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Oxygen transmission of multilayer EVOH films after microwave sterilization

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ABSTRACT

Classical industrial retort sterilization processes expose food packages to high temperature, moisture, and pressure conditions. Migration of water into hydrophilic polymers such as ethylene vinyl alcohol (EVOH) sharply reduces their oxygen barrier ability. This research studied the effect of short time microwave sterilization on oxygen transmission rates (OTR) of two multilayer films containing EVOH and compared with that of conventional retorting. Film A had a laminated structure of EVOH sandwiched between oriented polyethylene terephthalate (PET) and cast polypropylene (PP). Film B consisted of PET laminated to a 7-layer co-extruded structure of PP/tie/Nylon 6/EVOH/Nylon 6/tie/PP. The films were used as lidstocks for trays containing mashed potato and processed by microwave or retort sterilization to achieve lethality of $F_0 = 3$ min or $F_0 = 6$ min. For both films the classical retort treatments resulted in higher OTR than the microwave treatments. In all cases, the oxygen barrier property of film A was better than that of film B. Storage of the food packages for 2 months at room temperature helped with recovery of more than 50% of the oxygen barrier lost by the films. The oxygen barrier slowly deteriorated beyond 2 months in storage. Over the 12 months storage, the OTR for both films after $F_0 = 3$ min microwave process remained below 2 cc/m^2 day, a value comparable to commercially available polyvinylidene chloride (PVDC) laminated films currently used in the USA as lid film for shelf-stable products.

1. Introduction

A high oxygen barrier property is required in food packages to maintain shelf-stability of thermally processed foods. Ethylene vinyl alcohol (EVOH) copolymers are commonly used in food packaging as oxygen barriers. In a dry state, EVOH is an excellent barrier to oxygen (Zhang et al., 2001). However, EVOH is hydrophilic and its gas barrier ability deteriorates in high relative humidity (RH) conditions. Water molecules interact with the polar hydroxyl groups weakening the intermolecular and intramolecular hydrogen bonding, thereby facilitating segmental motion (Hodge et al., 1996). Plasticization of the polymer matrix by water at high RH results in an increase in oxygen transmission rates. Zhang et al. (2001) reported sharp increases in oxygen permeability of EVOH films of different mol% ethylene contents at RH above 75–80% measured at 15, 20, and 35 °C. Muramatsu et al. (2003) reported one hundred times increase in oxygen permeability as RH increased from 0% to 90% for EVOH film of 29 mol% ethylene measured at 20 °C. Oxygen permeation into food packages may cause rancidity and other oxidative degradation reactions in lipid-containing foods resulting in quality losses. Undesirable aroma compounds may also diffuse into a package with a compromised barrier, or desired aromas may diffuse out of a package, thereby affecting the sensory quality of food. It has been indicated by Koros (1990) that maximum oxygen ingress of 1–5 ppm is enough to limit the shelf life of canned meats, vegetables, soups, and spaghetti in storage at 25 °C for 1 year.

Retorting is the food industry's most common commercial sterilization process for prepackaged low acid (pH > 4.6) foods. The process exposes food packages to high moisture and high temperature conditions under pressures of up to 2.5 atm. The long retort processes may cause severe thermal impact to both the food and the package. EVOH is used in multilayer structures (flexible films and rigid trays) usually sandwiched between relatively thick layers of polyolefins such as polypropylene (PP) which act as moisture barriers. When used in flexible pouches or thin lid films for trays, the long exposure to water at sterilization temperatures causes severe losses to the barrier properties of EVOH containing films and makes them unsuitable for conventionally retorted foods. On the other hand, microwave (MW) heating generates thermal energy within the food, thus sharply reducing the time to raise the product temperature required to achieve thermal lethality to target bacteria (Bengtsson and Ohlsson, 1974). Guan et al. (2002) reported that it took only 8 min to raise the temperature of a macaroni and cheese product to 127 °C in a microwave-circulated water combination heating system, while it took 40 min for conventional hot water retort for the same sized trays. Guan et al. (2002) further

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reported that such a short microwave (MW) sterilization process resulted in much better color, texture and flavor for the macaroni and cheese product as compared to conventional retorting. Shorter processing times in MW sterilization processes also imply less exposure of package materials to the deteriorative effects of heat and moisture which have a direct influence on the oxygen barrier.

