

Oxygen Barrier and Enthalpy of Melting of Multilayer EVOH Films After Pressure-Assisted Thermal Processing and During Storage

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ABSTRACT: Pressure-assisted thermal processing (PATP) is an advanced thermal process involving application of elevated pressures above 600 MPa on a preheated food for a holding time of 3 to 5 min, causing the volumetric temperature of food to increase above 100°C, to inactivate bacterial spores and enzymes. This study evaluated the influence of PATP on two state-of-the-art multilayer EVOH films. Flexible pouches containing water as the food simulant were made from the two films and processed at 680 MPa for 3 min at 105°C and 680 MPa for 5 min at 100°C. Each film was investigated for its oxygen transmission rates (OTRs), melting temperature (T_m), enthalpy of melting (ΔH), and overall crystallinity before (control) and after processing. The changes in OTRs and total ΔH of the two films were also analyzed during a storage period of 240 days in ambient conditions after processing. Results showed a significant ($P < 0.05$) increase in the OTRs of the two films after PATP. However, PATP did not cause a significant ($P >$

0.05) change in the T_m and ΔH of the two films. The overall crystallinity of film A decreased, but improved slightly for film B after PATP. A recovery in the OTRs of the two films occurred during storage. The films also showed changes in the total ΔH measured during the storage period, which was used to explain the changes in the oxygen barrier properties. The OTR of both films remained below 2 cc/m² day, which is required in packaging applications for shelf-stable foods with a 1-year shelf life. This work demonstrates the advantages of using multilayer films containing EVOH as the barrier layer in PATP applications to produce shelf-stable foods. This work also highlights the advantage of, DSC analysis for studying the physical ageing of polymers during storage. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1538–1545, 2011

Key words: ethylene vinyl alcohol; oxygen transmission; PATP; morphology; food packaging

INTRODUCTION

The preservation of foods using thermal energy has been a major milestone in the history of food preservation. Thermal retorting is now the most popular method utilized in the food industry to sterilize prepackaged low acid (pH > 4.6) foods. However, retorting causes undesirable changes in the sensory and nutritional aspects of food. An emerging thermal processing technology, known as pressure-assisted thermal processing (PATP), has received great attention due to its ability to process low acid shelf-stable foods with increased sensory and nutritional benefits.^{1,2}

PATP involves application of elevated pressures above 600 MPa on a preheated food for a holding time of 3 to 5 min, causing the volumetric tempera-

ture of food to increase above 100°C, leading to the inactivation of spores and enzymes.³ The advantage of this technology is the rapid heating and rapid cooling of the food sample during hydrostatic compression and decompression, respectively.⁴ The synergistic effect of pressure and temperature leads to a decrease in exposure time of low acid foods to elevated temperature compared to that of the conventional retort system. In February 2009, PATP received U.S. Food and Drug Administration approval of a petition to preserve a low-acid food.⁵

One of the hurdles that must be surmounted before this technology to become commercially applicable is its compatibility with currently used flexible packaging pouches. PATP application would involve preheating these flexible packages containing food to an initial target temperature followed by high-pressure/high-temperature processing. Because packaging materials undergoing such extreme conditions may be severely damaged, shelf life of the processed food may decrease.¹ Juliano et al.³ described the general requirements for food packaging pouches for the application of various ranges of pressure and temperature treatments. Limited studies on the effect of PATP on polymeric based

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packaging material have been reported in the literature. A previous work¹ studied the effect of high-pressure/high-temperature sterilization on a few polymeric materials, and found that foil-laminated pouches showed minimal changes in terms of gas barrier, and mechanical properties after the influence of this sterilization technology. However, aluminum foil has the disadvantage of blistering under the influence of high pressure and also creates a potential problem for solid waste disposal because of its high mass density.⁶ The current polymer industry has the capability to produce nonfoil based multilayer polymeric films with high gas barrier properties which can withstand thermal sterilization processes. There is a definite need to explore the influence of PATP on such high barrier multilayer polymeric-based films.

Ethylene vinyl alcohol copolymers (EVOH) are semicrystalline materials widely used in food packaging for thermal processes. These materials have the advantage of being an excellent barrier to oxygen gas and aroma compounds, and have high thermal resistance and fast crystallization kinetics, as well as good optical characteristics. The hydroxyl group present in EVOH is responsible for the high cohesive energy offered by the molecule. This leads to a decrease in the available free volume for exchange of gas and thus the high oxygen barrier property. However, the hydrophilic nature of EVOH causes a significant decrease in its gas barrier properties when exposed to a high relative humidity (RH) environment. Hence, EVOH is commonly used in multilayer films protected by hydrophobic polymeric layers of polypropylene or polyethylene during sterilization operations.⁷⁻⁹

López-Rubio et al.⁷ studied the influence of high pressure processing on two commercially available EVOH copolymers. They concluded that this copolymer is scarcely affected by the application of high pressure processing. They also reported an improvement in barrier properties due to an increase in crystallinity of EVOH with 26 mol % of ethylene under the influence of high pressure. In another study, the oxygen barrier properties of Nylon 6/EVOH improved after pasteurization treatment using high pressure processing at 800 MPa for 10 min at 70°C.¹⁰ The current study builds on the previous studies by evaluating the impact of PATP on two state-of-the-art multilayer EVOH based packaging materials subjected to PATP.

