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# ORIGINAL PAPER



# Effects of Oxygen and Water Vapor Transmission Rates of Polymeric Pouches on Oxidative Changes of Microwave-Sterilized Mashed Potato

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**Abstract** Polymer-based packaging with low oxygen (OTR) and water vapor transmission rates (WVTR) can be used to limit oxidative chemical changes in packaged foods, especially for the 3- to 5-year shelf life required for military rations and long-duration space foods. Microwave-assisted thermal sterilization (MATS) produces higher quality food with a potentially longer shelf life as a result of volumetric heating and the associated shorter process time. This study investigated the effects of the package-MATS process interactions and the resultant package barrier properties on food quality, using a mashed potato model food following MATS process of F<sub>0</sub>= 9 min for 12 weeks at 50 °C. Two poly ethylene terephthalate (PET)-based (MFA, MFC) and one ethylene vinyl alcohol (EVOH)-based (MFB) retort pouches were tested, with OTRs of 0.20, 2.11, and 0.07 cc/m<sup>2</sup>·day and WVTRs of 2.64, 1.78, and 0.29 g/m<sup>2</sup>·day for MFA, MFB, and MFC, respectively; a foil double-sealed MFA pouch served as a control (MF0).

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Barrier properties did not influence oxygen content in polymer pouches during storage (p>0.05). From the third week to the fifth week of storage, significant differences (p<0.05) were observed in total color difference ( $\Delta E$ ) and oxidation indicators (TBARS, hexanal, and nonanal). The mashed potato treated in higher barrier property pouches exhibited less color change and oxidation than those in lower barrier property pouches. The performance of the MFC pouch was similar overall to that of the metal pouch. These findings suggested that high-barrier packages are suitable for MATS or other commercially sterile foods, particularly for long shelf-life purpose.

**Keywords** Barrier properties · Color change · Lipid oxidation · Microwave-assisted thermal sterilization · Polymeric pouch

#### Introduction

Retort is one of the most common heat processing techniques for the commercial sterilization of foods, which has increased the availability of safe foods over the past century (Ahmed and Ramaswamy 2007). A severe thermal treatment is required to reduce the target *Clostridium botulinum* spores that produce exotoxin in low acid foods (pH >4.6) to an acceptable level (more than 12 log reduction). The shelf life of conduction-heated low acid food in metal containers can be extended to 2–3 years (Robertson 2012) when sterilization is applied, but it is accompanied by undesirable quality degradation that occurs as a result of the high temperature and long-time retort process. Microwave-assisted thermal sterilization (MATS) provides a potential alternative for industrial-scale food sterilization. The advantages of MATS include more efficient heating, reduced come-up time, and shorter overall



thermal processing time due to volumetric heating with electromagnetic radiation at suitable frequencies (<u>Guan et al.</u> 2002).

A single mode of 915-MHz MATS pilot system was developed by researchers at Washington State University (Pullman, WA, USA). Previous studies on MATS processing demonstrate that quality is retained for a variety of foods, including asparagus, macaroni and cheese, salmon, chicken, rice, scrambled eggs, beef gravity, and mashed potatoes (Guan et al. 2002, 2003; Sun et al. 2007; Tang et al. 2008). Scheduled processes of packaged homogenous and nonhomogeneous foods have been accepted by the FDA (Dhawan et al. 2014). Since metal cannot be used for in-package microwave processing, the most suitable packaging for MATS must be polymer-based. Ensuring an extended shelf life for food involves the proper selection of packaging materials to withstand thermal processing and to maintain barrier properties. Oxygen permeation into food packaging may cause rancidity, especially in sterilized foods with high lipid content. Water loss may also contribute to quality degradation causing color loss, texture changes, or nutrition loss (Koros 1990).

The retort pouch used is a typical polymer-based packaging with a multilayer structure obtained from laminating different materials and characterized by high barrier properties, even if no metal foil is used. This type of packaging can be thermally processed like a metal can but provides a more convenient container, being lighter in weight, taking less storage space, and being transparent that allow consumers to see the food. Due to the larger surface to volume ratio for the food in a pouch compared to a cylindrical can, a shorter processing time is required. This usually results in improved taste, color, and flavor of commercially sterile foods (Rodriguez et al. 2003; Byun et al. 2010a). Previous works (Dhawan et al. 2014; Mokwena et al. 2009) conducted by our group showed that ethylene vinyl alcohol (EVOH) laminates and coated poly ethylene terephthalate (PET)-based pouches were successfully used for MATS processing, although the package barrier properties deteriorated. However, this effect was less profound than that observed in conventional retort processing with similar process lethality (Dhawan et al. 2014). If barrier properties are compromised, oxygen can enter in the packaging, causing lipid oxidation, and moisture loss can also occur (Mokwena et al. 2009).

The development of products and packaging that retain food quality for shelf lives of 3 to 5 years or at temperatures above 40-45 °C is a further challenge. These goals can be reached by understanding the effects of gas and water vapor barrier properties on the oxidative stability of packaged foods during storage. Only a few studies have correlated package barrier properties with the quality of thermally processed foods. Byun et al. (2010a, 2010b) examined the shelf life of retorted salmon and rice products packaged in different pouches. For salmon, the packaging materials were cast

polypropylene (CPP), PET/silicon oxide-coated nylon/CPP (SiOX), aluminum oxide-coated PET/nylon/CPP (AlOX) and PET/aluminum foil/CPP (FOIL) with different permeabilities. Rice products were prepared in pouches coated with organic or inorganic coated materials and tested under the same conditions during storage at 37.7 °C and 90 % RH for 12 weeks. Only slight differences (not significant) were observed in both the quantitative and sensory studies (Byun et al. 2010b).