The objective of this study was to determine the influence of MW sterilization processes on the oxygen transmission rate of two multilayer EVOH films during storage using conventional retorting for comparison.

2. Materials and methods

2.1. Experimental design

The experimental plan consisted of two thermal treatment methods (microwave and retort); two process lethality levels ($F_0 = 3$ min and $F_0 = 6$ min); and two film structures (film A and film B). For the retort treatment, only the $F_0 = 3$ min process was used. Preliminary tests showed that $F_0 = 6$ min retorting caused severe distortion and visible de-lamination in the lidstock films due to water penetration through the PP and PET layers into the EVOH layer. This observation is consistent with the fact that EVOH containing films are currently not used as flexible pouch or lidstock materials for thermally processed foods in the USA because of the severe thermal degradation during commercial industrial retorting practices. Thus, conventional (still) retorting for $F_0 = 6$ min was not included in the experimental design. Control samples for both films (i.e., films not exposed to any thermal treatment) were also evaluated in duplicate for comparison. The experimental plan is summarized in Table 1.

2.2. Description of multilayer EVOH films and rigid trays

Two multilayer films containing a thin layer of EVOH (EVAL™) as a barrier material were supplied by EVAL Company of America, Houston, TX. Film A was a laminated structure consisting of a 12 μm of EF-XL EVOH resin layer sandwiched between a 75 μm of cast polypropylene (cPP) layer on the side to be in direct contact with food and a 12 μm of biaxially oriented polyethylene terephthalate (PET) layer on the outer side (denoted PET//EVOH//PP). Film B consisted of PET laminated to a 7-layer co-extruded structure of 15 μm L171 EVOH resin between 10 μm nylon 6 homopolymer and 50 μm polypropylene homopolymer on both sides (denoted PET//PP/tie/Nylon 6/EVOH/Nylon 6/tie/PP). The tie layer between PP and nylon 6 was a maleic anhydride acid modified polypropylene. The EF-XL EVOH resin used in film A was biaxially oriented with 32 mol% ethylene, while L171 EVOH in film B was a non-oriented resin with 27 mol% ethylene. At 20 °C and 0% RH the two EVOH resins have oxygen permeability in the order of 0.002 cm^3 mm/m^2 24 h atm (EVAL Americas). Description of lamination and co-extrusion processes can be found in literature such as Frey (1986).

Rigid trays used for packing mashed potato were supplied by Rexam Containers, Union, MO, USA. The structure of the trays consisted of PP/regrind/tie/EVOH/tie/regrind/PP with a total wall thickness of about 1.8mm. The proportion of EVOH in the trays was about 1.4% by volume. The trays had a net volume of about 300 cm^3 and dimensions of $10.0 \times 14.0 \times 2.5$ cm.

2.3. Preparation of mashed potato

Mashed potato was prepared by mixing 15.4% instant mashed potato flakes (obtained from Washington Potato Company, Warden, WA, USA) with 84.6% deionized water. About 300 ± 0.2 g deaerated mashed potato at a temperature of 75 ± 1 °C was filled into the rigid trays described above. The filled trays were vacuum sealed with the lidstocks from film A and film B using a custom vacuum tray sealer (Rexam Containers, Union, MO, USA) with a top sealing plate temperature set at 193 °C, 305 mm Hg vacuum and a seal time of 3 s. The complete description of the vacuum sealer can be found in Guan et al. (2003). For both film A and film B, the PP side of the film was in direct contact with the food while the PET side was on the outside of the package.