Thermal sterilization treatments may impact the gas barrier, thermal properties, and morphology of packaging materials. These properties have a significant influence on the shelf life of the packaged products.¹¹ Increases in oxygen permeation into food packaging may severely affect the sensory properties of lipid-containing foods due to rancidity reactions.⁸

The enthalpy of fusion and melting temperature are important thermal properties of polymers, and can be used to characterize the crystallization of semicrystalline materials.¹² The crystallization mechanism influences the transmission of gases through food packaging films. X-ray diffraction studies assist in analyzing the morphological properties of the packaging materials in terms of percent of crystals. A higher crystal percentage of polymers would refer to greater orderliness of the polymeric chains, with lesser void spaces within the polymeric material. An increase in crystallinity of a polymer results in its superior gas barrier properties along with a greater stiffness and lower transparency.¹³

Thermal processing of the EVOH copolymer leads to a sharp initial increase in its oxygen permeability and also influences an increase in the steady state permeation of oxygen at a given relative humidity. This increase in gas permeability is attributed to moisture plasticization of the EVOH polymer, as well as an increase in the free volume in the polymer during the thermal process. This free volume increase causes an irreversible change in the film and morphology of the EVOH polymer.⁹ It is very important to understand the changes taking place in the polymer during a storage period after thermal processing as these modifications have an influence on the shelf life of the processed foods. Hence, studying the gas barriers and thermal properties of high-pressure/high-temperature processed films during a storage period at ambient conditions would reveal useful information concerning the free volume of the polymeric films. To the best of our knowledge, no research has been conducted that correlates thermal property changes in PATP processed films with oxygen barrier characteristics for storage periods over 200 days. Studies of this nature will help in the selection of polymeric films for sterilization applications requiring storage of a packaged food beyond 1 year.

Thus, the objective of this work is to determine the influence of PATP on two multilayer EVOH based high barrier films to improve the quality and shelf-life of many packaged foods. This study evaluated the impact of processing conditions on oxygen transmission rates, and on the thermal and morphological properties of packaging materials. This research also determined changes in oxygen transmission and overall melting enthalpy of the films during an 8-month storage period.

MATERIALS AND METHODS

Multilayer EVOH films

Two EVOH based multilayer films were developed by EVAL Company of America (Houston, TX). Film A is

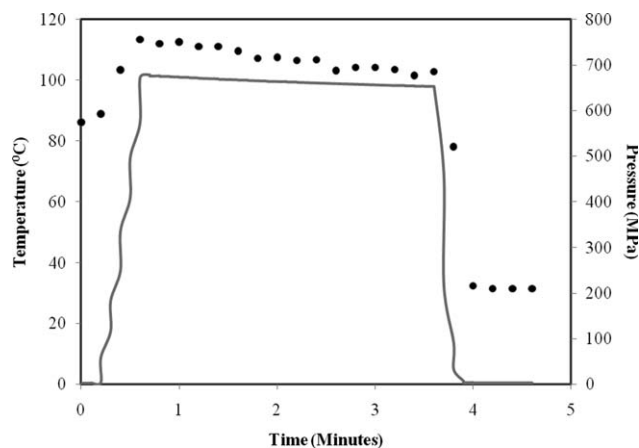


Figure 1 Representative temperature (●) and pressure (—) profile during PATP. The processing condition is 680 MPa for 3 min at 105°C.

laminated, and composed of an outer layer of 12 μm of biaxially oriented polyethylene terephthalate (PET), a middle layer of 12 μm of EF-XL EVOH resin layer (32 mol % ethylene); and an inner layer of 75 μm of cast polypropylene (cPP) placed in direct contact with food surface. Film A is also known as PET//EVOH//PP. Film B was a 7-layer structure laminated to an outer PET layer, and is denoted as PET//PP/tie/Nylon 6/EVOH/Nylon 6/tie/PP. Film B consists of a 15 μm layer of L171 EVOH resin (27 mol % ethylene) sandwiched between 10 μm nylon 6 homopolymer and 50 μm polypropylene homopolymer on both sides. The tie layer in film B was a maleic anhydride acid modified polypropylene. A previous study gives a detailed description of the structure of the materials.⁸ Flexible pouches with dimensions of 6 \times 4 inch were prepared from each of the above films.