Model foods have been used to study MATS heating profiles that can be used to predict food quality. One series of protein gel model foods involves the addition of ribose, glucose, lysine, and other compounds that form Maillardbrowning compounds when heated. This system has been used to study microwave heating patterns (Pandit et al. 2007; Zhang et al. 2014). The system was used as a chemical marker that reflected time-temperature accumulation through color changes or compounds formed during Maillard browning. Other researchs showed that lipid oxidation combines with Maillard reactions to influence browning, thus contributing to color changes in complex food systems (Zamora and Hidalgo 2005). Based on the above mentioned information, a mashed potato model food with added fat was selected to study the effect of barrier properties following MATS heating on food quality attributes.

The objectives of this study were (1) to develop a model food formulation for examining MATS food quality changes (color, lipid oxidation) under accelerated storage conditions and (2) to investigate how the barrier properties of polymeric pouches affect color changes and oxidative stability in MATS-processed model foods. These findings can then be used for the study, selection, or design of polymeric materials for commercial, thermally processed foods.

#### **Materials and Methods**

# **Materials and Reagents**

Potato flakes (Oregon Potato Co., Pasco, WA, USA), commercial olive oil (cold pressed, extra virgin), flaxseed oil (cold pressed), whey protein isolate (Purity 89.3 %, Now Foods Inc., Sparks, NV, USA), and glucose (Food grade, Purity 100 %, Now Foods Inc, Bloomingdale, IL, USA) were purchased for developing model food formulations. Trichloroacetic acid (TCA) and 2-thiobarbituric acid (TBA) were purchased from Avantor Performance Materials Inc. (Center Valley, PA, USA), butylated hydroxyanisole (BHT) from Acros Company (New Jersey, USA), and standard malondialdehyde (MDA) from Enzo Life Sciences (Farmingdale, NY, USA). Hexanal, 2-methyl butanal, and nonanal standards (GC level, purity >95 %) were obtained from TCI Chemicals (Portland, OR, USA).



#### **Model Food Formulation**

The chemical composition of the model food was based on average levels of nine typical thermally processed food items (USDA Nutrition Database, Table S1). The final mashed potato formulation (Table 1) was improved by selecting different combinations of added protein, lipids, or sugar in heating trials using an oil bath method following Dhawan et al. (2013). The test formulations were stored for 4 weeks at 50 °C before examining the color and oxidative changes. The model food was prepared just before processing. Hot water (~70 °C) was used to dissolve the glucose and salt, and then other ingredients were added in the following order: olive and flaxseed oil, whey protein isolate, and potato flakes to form a homogenous paste.

# Polymeric Pouches/Films and Barrier Properties

Freshly made mashed potato was vacuum-treated 3 to 5 times at 0.6 bar for 2 to 3 s to remove air using a UV 250 sealing machine (Koch Equipment, Kansas City, MO, USA). Then, 227 g of mashed potato was packed into MFA, MFB, and MFC pouches at a level 4 to 5 sealing temperature (scale 1 to 9) for 3 s at a vacuum of 0.8 bar. The pouch structures and other parameters are summarized in Table 2. No residual air/bubbles were observed inside the pouches after sealing. MFA was double-sealed at a vacuum of 1.0 bar for 10 s using a larger foil pouch as a control (MF0) for barrier properties. The pouch thickness and the thickness of the packaged samples were measured with a Model 15769 electronic disc micrometer (Flexbar Machine Co., Islandia, NY, USA).

The oxygen transmission rates (OTRs) and water vapor transmission rates (WVTRs) were measured with an Ox-Tran 2/21 MH and a Permeatran 3/33 permeability instrument (Mocon Inc., Minneapolis, MN, USA) following Dhawan et al. (2014). For the OTR measurements, conditions were set at 65 % RH, 23 °C, and 1 atm. Tests were conducted according to the ASTM standard D3985 method (1995). WVTR measurements were conducted at 100 % RH and 38 °C, according to the ASTM standard method F1249 (1990). Film specimens with a surface area of 50 cm² were cut from polymeric pouches and mounted inside the testing chambers. Both the OTR and WVTR of the pouches were measured using the continuous mode. Duplicate measurements were made before and after MATS processing.

**Table 1** Composition of mashed potato formulation

Components	Water	Potato flakes <sup>a</sup>	Whey protein	Flaxseed oil Olive oil=1:1	Glucose	Salt
Weight %	78.2	11	4.7	4.3	1.3	0.5

 $<sup>^{\</sup>rm a}$  The chemical composition of the potato flakes was 6.5 % water, 8.3 % protein, 0.4 % fat, 81.2 % carbohydrate, and 3.4 % sugar

#### Microwave-Assisted Thermal Sterilization

MATS was conducted using the pilot system (10 kW, 915-MHz, single mode) at Washington State University. A total of 64 packaged pouches (MFA=32, MFB=16, and MFC=16) were tested randomly in two batches (32 pouches for each batch). The processing procedures followed those of Dhawan et al. (2014) and Tang et al. (2008). The pouches were preheated for approximately 26 min at 61 °C, microwave heated for 7.4 min, and then were held at 124 °C for 4 min, with another 4 min of cooling in cold water. The target sterilization lethality was  $F_0=9$  min for all samples.