2.4. Microwave and retort heating procedures

A pilot scale 915-MHz single mode MW sterilization system developed at Washington State University (WSU, Pullman, WA, USA) was used for the thermal treatments (Tang et al., 2008). This system consisted of two 5-kW 915-MHz MW generators (Microdry Model IV-5 Industrial Microwave Generator, Microdry Inc., Crestwood, KY, USA); a pressurized MW heating vessel connecting two MW cavities; a water circulation heating and cooling system; and a control and data acquisition system. The pressurized MW heating vessel allowed batch treatments of four meal trays held in a MW transparent customized conveyor system. In operation, food trays were conveyed through the two MW cavities in a thin bed of circulating water. In each cavity, MW energy was applied from two MW applicators through a pair of MW transparent widows that were a part of the top and bottom walls of the heating vessel. One MW generator provided equal power to the pair of the applicators for each cavity via a T-splitter in the waveguides. A detailed description of waveguide arrangement is provided in Tang et al. (2006).

An over pressure 1.8 atm (26 psig) via compressed air was applied to the circulating water during heating and cooling to maintain the integrity of food packages. This system also enables the heating vessel to function as a hot water immersion still retort when MW power is not applied. The temperature of the circulating water was controlled via two plate heat exchangers, one for heating, and another for cooling. The exchangers were heated and cooled with steam and tap water, respectively. A Think & Do™ computer program (Entivity, Ann Arbor, Mich., USA) was used to control the modulating valves of the exchangers. More details of the MW heating system can also be found in Chen et al. (2007) and Tang et al. (2008).

Table 1
Experimental design for oxygen transmission tests after post-processing storage (numbers in the table shows replicates).

Thermal treatment	Process lethality	Film structure	Storage time (months)				
			0	1	2	3	12
Microwave	$F_0 = 3$ min	A	2	2	2	2	2
		B	2	2	2	2	2
	$F_0 = 6$ min	A	2	2	2	2	2
		B	2	2	2	2	2
Retort	$F_0 = 3$ min	A	2	2	2	2	2
		B	2	–	2	–	2

For temperature measurement during processing, four fiber optic sensor cables (FISO Technologies, Inc., Canada) were fed through pressure tight fittings on one of the pressure vessel walls; each sensor tip was inserted at the cold spot of one tray through polyimide tubing that prevented food from leaking out through the probe. The cold spot was predetermined using a chemical marker method and computer vision system described in Pandit et al. (2007). Meal trays moved through the two MW cavities on a conveyor belt at a speed that allowed the cold spot in the tray to reach 121 °C upon exiting the second MW cavity. During processing the circulating water temperature for heating and cooling, as well as the temperature of the mashed potato at the cold spot of the four trays, were displayed and recorded every second. The degrees of sterilization (F_0-values) were also shown on the screen. System over pressure was monitored using a pressure gauge.

Thermal treatment procedures were selected to achieve two levels of sterilization of $F_0 = 3$ min and $F_0 = 6$ min at the cold spot in the mashed potato. In general, the $F_0 = 3$ min process is the minimum for commercial sterility while $F_0 = 6$ min is generally used for commercial retail markets. The F_0 values were calculated using the General Method (Downing, 1996):

$$F = \int_0^t 10^{\left(\frac{T-T_R}{z}\right)} dt \qquad (1)$$

where T is the recorded temperature at the cold spot of the product (°C); T_R is the reference temperature (121.1 °C); z is the temperature increase required to reduce the thermal death time of the target microorganism, *Clostridium botulinum* spores type A and B, by one-log cycle (10 °C); and t is the heating time in minutes.

For MW sterilization, the output MW power for each of the two generators was maintained at 2.5 kW by regulating anode current to the magnetron. In the heating vessel the food product was first preheated to 75 °C using circulating hot water at 100 °C. The combined heating started when the MW power was turned on and hot water at 125 °C was circulated at a flow rate of 40 l/min. The holding stage began by maintaining the circulated water at 125 °C while the MW was turned off. After the desired holding period, the trays were cooled using circulating water at 80 °C under pressure, then by tap water at 20 °C at ambient pressure. To achieve a $F_0 = 3$ min thermal lethality at the cold spot, it required a total processing time of 9 min after preheating (excluding cooling) and 12 min to reach a $F_0 = 6$ min thermal lethality in the prepackaged mashed potato.