Pressure-assisted thermal processing

The pouches were filled with 50 mL distilled water (food simulant) and sealed with a minimum headspace using an impulse sealer (MP-12; J.J. Elemer Corp., St. Louis, MO) with a 4 s dwell time. Pouches were first preheated in water to 90°C in a tilting steam kettle (DLT-40-1EG, Groen; DI Food Service Companies, Jackson, MS) for 10 min. The pouches were then placed inside a cylindrical liner made of polypropylene (internal diameter 75 mm, external diameter 100 mm, height 21.5 mm; McMaster-Carr, Atlanta, GA); the liner was used as an insulator to prevent heat loss from the packaging material to the pressure walls during holding time at maximum pressure. The liner was temperature equilibrated before loading of pouches, to ensure that the temperature of the pouch/liner system was maintained at chamber temperature. The liner was then placed in the 1.7 L cylindrical high pressure chamber measuring 0.1 m internal diameter and 2.5 m height (Engineered Pressure Systems, Inc.,

Haverhill, MA), with pressure vessel walls and compression fluid set at 90°C to achieve sterilization process conditions. The compression fluid was 5% Houghton Hydrolubic 123B soluble oil/water solution (Houghton and Co., Valley Forge, PA). The high pressure unit was pressurized to operating pressure in a few seconds using an electrohydraulic pump (Hochdruck-Systeme GmbH, AP 10-0670-1116, Sigless, Austria). Three thermocouples (K-type; Omega Engineering, Inc., Stamford, CT) were used to measure the temperature of the liner containing the sample and pressure medium.

PATP processing conditions for the EVOH pouches were 680 MPa for 3 min at 105°C and 680 MPa for 5 min at 100°C. Figure 1 shows the temperature-pressure profile during processing at 680 MPa for 3 min holding time at 105°C.

Oxygen transmission rate

Oxygen transmission rates (OTRs) were measured using an Ox-Tran 2/21 instrument (Modern Control, Minneapolis, MN) at 23°C and 55 \pm 1% RH, according to the ASTM standard method D 3985.¹⁴ The pouches were first cut into films with a measurement area of 50 cm² and then mounted inside the testing chambers. The OTR of the untreated and PATP processed pouches were measured in replicates. The OTR of the films processed at 680 MPa for 5 min holding time at 100°C was also measured after 15, 30, 60, and 240 days of storage at ambient conditions. This timeline to measure the OTRs during storage was selected because EVOH based films undergo dynamic changes immediately after a thermal process, and the lag time required by EVOH films to reach steady state oxygen permeability is greater than 200 days.⁹

Thermal analysis

The thermal transition of the EVOH films before and after processing was analyzed using a differential scanning calorimeter (DSC, Q2000; TA Instruments, New Castle, DE). The pans containing 2 \pm 0.2 mg of the EVOH multilayer samples were heated from 20 to 300°C at a rate of 10°C/min. Melting temperature (T_m , °C) and the enthalpy of melting (ΔH , J/g) of the polymers present in the multilayer EVOH films were determined using DSC thermograms. The T_m was determined from the peak temperature of the endotherm and the ΔH was determined by integrating the respective melting endotherm using the instrument's software. The sum of the ΔH of the polymers present in film A was used to calculate its total ΔH [$(\Delta H_{\text{total}})_A = \Delta H_{\text{PET}} + \Delta H_{\text{EVOH}} + \Delta H_{\text{PP}}$]. Similarly, the sum of the ΔH of the polymers present in film B was used to calculate its total ΔH [$(\Delta H_{\text{total}})_B = \Delta H_{\text{PET}} + \Delta H_{\text{EVOH}} + \Delta H_{\text{Nylon}} + \Delta H_{\text{PP}}$].

The total ΔH of the films processed at 680 MPa for 5 min at 100°C was also determined during storage. All measurements were made in replicate.

X-ray diffraction

X-ray diffraction patterns for all the untreated and processed films were obtained using a Siemens D-500 diffractometer (Bruker, Karlsruhe, Germany). The diffractometer was operated at a wavelength of 0.15 nm and the copper target tube was set at 35 KV and 30 mA. The dimension of the multilayer EVOH sample required for recording the diffraction patterns was 2 inch \times 2 inch. The intensity of diffraction was recorded as a function of increasing scattering angle from 8 to 35°C with a step angle of 0.05°C and scan time of 3 s per step. The XRD patterns provided an estimate of the crystallinity percentage in the films.

Data analysis

The OTR and enthalpy of melting data for the two films before and after processing were studied using a complete randomized design. The data was analyzed using the general linear model (GLM) and the significant differences ($P < \alpha$) in properties of the films were determined through the Fisher's least significant difference (LSD) test ($\alpha = 0.05$). Data analysis was conducted with the statistical software SAS version 9.2 (SAS Inst. Inc., Cary, NC).

RESULTS AND DISCUSSION

Film characterization after PATP

This section will discuss the oxygen barrier and structural changes suffered by the two multilayer EVOH films immediately after PATP.