# **Accelerated Storage and Sampling Strategy**

The processed samples were stored at 50 °C inside an incubator (ED 53-UL, Binder Inc., Bohemia, NY, USA) at 16-20 % RH, as measured by a hygrometer (Acu-Rite, Heidenhain Corp., Schaumburg, IL, USA). The total storage time was 12 weeks, and duplicate pouches were taken out and measured each time. The 50 °C storage temperature was selected to accelerate the degradation of food quality parameters (Robertson 2012). Color parameter measurements were taken at five locations (Fig. 1): Top surface layer (TOP), middle geometric center (MID), edge and corner (EDG), back hot spot area (HOT), and back cold spot area (COLD), defined by the pouch position during processing. Different sampling locations were used based on microwave heating uniformity. Selected sampling locations were related to the heating patterns of the MATS system (Luan et al. 2013). For the pH, redox potential (ORP), thiobarbituric acid-related substances (TBARS) and volatile measurements, samples were taken only from the TOP, MID, and EDG.

# Weight Loss

Weight loss (n=2) was calculated as the percentage of weight loss (%) for treated pouches following processing (week 0) and at different storage intervals (weeks 2, 3, 4, 5, 7, 8, and 12) using a GK703 balance (Sartorius, Goettingen, Germany).

# **Oxygen Content**

An OxySense 325i (Oxysense Inc., Dallas, TX, USA) noninvasive oxygen analyzer system was used to track the oxygen



 Table 2
 Structure and dimensions of selected pouches

Pouch	Pouch type	Structure	Dimensions (mm×mm)	Pouch thickness $(\mu m, n=5)$	Sample thickness (mm, <i>n</i> =8)
MFA	Stand-up	Composite coating 1 µm/PET 12 µm/composite coating 1 µm/Nylon/PP	185×129	96.4±1.8	14.2±0.42
MFB	Flat	Nylon 15 μm/27 % EVOH 15 μm/ CPP 60 μm	181×133	91.8±2.2	$13.3 \pm 0.48$
MFC	Flat	HB-PET 12 μm/Nylon 15 μm/CPP	181×133	$107.6 \pm 0.9$	$13.3 \pm 0.25$
MF0	Flat-Foil	PET12μm/Aluminum 9 μm/BOPA 15 μm/RCPP 80 μm	230×190	114.8±1.8	$14.1 \pm 0.40$

HB-PET hyperbranched polyester, BOPA biaxially oriented nylon, RCPP retort cast polypropylene

concentration in the packaged food at the TOP location. The OxySense 325i was the main analyzer with a hand-held pen containing a built-in temperature sensor. This was used to measure fluorescent radiation released from the oxygensensitive film (Oxygen Dot, Oxysense Inc.) attached to the inside of the package, reflecting the oxygen concentration inside the package. In our study, the oxygen dot was fixed to the center of the pouch's inner surface before filling with the mashed potato. After processing, the inner side of the oxygen dot was in direct contact with the food surface at the center of the TOP region. Sensor calibration was performed using pure nitrogen and ambient air as standards. Measurements were performed (n=2) before and after MATS processing at weeks 1, 2, 3, 4, 5, 7, 8, and 12, with three repeated measurements. Oxygen content was expressed in parts per billion.

# pH and Redox Potential

The pH and redox potential value were measured using a pH meter (FE20/EL20, Mettler Toledo, Columbus, OH, USA) and a portable pH/ORP/redox meter (SevenGo2-FK, Mettler Toledo, Columbus, OH, USA). Samples were prepared by

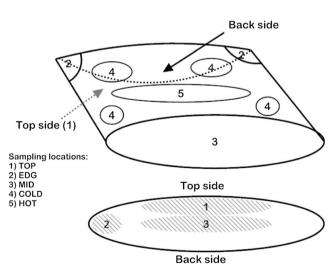


Fig. 1 Diagram of different sampling locations within pouch samples



vortexing 1 g of treated mashed potato in 5 ml of distilled water. Measurements were conducted immediately after processing and then at weeks 1, 2, 3, 5, 7, and 12. Each value was the mean of duplicate determinations at each sampling location in treated pouches (n=2); hence, the average was the mean of six measurements from three locations.