To simulate conventional still retort processing the system was used without turning on the MW power generators. The same procedures for filling, preheating, and water heating and cooling were used to achieve a $F_0 = 3$ min at the cold spot. It took a total heating time of 28 min to achieve an $F_0 = 3$ min at the cold spot in trays for the still retort treatments. Fig. 1 shows representative temperature profiles at the cold spot of the trays for both MW and still retort processes.

The MW and retort sterilized trays were shipped overnight to the Kuraray Research and Technical Center of EVAL Company of America in Pasadena, TX via FEDEX for analysis of O_2 transmission rates. Due to the limitations in processing capacity of the heating system, samples for the $F_0 = 3$ min and $F_0 = 6$ min treatments were processed and shipped on different dates. Trays marked for control (no heat treatment) and for 0 months storage were analyzed immediately when they arrived at Kuraray Research and Technical Center. The remaining food trays were stored at ambient conditions (~20 °C and 65% RH) until analyses were conducted at specified time intervals over a 12-month period as indicated in Table 1.

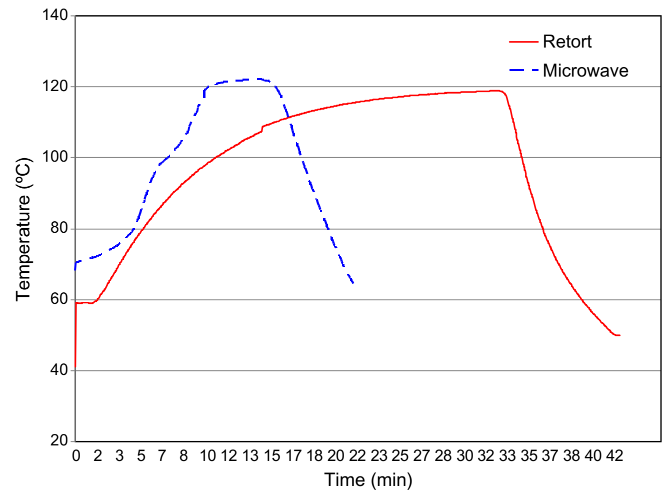

Fig. 1. Representative temperature profiles for the cold spot of mashed potato in trays during microwave and retort treatments ($F_0 = 6$ min).

2.5. Determination of oxygen transmission rates of films

O_2 transmission rates (OTR) were analyzed in MOCON OX-TRAN 2/20 devices (MOCON, Inc., USA) which used the ASTM D3985 standard method (ASTM, 1995). OTR represents the ease with which oxygen passes the films when submitted to a gradient in the partial pressure of O_2 across the films. It is expressed as the quantity (Q) of O_2 molecules passing through a film surface area (A) during time (t) at steady state under a partial pressure difference (Δp) in O_2 between the two surfaces of the sample (Massey, 2003):

$$OTR = \frac{Q}{A t \Delta p} \qquad (2)$$

Trays containing mashed potato were selected at random and the lidstock films were peeled off and food residues were cleaned by rinsing with distilled water and wiping with a paper towel. A single film specimen was cut out from each tray lid to have a measurement area of 50 cm^2. The specimens were mounted onto the diffusion cells inside which 100% oxygen (test gas) was routed through the PET side of the film specimens while a mixture of 98% N_2 and 2% H_2 (carrier gas) passes on the PP side. As the oxygen permeated through the film sample, it was picked up by the carrier gas and carried through a coulometric sensor. The amount of oxygen contained in the carrier gas at equilibrium was measured. It took 14–30 days to reach the equilibrium state. The test conditions used in the MOCON OX-TRAN 2/20 system were 20 °C and 65% RH, similar to the room storage conditions. Duplicate film samples were tested after 0, 1, 2, 3, and 12 months storage. Analysis of variance was performed on the data to determine statistical significance between treatment effects.

3. Results and discussion

Table 2 summarizes the O_2 transmission rate data for all treatments studied. In general, oxygen transmission in the multilayer EVOH films increased many fold after the thermal processes; it was recovered to a certain degree during the first 2 months storage, and was stabilized or increased during 12 months in storage.