Oxygen transmission rate

The OTR of films A and B before (control) PATP were 0.24 and 0.11 cc/m² day, respectively. Similar OTR values were observed by Mokwena et al.⁸ for the two films before thermal processing. These values were significantly lower than those of commercially available polyvinylidene chloride or silicon oxide coated barrier films of similar thickness. These commercially available films are currently being used to construct pouches for thermal processing of sterilized foods. Results from Mokwena et al.⁸ also showed that thermal sterilization influenced the OTRs of both films.

OTR for the two EVOH films was observed immediately after the two PATP processing treatments. A comparison of OTR of the two films before and im-

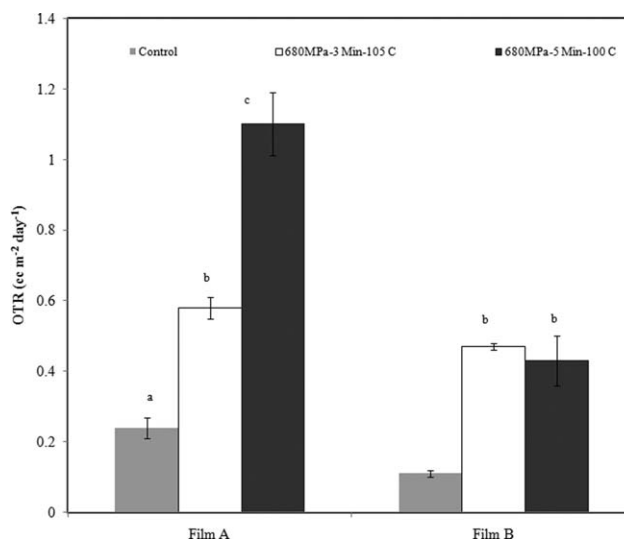


Figure 2 Oxygen transmission rate of films A and B as influenced by the two PATP conditions. Mean values with different letters are significantly different ($P < 0.05$).

mediately after PATP for the two processing conditions is shown in Figure 2. There was a 2.5-fold and fivefold increase in the OTR of film A after the 3 min and 5 min PATP processes, respectively. The OTR values of film A significantly increased ($P < 0.05$) with increased holding time under maximum pressure. The OTR value for film B increased nearly four times after PATP. Results for film B suggest that its barrier properties were not influenced by the increase of holding time at maximum pressure. The superior oxygen barrier property of film B with 28 mol % ethylene, compared to film A with 32 mol % ethylene, is in agreement with the study conducted by López-Rubio et al., who observed slightly better barrier properties after high pressure processing for the monolayer EVOH copolymer with lower ethylene content.⁷ Also, the influence of individual layers in the multilayer structure of film B would have played a crucial role in outperforming film A in terms of the oxygen barrier properties after the thermal process.

The increase of OTR in EVOH films could be attributed to the poor moisture resistance of EVOH copolymers. In one study, the authors observed that a decrease in the barrier properties of films after high-pressure/high-temperature treatment was due to thermal damage of polymers during preheating.¹ The preheating step in the current study involved heating for 10 min at 90°C with similar results. It was found that preheating exposed the EVOH copolymer to a high relative humidity environment causing the plasticization of the hydrophilic EVOH layer, which led to a decrease in the polymer chain-to-chain interactions, resulting in an increase in the free volume. These modifications may be responsible for the deterioration of oxygen barrier properties.

TABLE I
Values of OTR Obtained for Polymeric Packaging Films in Different Studies After High-Pressure/High-Temperature Processing

Film	Preheating		High pressure conditions			Oxygen transmission rate			References
	T (°C)	Time (min)	Pressure (MPa)	T (°C)	Time (min)	OTR (cc/day m ² atm)	RH (%)	T (°C)	
PET/EVOH/PP	90	10	680	100	5	1.1 ± 0.09	55	23	Present study
PET//PP/tie/Nylon6/ EVOH/Nylon 6/tie/PP	90	10	680	100	5	0.43 ± 0.07	55	23	Present study
PET/AlO _x /CPP	90	11	688	121	3	19.6 ± 0.7	a	a	Koutchma et al. ¹
Biaxial Nylon/EVOH	90	12.2	688	121	3	2.0 ± 0.3	a	a	Koutchma et al. ¹
PET/Al/PP	90	8.8	688	121	3	0.4 ± 0.15	a	a	Koutchma et al. ¹
Nylon/Al/PP	90	a	688	121	3	0.44 ± 0.05	a	a	Koutchma et al. ¹
EVOH (26 mol % ethylene)	a	a	800	75	5	0.62	0	23	Lopez-Rubio et al. ⁷

^aValues were not reported.

However, the plasticizing effect is time dependent when the EVOH layer is protected by hydrophobic polymer layers.¹⁵ Both films used in this study were protected by polypropylene, which is a good water barrier. Hence, the increase of OTR in both films A and B is far below the 2 cc/m²day limit required for packaging application for sterilized food products.⁸

Table I compares the OTR of different films after high-pressure/high-temperature processing observed from various studies. The aluminum foil-laminated films studied by Koutchma et al.¹ performed the best in terms of the OTR after processing at 688 MPa and 121°C for 3 min. Nevertheless, the EVOH based films utilized in this study had OTR values comparable to the foil-based films. These results suggest that multilayer EVOH films have the potential to replace foil-based films whose drawbacks have been previously discussed.

