system is also recommended due to the limiting application of iron based oxygen scavenger systems for food manufacturing processes using metal detectors and transparent packages.

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