3.1. Effect of thermal treatments

A comparison of O_2 transmission rates of the two films before and immediately after thermal processing is shown in Fig. 2. Before ther-

Table 2
Oxygen transmission rates (cc/m^2 day) for EVOH films after microwave and retort sterilization.

Storage time (months)	Film A			Film B		
	Microwave (F_0 = 3 min)	Microwave (F_0 = 6 min)	Retort (F_0 = 3 min)	Microwave (F_0 = 3 min)	Microwave (F_0 = 6 min)	Retort[a] (F_0 = 3 min)
Control[b]	0.16 ± 0.01[a]			0.096 ± 0.01[a]		
0	0.79 ± 0.01[a]	1.58 ± 0.38 [ab]	1.75 ± 0.04[ab]	1.58 ± 0.22[ab]	2.30 ± 0.32[b]	4.57 ± 0.59[c]
1	0.62 ± 0.004[a]	0.72 ± 0.01[a]	1.35 ± 0.16[b]	1.40 ± 0.30[b]	1.19 ± 0.01[b]	–
2	0.44 ± 0.23[a]	0.66 ± 0.03[ab]	0.85 ± 0.03[bc]	1.05 ± 0.04[d]	0.81 ± 0.05[cd]	0.83 ± 0.17[cd]
3	0.73 ± 0.03[a]	0.77 ± 0.004[a]	0.83 ± 0.01[ab]	0.92 ± 0.02[b]	1.28 ± 0.11[c]	–
12	0.80 ± 0.07[a]	0.79 ± 0.03[a]	2.30 ± 0.21[c]	1.36 ± 0.11[bc]	1.09 ± 0.136[b]	1.33 ± 0.34[bc]

Values with different letters within a row are significantly different.
[a] No data was collected at 1 and 3 months of storage.
[b] Control films received no heat treatment.

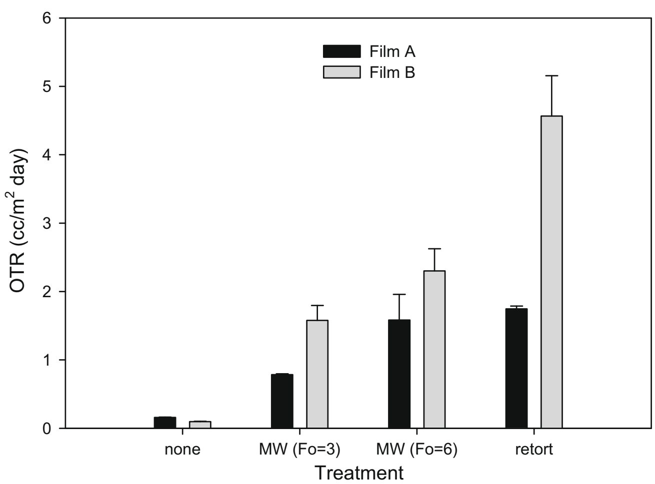

Fig. 2. Initial post-processing oxygen transmission rate of film A and B as influenced by microwave and pressurized hot water treatments.

mal treatments the O_2 transmission rates of film A and film B were 0.160 and 0.096 cc/m^2 day, respectively. These values are significantly lower than the O_2 transmission rates of 0.3–2.3 cc/m^2 day reported by commercial packaging companies for similar thickness of laminated polyvinylidene chloride (PVDC, commonly referred to as Saran) barrier film or silicon dioxide (SiOx) coated films currently used as lid films and flexible pouch materials for thermally processed shelf-stable foods in retail markets. MW and retort processes had adverse impacts on the oxygen barrier of both films as indicated by the increased O_2 transmission rates observed immediately after processing. The O_2 transmission rate (OTR) of film A increased 5-fold and 10-fold for the F_0 = 3 min and F_0 = 6 min MW processes, respectively, and increased by about 11 times due to the hot water retort (F_0 = 3 min) treatment. The O_2 transmission rate of film B increased by about 16 and 24 times, respectively, for F_0 = 3 min and F_0 = 6 min MW processes, and about 47 times for the retort treatment. That is, the O_2 transmission rate after the F_0 = 6 min MW process was about twice that of the F_0 = 3 min MW process for film A and about 1.5 times that of F_0 = 3 min process for film B. The O_2 transmission rate immediately after retort treatment was twice that of the MW treatment for film A (F_0 = 3 min) and almost three times that of the MW process for film B. Thus, the short time MW sterilization process sharply reduced the adverse thermal processing impact to both EVOH films as compared to conventional retorting. The positive correlation between exposure time to water and loss of barrier in the films was also observed for the two microwave processes (i.e., 9 min for F_0 = 3 min and 12 min for F_0 = 6 min).