Thermal analysis

The thermal characteristics of the films after PATP were studied using DSC experiments. Table II sum-

TABLE II
Melting Temperature and Enthalpy of Melting for the EVOH Layer in Films A and B, Untreated, and After PATP

Film	Treatment	T_m (°C)	ΔH (J/g)
A (32 mol % ethylene)	Control	182.8 ± 0.3 ^a	6.5 ± 0.2 ^b
	680 MPa, 3 min, 105°C	182.2 ± 0.1 ^a	6.7 ± 0.1 ^b
	680 MPa, 5 min, 100°C	182.6 ± 0.3 ^a	5.8 ± 0.8 ^b
B (27 mol % ethylene)	Control	186.1 ± 0.2 ^c	4 ± 0.6 ^d
	680 MPa, 3 min, 105°C	186.1 ± 0.1 ^c	4.1 ± 0.8 ^d
	680 MPa, 5 min, 100°C	186.1 ± 0.1 ^c	4.4 ± 0.5 ^d

Values are means ± 1 standard deviation. Means with different letters within a column are significantly different ($P < 0.05$).

T_m = melting temperature; ΔH = enthalpy of melting.

marizes the melting temperature and enthalpy of melting for the two films before and after the combined temperature and pressure treatment. The PATP processes had no influence on the melting temperature (T_m) and melting enthalpy (ΔH) of the EVOH layer in both films A and B.

The results for film B containing 27 mol % ethylene are in agreement with the study conducted by López-Rubio et al.,⁷ who observed no significant difference in the melting behavior of high pressure processed monolayer EVOH containing 26 mol % ethylene. On the other hand, the results of film A are also in agreement with the thermal characteristics of a multilayer film of nylon/EVOH/polyethylene processed at 690 MPa at 95°C for 10 min in another study. No significant difference was shown between the untreated film and the high pressure processed EVOH film containing 32 mol % ethylene.¹⁶ The above results indicate that PATP did not influence the thermal characteristics of the EVOH layer in films A and B.

X-ray diffraction

The XRD patterns for film A for the two PATP processing conditions are presented in Figure 3. The XRD diffractograms show a decrease in peak intensities after both of the PATP treatments, leading to a decrease in the overall crystallinity of film A. This decrease is reflected in the loss of the film's gas barrier property after the PATP treatments, as a decrease in crystallinity results in a loss of orderliness in the polymeric chains, in turn causing a decrease in the tortuous path for the gas to travel through the film. This decrease in tortuosity promoted by the crystalline phase causes more gas to flow through the film, leading to quality deterioration of the food.^{13,17}

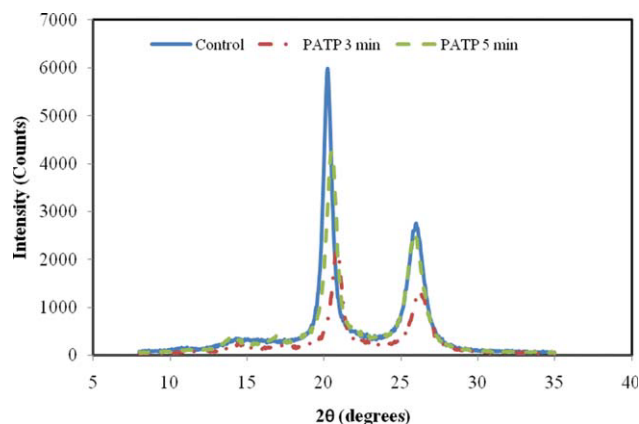


Figure 3 X-ray diffraction patterns for film A before and after the two PATP treatments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The XRD patterns for film B for the two PATP processing conditions are presented in Figure 4. Unlike film A, the film B showed a small improvement in overall crystallinity. In another study, the authors observed similar results, in which high pressure processing caused an increase in the percentage of crystallinity of EVOH with 26 mol % ethylene.⁷ However, the improved crystallinity does not explain the loss of the gas barrier property for film B after PATP. Hence, more studies involving measurement of the morphology in the polymeric film are required to gain a clearer understanding of the behavior of the gas barrier properties for a given polymeric film.

Film characterization during long-term storage

This section reports the influence of storage on the PATP processed multilayer EVOH films. The alterations suffered by the films are explained by means of oxygen transmission rate, and total melting enthalpy.