#### **Color Measurements**

A Minolta CR 200 colorimeter (Konica Sensing America Inc., Ramsey, NJ, USA) was used to measure the CIE parameters lightness L\*, redness a\*, and yellowness b\*. Measurements were conducted before and after MATS processing and at weeks 1, 2, 3, 5, 7, and 12. Samples (n=2) were measured twice at a predetermined pouch location, with four replicates for each location. The total color difference  $\Delta E$  and the Browning index (BI) values were calculated using the average from five sampling locations for CIE L\*, a\*, and b\* values. Calculations for  $\Delta E$  and BI were based on Eqs. 1 and 2 (Kong et al. 2007; Wang et al. 2013):

$$\Delta E = \sqrt{\left(L^* - L_0^*\right)^2 + \left(a^* - a_0^*\right)^2 + \left(b^* - b_0^*\right)^2} \tag{1}$$

$$BI = [100(x-0.31)]/0.172$$
 where  $x = \frac{(a+1.75L)}{(5.645 L + a-3.012 b)}$  (2)

The value of  $\Delta E$  indicates the difference between the two colors according to the scale below (Wang et al. 2013):

 $\Delta E$ <0.2: no perceptible difference

 $0.2 < \Delta E < 0.5$ : very small difference

 $0.5 < \Delta E < 2$ : small difference

 $2 < \Delta E < 3$ : fairly perceptible difference

 $3 < \Delta E < 6$ : perceptible difference

 $6 < \Delta E < 12$ : strong difference

 $\Delta E > 12$ : different colors

#### Thiobarbituric Acid-Related Substance Measurement

The TBARS values were measured following the procedures of Sun et al. (2001), with some modification. Specifically, a 2.5 g sample was mixed with 10 mL, 50 g/L TCA and vortexed for 1 min. The homogenate was centrifuged at 10, 000 rpm (13,000×g, VWR Galaxy 14D microcentrifuge, Radnor, PA, USA) for 10 min. The supernatant obtained (250 µL) was used for the TBA reaction with 2.5 ml TBA buffer solution (5 g/L TBA 50 g/L TCA=1:1) in a 15 ml test tube, with 20  $\mu$ L 1 % (w/w) BHT added to prevent further oxidation during heating. Subsequently, the test tubes were incubated for 60 min in a water bath at 90 °C, cooled in ice water for 10 min, and then centrifuged at 10,000 rpm (13,  $000 \times g$ ) for 5 min before measurement by a spectrometer (Ultraspec 4000, Pharmacia Biotech Inc., Piscataway, NJ, USA) at both 532 and 450 nm. The MDA standard solutions (concentration 0, 0.9, 1.8, 3.6, and 7.2 g/L) were tested using the method described above to obtain the standard curve. Results were expressed as mg MDA/kg sample. Duplicate samples from predetermined locations were tested after processing at storage times of 1, 2, 3, 5, 7, and 12 weeks.

#### **Volatile Analysis**

The identification and quantification of volatiles were carried out using headspace solid-phase microextraction and gas chromatography (HS-SPME-GC). The sample was prepared with 1.8 g mashed potato, 1.3 g sodium chloride, and 3 mL distilled water in a 15-mL headspace vial with an open hole cap and Teflon-faced silicone septa. The SPME fiber applied was a 65-um polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber (Fused Silica 24 Ga, Supelco, Bellefonte, PA, USA). SPME extraction lasted for 60 min at room temperature (23 °C). Volatiles were thermally desorbed for 2 to 5 min using an SPME liner and set in the splitless mode into the injection port of a HP5890/5970 GC/FID or GC/MS system (Agilent, Avondale, PA, USA) equipped with a DB-1 column (60 m×0.32 mm id, 0.25 um film thickness, J&W Scientific, Folsom, CA, USA). The GC procedure followed Iyer et al. (2010) using helium as the carrier gas. The injector and detector temperatures were 200 and 250 °C, respectively. The column temperature was initially maintained at 33 °C for 5 min before being increased to 50 °C at a rate of 2 °C/min and then to 225 °C at a rate of 5 °C/min. Volatile compounds were identified by comparing MS spectra against a Wiley-NBS library. Hexanal, nonanal, and 2-methyl butanal were then quantified by FID using the external standard method. Duplicate samples from predetermined locations were measured immediately after processing and at weeks 1, 2, 3, 5, 7, and 12.

#### **Statistical Analysis**

Statistical analysis was conducted using the analysis of variance (ANOVA) function in SAS software (version 9.1, SAS Institute Inc., Cary, NC, USA). Fisher's least significant difference procedure was used to compare differences between mean values and interpret the effects of package barrier properties, storage time, and sampling location on the quality parameters. Significance was defined at a level of p < 0.05.

# **Results and Discussion**

# Visual Observation of Packaged Mashed Potato After Microwave-Assisted Thermal Sterilization Processing

Results showed that the mashed potato turned from a homogeneous paste into a soft gel after processing with a thin layer of oil forming on the top surface. This might be explained by the chemical changes induced by heating process such as starch gelatinization and protein coagulation, etc. Although there were some observable color differences in the HOT and COLD regions, there was no obvious overburn. The MFA and MFC pouches showed no visual damage, but the MFB pouches exhibited minor deformation and clouding at the pouch surface, due to the moisture sensitivity of the EVOH material. The attached oxygen dots were immersed in the mashed potato surface. The dots and the packaging maintained their integrity after the pouches were subjected to MATS.