The sharp increase in the O_2 transmission rates due to thermal processing is unique to EVOH laminated films and can be detrimental when used in flexible packages that need to go through conventional retort processing in production of shelf-stable low acid foods. The above results imply that food products processed to a lethality of F_0 = 6 min by conventional retort would experience more deterioration resulting from oxidation processes during storage when packaged in these types of films, as compared to those processed by F_0 = 3 min and MW processes.

The differences in O_2 transmission rate due to the thermal treatments may be explained on the basis of plasticization resulting from water absorption by the EVOH layer during processing. It is possible that the amount of water absorbed by the films was directly proportional to processing time. Due to the short times utilized in MW heating (i.e., 9 min processing time) the films might have absorbed less moisture than those processed by retort (i.e., 28 min total processing time).

To support the above speculation, separate moisture absorption experiments were conducted to determine how much water was absorbed by the two films when immersed in water at 121 °C for durations similar to those used in this study. The results from these absorption experiments indicated that exposing film A to water at 121 °C for 10 min (similar exposure times to the MW sterilization treatment used in this study) resulted in moisture uptake of about 4.3% by weight. Exposing film A for 30 min (corresponding to retorting for F_0 = 3 min) resulted in 6.2% moisture uptake. Similarly, film B absorbed about 2.9% and 4.6% moisture when exposed to water for 10 and 30 min, respectively.

Hernandez and Giacin (1998) reported 60 times increase in O_2 transmission rate for a film structure of 12 μm PET/15 μm EVOH/60 μm cPP (similar to that of film A) after retorting for 20 min at 125 °C. The authors also reported very limited effect of thermal treatment on oxygen barrier properties of SiOx coated film (i.e., 12 μm PET/SiOx/60 μm cPP) and PVDC multilayer film (i.e., 12 μm PET/15 μm PVDC/15 μm Oriented Nylon /60 μm cPP), where O_2 transmission rates increased by only 1.4 times after retort. PVDC and SiOx films are commonly used in lidstock films and flexible pouches. Despite the better performance during retort PVDC contains chlorine and at high temperatures (e.g., during incineration) it undergoes thermal degradation, producing toxic and corrosive products (Wright et al., 1995). PVDC is also more difficult to process and requires special equipment for extrusion. SiOx films, on the other hand, have limited flex and crack resistance, which is not easily detected without stress testing of packaging material, and production costs are relatively high (Lange and Wyser, 2003).

3.2. Effect of film structure

It is evident from Table 2 that the O_2 transmission rates of film A and film B before heat treatments were statistically comparable. But after thermal treatments the O_2 transmission rate of film B was higher than that of film A. In particular, after the retort treatment the O_2 transmission of film B was 2.6 times higher than that of film A. For the MW treatment the ratio of O_2 transmission rate of film B to that of film A ranged from 1.5 to 2 depending on the severity of the process. Film A consisted of a biaxially oriented EF-XL EVOH resin while film B consisted of a non-oriented L171 EVOH resin. Molecular alignment that occurs during biaxial orientation generally improves crystallinity, which results in a more tortuous path for oxygen and water vapor permeation, hence the lower O_2 transmission rates observed for film A. The differences between the two films cannot be adequately attributed to plasticization of the EVOH barrier layers by water. It is likely that different factors arising from the individual layers used in each multilayer film structure combined to influence how the oxygen barrier was affected during thermal processing. The unique multilayer structures of the two films likely provided different mechanisms for protecting the oxygen barrier of the EVOH layers as a result of the thermal processes.