Oxygen transmission rate

The OTRs of the two films were measured before (control) processing, after PATP at 680 MPa for 5 min at 100°C, and during a storage period of 240 days (Table III). Generally, there was a recovery in the oxygen barrier properties of the films during the

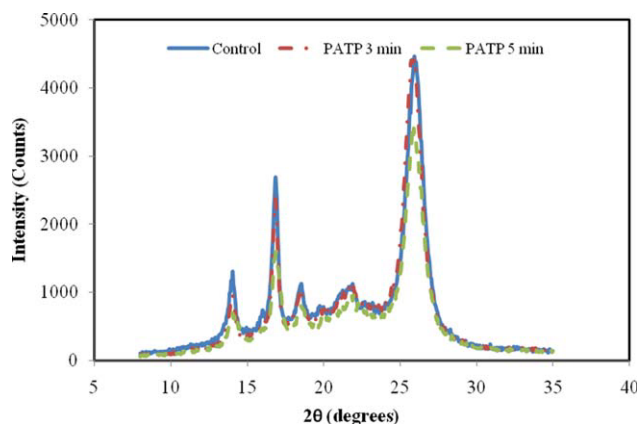


Figure 4 X-ray diffraction patterns for film B before and after the two PATP treatments. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

storage period after the initial increase of OTR measured immediately after processing. The rate of recovery of the oxygen barrier properties was slower during the initial storage period, but increased during the storage period of 60 to 240 days. However, overall, the barrier properties of the films were not completely recovered during the storage study and the preprocessing values were not attained. Nevertheless, this study shows an improvement in the gas barrier properties of thermally processed multilayer films during storage, which will help extend the shelf-life of packaged foods.

The OTR values for film A observed after a storage period of 15 days did not change significantly ($P > 0.05$) compared with the initial postprocessing value. On the other hand, at the end of 30 days storage, there was a significant decrease in OTR measured for film A ($P < 0.05$) (Table III). This observation is in agreement with the study conducted by Mokwena et al.,⁸ who observed a similar improvement in oxygen barrier properties of film A after microwave sterilization. As the authors describe, the difference in the vapor pressure between the EVOH layers and the storage environment force a moisture migration from the film to attain equilibrium conditions. This migration would have facilitated an improvement in the oxygen barrier property of the film. The film A reached a quasi-equilibrium condition between day 30 and day 240 of storage and,

TABLE III
OTR Values ($\text{cc}/\text{m}^2 \text{ day}$) for the Multilayer EVOH Films After PATP at 680 MPa and 100°C for 5 min

Film	Control	Storage time (days)				
		7	15	30	60	240
A	0.24 ± 0.03^a	1.1 ± 0.09^b	1.06 ± 0.07^b	0.84 ± 0.11^c	0.86 ± 0.01^c	0.71 ± 0.04^c
B	0.11 ± 0.01^a	0.43 ± 0.07^{bc}	0.4 ± 0.05^{bc}	0.43 ± 0.02^{bc}	0.47 ± 0.18^b	0.26 ± 0.01^{ac}

Values are means ± 1 standard deviation. Means with different letters within a row are significantly different ($P < 0.05$).

TABLE IV
Melting Enthalpy (J/g) of Individual Components and the Total Melting Enthalpy for Multilayer EVOH Films After PATP at 680 MPa and 100°C for 5 min During Storage

Film	Components/total	Storage time (days)			
		Control	7	60	240
A	PP	41.81 ± 0.99	30.12 ± 4.72	37.97 ± 0.64	34.84 ± 0.79
	EVOH	6.67 ± 0.74	6.17 ± 0.77	7.28 ± 0.62	7.03 ± 0.65
	PET	4 ± 1.06	3.86 ± 0.09	5.31 ± 0.86	4.42 ± 0.12
	Total melting enthalpy	52.48 ± 0.8 ^a	40.15 ± 5.59 ^b	50.56 ± 2.13 ^a	46.29 ± 1.56 ^{ab}
B	PP	32.08 ± 1.04	28.37 ± 0.56	26.51 ± 2.27	35.85 ± 4.89
	EVOH	4.37 ± 0.31	4.72 ± 0.01	4.2 ± 0.02	5.11 ± 0.48
	Nylon	5.8 ± 1.35	5.52 ± 0.26	5.15 ± 0.18	6.43 ± 1.05
	PET	2.98 ± 0.55	3.35 ± 0.15	2.58 ± 0.09	3.79 ± 0.3
	Total melting enthalpy	45.23 ± 3.27 ^{ab}	41.96 ± 0.98 ^{ab}	38.44 ± 2.52 ^a	51.18 ± 6.73 ^b

Values are means ± 1 standard deviation. Means with different letters within a row are significantly different ($P < 0.05$).

hence, no significant changes were seen in the oxygen barrier properties.