# Package Barrier Properties After Microwave-Assisted Thermal Sterilization Processing

In our previous study, Dhawan et al. (2014) observed increments in OTR of two PET-based polymeric films subjected to both retort and MATS processes. The overall crystallinity of polymer increased up to 5 % after thermal sterilization; however, fractional free volume of polymer increased by the thermal treatment leading to increase in oxygen and water vapor transmission rates of films (Dhawan et al. 2014). Results in the present study showed that both the OTR and WVTR of all polymeric pouches increased (Table 3). The OTR of all three pouches and the WVTR of MFA pouch increased significantly (p<0.05). This is consistent with our previous study. Furthermore, both the OTR values and the WVTR values of three pouches were found to be significantly different (p<0.05) from each other after MATS processing: the OTR values in the MFB pouches were significantly higher (p<0.05) than in the MFA and MFC pouches (10 times higher and 31 times higher, respectively). The OTR of the MFA pouches was also significantly higher than that of the MFC pouches (p<0.05). Significant differences (p<0.05) in WVTR



**Table 3** OTR and WVTR values of polymer pouches before and immediately after MATS

Polymeric pouch	OTR		WVTR		
	Before MATS	After MATS	Before MATS	After MATS	
MFA	0.050±0.007 bB	0.197±0.026 aB	5.190±0.106 bA	8.730±0.007 aA	
MFB	1.120±0.014 bA	$2.108 \pm 0.088 \ aA$	$4.120 \pm 0.092 \text{ aB}$	$4.480 \pm 0.255 \text{ aB}$	
MFC	$0.018\pm0.001~bC$	$0.068 \pm 0.010~aC$	$0.440 \pm 0.200~aC$	$0.700 \pm 0.134~aC$	

Means with different letters are significantly different (p<0.05) after process (lowercase) and between different pouch types (uppercase)

OTR oxygen transmission rates, WVTR water vapor transmission rates, MATS microwave-assisted thermal sterilization

values were found in the sequence—MFA>MFB>MFC. The WVTR of MFA was more than twice than that of MFB and 4.5 times than that of MFC. The OTR and WVTR values measured after processing were used as reference pouch barrier properties during storage.

#### Weight Loss

The weight loss in the pouches was primarily due to the moisture migration from the mashed potato and passes through the polymeric film. The average weight loss for MFA, MFB, and MFC were 2.64, 1.78, and 0.29 g/week, respectively, with no loss for the control MF0. Figure 2 shows that after 12 weeks storage, the weight loss of MFA, MFB, and MFC had reached  $14.2\pm2.2$ ,  $9.2\pm1.0$ , and  $1.5\pm0.4$  %, respectively, of the original weight. This weight loss was highly related to the pouch WVTR. Increasing the WVTR (i.e., the worse water vapor barrier) led to faster moisture loss (Table 3). This high weight loss may be due to the high temperature and lower humidity in storage, increasing the rate of water vapor loss. A better water vapor barrier can prevent extensive water loss and therefore prevent changes in food texture and mouthfeel. This may also reduce the rate of chemical degradation (Nelson and Labuza 1994).

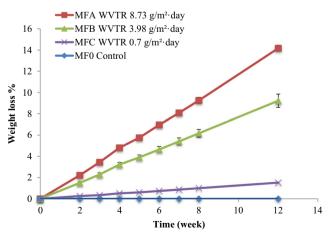


Fig. 2 Weight loss in 4 types of pouch during 12 weeks storage at 50 °C



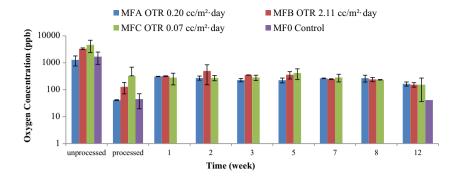
# **Oxygen Content**

Oxygen content is a major factor affecting oxidative status within packaged systems since it directly shows the amount of oxygen to which a food is exposed (Chaix et al. 2014). In this study, we monitored changes in oxygen content to determine any association between the oxidation of mashed potato, the barrier properties of pouches, or sealing problems. Figure 3 uses a semi-log Y axis to depict changes in oxygen content. The initial oxygen amounts inside the pouches varied significantly even though the same sealing conditions had been applied. The average oxygen content before MATS processing was 1270 ppb for MFA, 3315 ppb for MFB, 4600 ppb for MFC, and 1690 ppb for MF0. After MATS processing, these values decreased significantly to 40, 130, 320, and 45 ppb, respectively (p<0.05). This reduction is explained by the high temperature and pressure conditions of thermal processing, leading to oxygen diffusion and oxidation reactions.

During the first week, the oxygen content for MFA increased (p<0.05) to 310 ppb, while MFB increased (p<0.05) to 320 ppb and MFC decreased to 280 ppb. During the remaining storage time, no significant changes (p>0.05) were observed in oxygen content for any of the polymeric pouches. This indicates that regardless of deviations in the initial oxygen amounts and barrier properties, the oxygen content in the mashed potato surface inside the polymeric pouches might have reached equilibrium after the first week of storage. This was most likely due to the ingress of oxygen as well as the diffusion and solubility of oxygen in the food system (Chaix et al. 2014). Furthermore, prediction of the oxygen content changing in such food system is a challenge also because of the various components in the food formulation, which lead to complex oxidation reactions.

In the control pouches, the oxygen content was measured only after processing and at the end of the storage since the foil layer is impermeable to light. The oxygen content in MF0 pouches was found to be significantly lower than other pouches (p<0.05). However, there were no significant changes during storage (p>0.05) for all the types of pouches used.