Visual observations of the films after some of the severe heat treatments have shown certain degrees of damage in both films, manifested as wrinkling/wavy patterns and clusters of small blister-like swelling. Typical damages are shown in Fig. 3 for films exposed to $F_0 = 3$ min retort treatment. These observations may be an indication that there were some variations and potential loss of adhesion strength between some adjacent layers within the film structures. A sufficient explanation based on changes in internal structures of the films after thermal treatments is not possible without further microstructure examination of the films.

3.3. Changes in oxygen transmission rates during long term storage

The changes in O_2 transmission rates of the multilayer EVOH films during storage over 12 months are shown in Fig. 4. During the entire 12 months storage period the oxygen barrier of the films was recovered only partially and the pre-processing O_2 transmission rates were not reached. In general, O_2 transmission rates in the multilayer EVOH films decreased between 0 and 2–3 months of storage. The O_2 transmission rate of film A processed by MW heating decreased to just over half the initial post-processing value for the $F_0 = 3$ min process, and decreased by about 2.5 times for the $F_0 = 6$ min process during the first 2 months. The O_2 transmission rate for film A processed by retort heating reduced to about half the initial post-processing value. Sharper reductions were observed for film B, especially after the retort treatment with reduction of over five times from 4.57 to 0.83 cc/m^2 day. The MW treatment of film B resulted in reductions of about 1.5 times for $F_0 = 3$ min process and almost three times for the $F_0 = 6$ min process. It is likely, that during the initial 2–3 month in storage the much higher vapor pressure in the EVOH layer of the film than that of storage environment forced moisture to migrate through the outer layers to reach equilibrium condition.

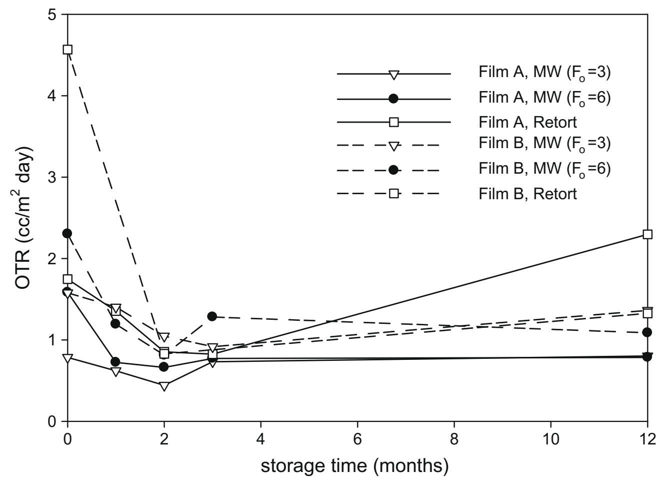

Fig. 4. Oxygen transmission rate of film A and B after microwave and retort processes for $F_0 = 3$ min during storage of mashed potato at 20 °C.

Between 2–3 and 12 months the O_2 transmission rates for the films either increased sharply or remained fairly constant. The retort treatment appears to have more effect on the O_2 transmission rate of film A during subsequent storage beyond 2 months as demonstrated by a very high value at 12 months. Conversely, the value for the MW treated film A increased slightly between 2 and 3 months and remained fairly constant between 3 and 12 months. Film B, on the other hand, revealed a slight increase in O_2 transmission for both the retort and MW heated films. It is interesting to note that, except for film A processed by retort treatment, quasi-equilibrium conditions were maintained during long term storage after 2–3 months.

The observed changes in the O_2 transmission rates during entire 12 months storage are controlled by a dynamic process of moisture migration from the EVOH layer through PET to the ambient environment and moisture migration from the mashed potato inside the trays through PP to the EVOH layer. Tsai and Wachtel (1990) stated that equilibrium oxygen permeability of retorted EVOH during storage is determined by both the amount of moisture absorbed during thermal processes and the intrinsic equilibrium moisture content of the EVOH layer at the storage temperature. It is also possible that certain structural changes in the multilayer EVOH films took place during the storage period. In particular, upon cooling from the processing temperature, the EVOH film could have lost an amount of water that was beyond its hold-capacity at the storage temperature. Moisture migration within the film (via slow diffusion until a quasi-equilibrium condition) should be associated with dehydration in some regions of the EVOH films leading to localized re-crystallization of EVOH structure, thus, the observed reduction in the O_2 transmission rates