On the other hand, the study of storage between 30 and 240 days showed a significant improvement ($P < 0.05$) in the oxygen barrier property for film B (Table III). The significant improvement in the barrier properties of film B during this storage period suggests that it would require more time to attain its quasi-equilibrium state. It is exciting to note that there was no significant difference ($P < 0.05$) between the preprocessing OTR for film B with the postprocessing value obtained after storage for 8 months (Table III). This improvement in the oxygen barrier property will have a positive impact on the shelf life of PATP processed packaged foods. To prove this further and to add more insight on the possible reasons for improvement in the OTR, a thermal analysis was performed during storage to study the crystallization mechanism of the semicrystalline polymers. However, the OTR values for the two films during the storage period was way below 2 cc/m² day, the value required for packaging applications for shelf-stable foods.⁸

Thermal analysis

To increase our understanding about the behavior of the oxygen barrier properties and the morphology of the films during storage, the total ΔH was measured during the 240-day storage period. Table IV highlights the results obtained for the two films after processing at 680 MPa and 100°C for 5 min. The $(\Delta H_{\text{total}})_A$ decreased significantly ($P < 0.05$) immediately after processing. This decrease in the $(\Delta H_{\text{total}})_A$ could have led to a decrease in crystal size and crystallinity and, hence, led to a significant increase in the OTR immediately after processing. On the other hand, film B also showed a decrease in the $(\Delta H_{\text{total}})_B$ after processing but the change was not significant ($P > 0.05$).

During a storage period of 60 days, the film A showed a significant increase ($P < 0.05$) in the $(\Delta H_{\text{total}})_A$ compared to the previous measurement (Fig. 5); whereas the $(\Delta H_{\text{total}})_B$ value remained nearly the same for film B ($P > 0.05$) (Fig. 6). It can be inferred that the change in the $(\Delta H_{\text{total}})_A$ could have led to an increase in the crystallinity of the polymers, thereby causing a recovery in its oxygen barrier property at the end of 60 days.

The $(\Delta H_{\text{total}})_B$ at the end of 240 days showed a significant increase ($P < 0.05$) compared to the previous value obtained at the end of 60 days, which could be related to the significant decrease ($P < 0.05$) in its OTR value at the end of the storage period.

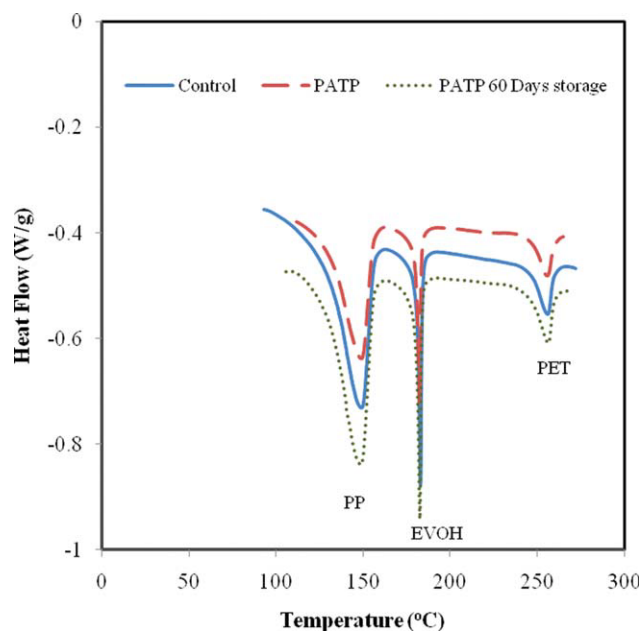


Figure 5 The total melting enthalpy of film A after PATP (680 MPa for 5 min at 100°C) during a storage period of 60 days at room temperature. The DSC scan rate ranged from 20 to 300°C at a rate of 10°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

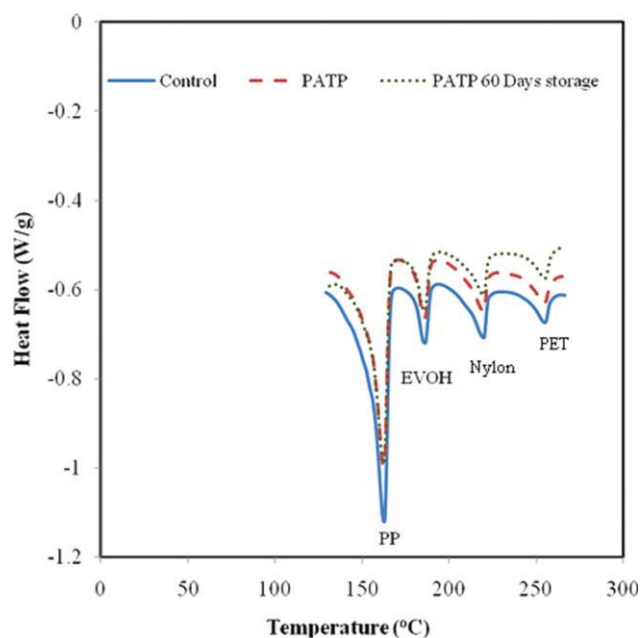


Figure 6 The total melting enthalpy of film B after PATP (680 MPa for 5 min at 100°C) during a storage period of 60 days at room temperature. The DSC scan rate ranged from 20 to 300°C at a rate of 10°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Conversely, for film A, there was only a slight decrease in the $(\Delta H_{\text{total}})_A$ and, hence, the change in its barrier property during this period was not significant ($P > 0.05$). These changes in total ΔH could be attributed to the physical ageing of polymers present in the films A and B. During physical ageing, the polymeric layers exhibit slow thermodynamic changes to attain a lower-free energy state; these modifications lead to significant changes in the mechanical and gas barrier properties of the food packaging film. The molecular rearrangement during ageing causes a slow decrease in the free volume within the polymer matrix through which the gas molecules move, and the level of changes depends on the thermal history and thickness of the polymers present in the film.¹⁸

This study shows that the microstructural changes within the polymeric layers during storage can be utilized to explain the variation in barrier properties of films utilized for sterilization applications.