**Fig. 3** Oxygen content change in the TOP surface of samples during 12 weeks storage at 50 °C



The interaction effect of storage time and pouch barrier properties was also found to be not significant (p>0.05). In summary, the oxygen content indicated the possible oxygen ingress at the beginning of the storage, which can be correlated to barrier properties. But, no further correlation was found after 1 week of storage, possibly due to the complex oxidation reactions and other factors mentioned above. To our knowledge, this study represents the first examination of the oxygen content in packaged thermally processed foods.

#### pH and Redox Potential

Our findings show that pH decreased (p<0.05) gradually during storage. For all samples, it remained in the range from 6.1 to 5.7. For the ORP, the values of all samples ranged from 160 to 210 mV. The ORP values were linked to the dissolved oxygen and chemical reactions in mashed potato (Giroux et al. 2008). However, there was no clear pattern from effects of barrier properties, and no significant sampling location effects (p>0.05) were observed.

# **Color Change**

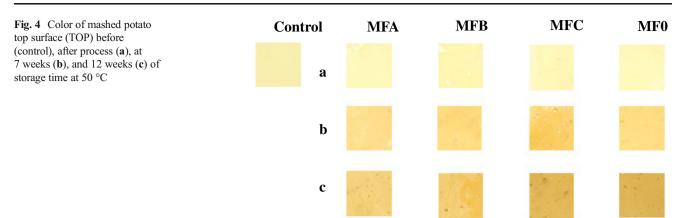
The color values of the freshly made mashed potato were measured as brightness L\*  $60.6\pm3.5$ , redness a\*  $-2.6\pm0.2$ , and yellowness b\*  $8.9\pm0.5$ . After MATS processing, the L\*, a\*, and b\* values increased to  $69.9\pm3.8$ ,  $0\pm0.4$ , and  $15.4\pm0.8$  (as a general average for all pouches), respectively. During storage, the color changed from light yellow to dark brown. Figure 4 displays digital images of TOP in MFA–MF0 pouches after processing at 7 and 12 weeks of storage.

To further characterize the color changes, Fig. 5a, b showed the total color difference ( $\Delta E$ ) and browning index (BI) plotted against storage time.  $\Delta E$  is one of the most widely used color parameter, and during storage,  $\Delta E$  increased with storage time (p<0.05). By the fifth week, the  $\Delta E$  values for MFA and MFC reached 12.44 and 12.15, respectively. According to the  $\Delta E$  scale table,  $\Delta E$  values for MFA and MFC had changed to different colors. At the same time, the  $\Delta E$  values for MFB and MFO were less than 12. The  $\Delta E$  values for MFA, MFB, and MFC differed significantly (p<0.05) from the

control, but did not differ significantly (p>0.05) from each other. However, by the 12th week, the  $\Delta E$  values for MFC and MF0 showed no significant difference between them (p>0.05). The BI value represents the purity of the brown color, which is an important indicator for a browning reaction. The BI values at the 12th week for each type of pouch showed a sequence of MFB (72.18)>MFA (66.12)>MFC (65.88)> MF0 (65.49). The BI value for the MFB pouch was significantly higher than the other pouches (p < 0.05). Generally, great changes in color were observed in the short time of accelerated storage of the model food. Barrier properties did significant influences (p<0.05) on both  $\Delta E$  and BI values, and no significant interaction effect was found between the barrier properties and storage time (p>0.05). The MFC pouch was the closest to the control metal pouch in terms of color preservation, especially at the end of storage.

The color change in the mashed potato model food was significant in all barrier pouches tested. These changes resulted from the combined effect of browning and lipid oxidation reactions. The extent of lipid oxidation was limited by the oxygen to which the mashed potato was exposed. Hence, the MFA and MFB pouches had higher  $\Delta E$  and BI values than the lower-OTR MFC and control. High WVTR pouches underwent more moisture loss than low WVTR pouches, which may also alter color change. Muizniece-Brasava et al. (2013) reported that moisture loss significantly affected color changes in thermally processed potato slices. They studied two packaging materials (polyamide/polyethylene and aluminum/polyethylene) during storage of 4 months at 18 °C. This may explain why, in the present study, the  $\Delta E$  value for MFA increased faster compared with MFB at the end of storage. Consequently, color changes appeared to be affected by both oxygen and water barrier properties. Therefore, higher barrier properties are preferred to maintain the color of mashed potato. Color measurements were conducted at five different locations (Fig. 1). The  $L^*$  value at TOP and COLD was higher than at other sampling locations. The a\* and b\* values at MID and HOT were higher than at other sampling locations. Generally, the color differences among the various locations within the pouch became less profound after 7 weeks of storage.