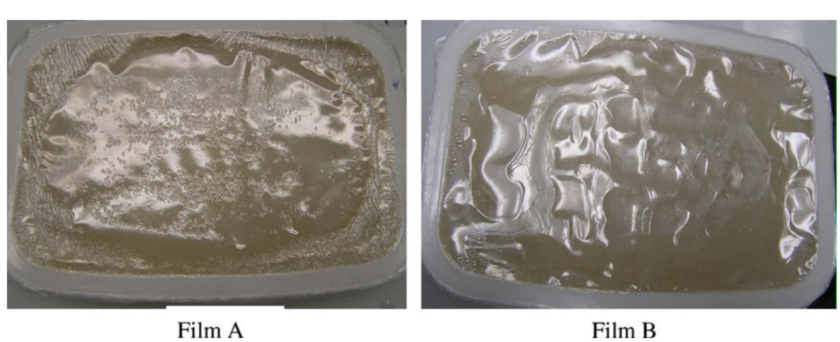

Fig. 3. Visual damage on film A and B after $F_0 = 3$ min retort treatment.

within the first 2–3 months. The reason for a steady increase of O_2 transmission rate of film A between 2 and 12 months after retorting (as shown in Fig. 4) remains unknown.

The differences observed for the two film structures during long term storage could be influenced by properties of the protective layers. The thickness and moisture transmission rates of the protective layers directly influence moisture absorption by the films during thermal processing and moisture loss during storage. The EVOH layer in film A was separated from its outside environment by a 12 μm PET layer (i.e., out-12 μm PET//12 μm EF-XL//75 μm PP-food), while additional layers of PP and nylon 6 served as moisture barrier from the external environment in film B (out-12 μm PET//50 μm PP/6 μm Nylon 6/15 μm L171/6 μm Nylon 6/50 μm PP). Nylon 6 is a poor barrier to moisture, and the moisture transmission rate in PP resin is several times smaller than that of PET (Osborn and Jenkins, 1992). The thinner and outer protective layers in film A dictate that moisture absorption into the EVOH layer was faster during processing, but the moisture also escaped more easily from the film during storage when the ambient environment was at a lower RH than the water activity of the food inside. This might have helped in reducing O_2 transmission rates in film A to a lower level than in film B at the end of the first 2 months of storage. Therefore, the positioning of the EVOH layer within the multilayer structure can be a design strategy to reduce hydration of EVOH layer and consequently limit oxygen permeability into packages as discussed by Zhang (1998).

In practical applications, the lack of full barrier recovery during storage can lead to substantial additional oxygen permeating into the package resulting in possible deterioration of oxygen sensitive foods, especially during the first 2 months of storage. Nevertheless, over the 12 months storage, the O_2 transmission rates for both films after a $F_0 = 3$ min MW processing remained below 2 cc/m^2 day, a value comparable to commercially available PVDC laminated films currently used in the USA as lidstock film for shelf-stable products.

4. Conclusion

The oxygen barrier of the two films deteriorated during hot water retort and MW processing. However, the retort processing resulted in higher oxygen barrier deterioration than the MW treatment. This implies that MW processing, with its shorter processing times, can be used to reduce hydration of the EVOH layer during processing which in turn will result in less deterioration of the oxygen barrier property. Although data showed that film A absorbed more water during thermal processing, the oxygen barrier was better than that of film B during storage, possibly due to the location of the EVOH barrier layer in the multilayer structure. For all thermal processes, the oxygen barrier of the films decreased considerably during the first 2 months of storage but the original O_2 transmission properties were not recovered during the entire storage period. Over the 12 months storage, the O_2 transmission rates for both films after a $F_0 = 3$ min microwave processing remained below the 2 cc/m^2 day value comparable to commercially available PVDC laminated films currently used in the USA as lidstock film for shelf-stable products.

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