CONCLUSIONS

PATP had a significant influence on the oxygen barrier properties of the two films. The state-of-the-art seven-layer film B (PET//PP/tie/Nylon 6/EVOH/Nylon 6/tie/PP) containing 27 mol % ethylene showed superior oxygen barrier properties compared with film A throughout the study. The changes in overall crystallinity observed from the XRD diffractograms help explain the change in oxy-

gen barrier property after PATP. On the other hand, the thermal characterization of the films with DSC did not show significant changes in the T_m and ΔH after the thermal process. However, the changes in total ΔH of the EVOH based multilayer films during storage correlated to the changes in their oxygen barrier properties. Thus DSC analysis is recommended as a useful technique to reason out the recovery of the oxygen barrier properties in the thermal processed packaging films during the storage period. The improvement of OTR in the films during storage would help further improve the shelf life of PATP processed food. Overall, flexible plastic pouches containing EVOH as the barrier layer is a suitable choice as packaging material for PATP.

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References

- Koutchma, T.; Song, Y.; Setikaite, I.; Juliano, P.; Barbosa-Cánovas, G. V.; Dunne, C. P.; Patazca, E. J. *Food Process Eng* 2009, 2, 138.
- Juliano, P.; Toldrà, M.; Koutchma, T.; Balasubramanian, V. M.; Clark, S.; Mathews, J. W.; Dunne, C. P.; Sadler, G.; Barbosa-Cánovas, G. V. *J Food Sci* 2006, 71, 52.
- Juliano, P.; Koutchma, T.; Sui Q.; Barbosa-Cánovas, G. V.; Sadler, G.; *Food Eng Rev* 2010, 2, 274
- Ratphitagsanti, W.; Ahn, J.; Balasubramanian, V. M.; Yousef, A. E. *J Food Prot* 2009, 72, 775.
- Food Processing. Pressure-Assisted Thermal Sterilization Accepted by FDA 2009. Available at: <http://www.foodprocessing.com/articles/2009/032.html>. Last accessed July 5 2010.
- Han, J.; Yuan, J. *Advances in Packaging for Nonthermal Processes*; Blackwell: Ames, IA, 2007.
- López-Rubio, A.; Lagarón, J. M.; Hernández-Muñoz, P.; Almenar, E.; Catala, R.; Gavara, R.; Pascall, M. A. *Innov Food Sci Emerg Technol* 2005, 6, 51.
- Mokwena, K. K.; Tang, J.; Dunne, C. P.; Yang, T. C. S.; Chow, E. *J Food Eng* 2009, 92, 291.
- Tsai, B. C.; Wachtel, J. A. In *Barrier Polymers and Structures*; Koros, W. J., Ed.; American Chemical Society: Washington DC, 1990; Chapter 9.
- Halim, L.; Pascall, M. A.; Lee, J.; Finnigan, B. *J Food Sci* 2009, 74, 9.
- López-Rubio, A.; Giménez, E.; Gavara, R.; Lagarón, J. M. *J Appl Polym Sci* 2006, 101, 3348.
- Kong, Y.; Hay, J. N. *Eur Polym Mater* 2003, 39, 1721.
- Yoo, S.; Lee, J.; Holloman, C.; Pascall, M. A. *J Appl Polym Sci* 2009, 112, 107.
- American Society for Testing and Materials. *Standard Test Method for Oxygen Gas Transmission Rate Through Plastic Film and Sheet Using a Coulometric Sensor*; American Society for Testing and Materials: Philadelphia, PA, 1995. ASTM D 3985–95.
- López-Rubio, A.; Lagarón, J. M.; Giménez, E.; Cava, D.; Hernández-Muñoz, P.; Yamamoto, T.; Gavara, R. *Macromolecules* 2003, 36, 9467.
- Schauwecker, A.; Balasubramanian, V. M.; Sadler, G.; Pascall, M. A.; Adhikari, C. *Packaging Technol Sci* 2002, 15, 255.
- López-Rubio, A.; Gavara, R.; Lagarón, J. M. *J Appl Polym Sci* 2006, 102, 1516.
- Martino, V. P.; Ruseckaite, R. A.; Jiménez, A. *Polym Int* 2009, 58, 437.