#### Thiobarbituric Acid-Related Substances

TBARS values were tested at both 532 nm (pink color) and 450 nm (yellow color) (Fig. 6). Comparing unprocessed with processed mashed potato, the TBARS value for MFA and MFB increased (p>0.05), while the value for MFC decreased (p>0.05), but the value for MF0 decreased significantly (p<0.05). During storage, the TBARS value increased to the highest level at the third week for MFA, MFB, and MFC and

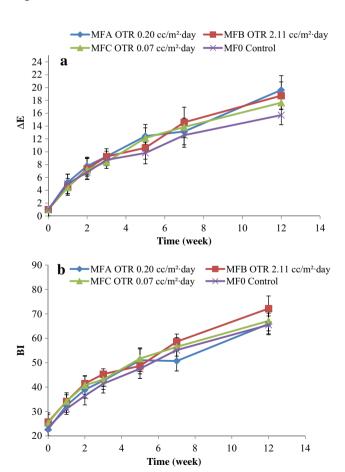


Fig. 5 Changes in color parameters (a  $\Delta E$ , b BI) during 12 weeks of

storage at 50 °C

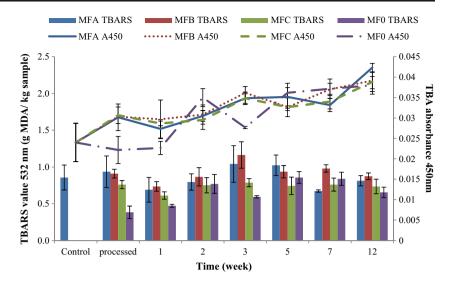
at the fifth week for MF0. After the fifth week, the TBARS values for all pouches decreased. Similar observations have been reported for fish products in cans, with values decreasing during storage or the late part of storage (Bindu et al. 2007; Dhanapal et al. 2010). This is probably because of the dilution of secondary lipid oxidation products by oil or water and because of the reactions with other compounds such as amino acids (Bindu et al. 2007; Dhanapal et al. 2010).

The MATS-processed mashed potato in our study contained a high level of moisture and additional protein. Therefore, it is likely that further reactions and dilution reduced the TBARS value after 5 weeks of storage. The absorbance at 450 nm for all pouches increased continuously with storage time (Fig. 6). Absorbance by the 12th week was significantly higher (p<0.05) than at other sampling times. However, the TBA reaction might be considered as nonspecific: other compounds such as sugars or HMFs from browning reactions might interfere with the results (Guillén-Sans and Guzmán-Chozas 1998). Hence, the absorbance value at 450 nm may be the appropriate indicator for lipid oxidation as well as for browning reactions.

In terms of pouch types, since barrier properties were found to be significantly interacted with the storage time (p < 0.05), the simple effect of different pouches were interpreted. The TBARS values for MFC and MF0 were lower than those of MFA and MFB. The TBARS value for MFC showed no significant difference (p > 0.05) from the MF0 treatment during storage. Only after processing at time=0 was the value for MFC shown to be significantly higher than for MF0. The TBARS value for MFC was significantly lower (p < 0.05) than that of MFA at the fifth week and MFB at the third week. However, the TBARS value for MFA and MFB showed no significant differences (p>0.05) during the entire storage time, but each of these values was significantly (p<0.05) higher than that for MF0, except for the fifth week. Byun et al. (2010a) found that the TBARS values for CPP pouchpackaged salmon was significantly higher (p<0.05) than for those in AlOX, SiOX, and FOIL pouches. The CPP pouch had more than 100 times the oxygen permeability (>920 g μm/



**Fig. 6** Changes in TBA value (532 nm) and absorbance (450 nm) before, after MATS process, and during 12 weeks storage at 50 °C



 $\rm m^2$  day) of the other three pouches. The AlOX, SiOX, and FOIL pouches, with similar oxygen barrier properties, showed no significant differences (p>0.05) over 8 weeks of storage. All selected pouches in the present study had barriers with OTR values less than 2.11  $\rm cc/m^2$  day, and within this range of OTR, the mashed potato in the higher barrier pouches undergoes less oxidization than those packaged in lower barrier pouches. The TBARS values at different sampling locations

also showed no significant differences (p>0.05) between the TOP, MID, and EDGE locations.

#### **Gas Chromatography Volatiles**

Volatile compounds are formed during the thermal processing and storage. At high concentrations, these can be indicators of food flavor or lipid oxidation (Viljanen et al. 2011; Roldan

Table 4 Changes in volatile content before and after MATS and during 12-week storage

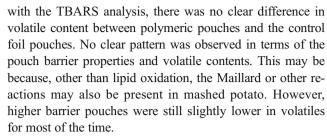
Indicator	Storage time	Package pouch				
	(week)	MFA	MFB	MFC	MF0	
Hexanal (μg/kg sample)	Control	77.4±2.3 a				
	0	42.0±3.5 b	79.1±11.1 a	51.6±8.2 b	56.8±2.1 b	
	1	32.6±5.2 b	43.4±2.6 a	41.7±3.2 b	35.0±2.8 b	
	3	36.8±5.8 a	24.4±7.6 b	40.6±5.7 a	20.5±2.4 b	
	5	31.1±6.1 ab	44.3±18.7 a	30.3±6.9 ab	21.3±1.6 b	
	12	22.1±11.6 a	63.8±28.5 a	36.4±14.8 a	57.3±12.4 a	
2-Methyl-butanal (µg/kg sample)	Control	ND c				
	0	491±203 ab	788±273 a	$492 \pm 178 \ ab$	232±88 b	
	1	$809 \pm 104 a$	1084±212 a	891±175 a	800±153 a	
	3	$776 \pm 182 a$	1012±141 a	969±49 a	887±134 a	
	5	1007±198 a	687±44 a	974±324 a	984±104 a	
	12	644±116 b	885±90 a	615±85 b	714±127 ab	
Nonanal (μg/kg sample)	Control	18.1±1.9 c				
	0	63.4±5.8 ab	60.5±2.2 b	75.3±12.0 a	62.4±10.3 ab	
	1	78.5±15.9 a	88.6±19.7 a	93.6±46.5 a	101.3±32.4 a	
	3	59.2±32.3 a	68.2±45.1 a	49.2±15.2 a	52.9±11.1 a	
	5	30.6±9.5 a	26.4±11.7 a	28.2±9.1 a	26.5±8.1 a	
	12	$18.1 \pm 12.0$ a	17.6±8.7 a	15.4±8.9 a	9.1±4.3 a	

Controls are samples before process, and 0 week represents samples immediately after process, values are expressed as mean $\pm$ standard deviations with n=6. Interactions were found between storage time and the pouch types (barrier properties) for hexanal (p<0.05) and 2-methyl-butanal (p<0.05). Means with different letters are significantly different within row (p<0.05). Controls are compared with 0-week samples



et al. 2014). The changes in hexanal, nonanal, and 2-methyl butanal contents during the 12 weeks of storage are shown in Table 4. The initial contents of hexanal and nonanal were  $77\pm$ 2.3 and 18±1.9 μg/kg, respectively. No 2-methyl butanal was detected initially. The hexanal content of processed model food decreased significantly (p<0.05) after MATS processing for all pouches except for MFB. However, the nonanal and 2methyl butanal content increased (p < 0.05). The changes in hexanal, nonanal, and 2-methyl butanal contents followed different patterns during storage. This may be because hexanal is formed by the oxidation of linoleic acid, but nonanal was formed from oleic acid (Viljanen et al. 2011). In addition, 2methyl butanal is mainly used as an indicator for Strecker degradation, which is part of the Maillard browning reaction (Martin and Ames 2001). The increased content of volatiles after processing mainly resulted from the thermal effect of MATS. The original hexanal content was higher than other volatiles since it is naturally present in potato. More statistical analysis comparing contents of the three volatiles at beginning of storage and those at end of the storage were also interpreted (data discussed in the following description but not shown in Table 4). For all types of pouches, the nonanal content dropped sharply (p < 0.05) after storage. The hexanal content for MFA and MFC also dropped significantly (p < 0.05). The 2-methyl butanal content at the 12th week was not significantly (p>0.05) different from the start of storage, but this was significantly higher (p<0.05) for MF0 pouch. Similarly to the TBARS results, the reduction in hexanal and nonanal contents was likely due to further reactions during high temperature storage (Roldan et al. 2014). Viljanen et al. (2011) compared results from sensory and volatile analyses for high pressureprocessed tomato puree at increased storage temperatures. They found that a reduction in aldehydes content was concomitant with a loss of fresh tomato odor. Hence, in the present study, the reduction of the volatiles may also indicate the flavor loss of the mashed potato. The increase in 2-methyl butanal content correlated with increasing TBA 450 nm absorbance in the first 5 weeks.

Compared to the other types of pouch, mashed potato packed in MFA and MFB had a higher hexanal content. At 0 to 1 week, MFB was significantly (p<0.05) higher in hexanal than in the other pouches. By the third week, the differences between MFA and MFC or between MFB and MFO were not significant (p>0.05), while that difference between MFA and MFC was. Furthermore, in the 5th to 12th week, the only significant difference (p<0.05) was observed between MFB and MFO at the 5th week. The nonanal content overall showed no significant differences between the different pouches. Only just after processing did MFC show a significantly higher nonanal content (p<0.05) than that of MFB. For 2-methyl butanal, a significant difference (p<0.05) was found between MFB and MFO after processing, and between MFB and both MFA and MFC at the end of the storage. Compared



Our findings also indicate that location within the pouch had some effect. At the 12th week, the hexanal content in the TOP location was significantly (p<0.05) higher than at the MID and EDGE locations. For nonanal, there were significant differences (p<0.05) between the TOP, MID, and EDGE in the second and third week. No differences were observed for 2-methyl butanal at different sampling locations at any time.

#### **Conclusions**

A mashed potato model food has been developed for studying microwave-assisted thermal sterilized food as influenced by different packaging barrier levels during the accelerated shelf life. For the purpose of designing polymeric packages to replace metal packaging for long-term storage, three types of polymeric pouches and a nonpermeable foil pouch were selected to evaluate the changes in barrier properties and food quality during storage. The findings have shown that weight loss, oxygen content, color change, and oxidation indicators (TBARS, volatile compounds) of mashed potato were associated with the barrier properties. However, there was no clear association between the pH value, redox potential value of mashed potato and the packaging barrier properties. Sampling location was found to have no significant influences on most factors. Thus, overall, in terms of mashed potato quality, pouches with lower transmission rates maintained better, and a barrier property such as MFC with an OTR of 0.07 cc/m<sup>2</sup> day and a WVTR of 0.29 g/m<sup>2</sup> day was found to be similar to the control pouch material MF0. The elevated temperature in this study promoted rapid chemical reactions and created a relatively high moisture loss. Therefore, a limitation of this study is that these further reactions may not usually occur under normal conditions. Hence, storage studies at lower temperatures are suggested with further sensory evaluation needed to complete this shelf life study of MATS-processed foods.

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