



## Pressure-assisted thermal sterilization effects on gas barrier, morphological, and free volume properties of multilayer EVOH films



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### ABSTRACT

Pressure-assisted thermal sterilization (PATS) alters the morphology and free volume distributions of polymers leading to a decrease in gas-barrier properties of polymer packaging materials, and hence compromising the quality and shelf life of PATS processed foods. Two multilayer ethylene–vinyl alcohol (EVOH) films, intended for high pressure applications, were investigated to understand the influence of free volume characteristics and film morphology on gas-barrier properties of PATS processed EVOH films. X-ray diffraction (XRD) and positron annihilation lifetime spectroscopy (PALS) were applied to investigate film morphology and free volume characteristics, respectively. Film A was comprised of polyethylene terephthalate (PET)/EVOH/polypropylene (PP). Film B consisted of PET laminated to a co-extruded structure of PP/tie/Nylon6/EVOH/Nylon6/tie/PP. Both oxygen and water vapor transmission rates increased in the two films after the selected treatments. However, the increase in film A is much larger which can be understood from the change in free volume distributions measured by positron lifetime and overall crystallinity observed from X-ray diffraction. This work shows that PALS and XRD are suitable tools to reason out the gas-barrier changes in multilayer EVOH films after PATS treatment.

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### 1. Introduction

Pressure-Assisted Thermal Sterilization (PATS) is an emerging thermal processing technology for sterilizing prepackaged low-acid (pH > 4.6) foods. Pressures in the range of 600–800 MPa and initial chamber temperature of 60–90 °C is utilized to ensure the inactivation of spores and enzyme. This synergistic effect of temperature and pressure helps reduce the total processing time and reduces the exposure of food products to high temperature compared to the conventional thermal retort system. The lower food processing times help improving the sensory and nutritional characteristics of low-acid shelf-stable foods. In February 2009, US Food and Drug Administration approved a petition to preserve a low-acid food using PATS (Bermúdez-Aguirre and Barbosa-Cánovas, 2011).

PATS require food to be packaged during processing and ethylene vinyl alcohol copolymers (EVOH)-based multilayer polymeric films have been found to be suitable candidates of packaging material for withstanding high pressure and temperature (López-Rubio et al., 2005a). However, a previous study showed that deterioration in oxygen barrier properties of EVOH-based films has

been observed after PATS treatment and during storage which could have an impact on the quality and shelf life of PATS processed foods. This loss of oxygen barrier property in EVOH films has been correlated to the changes in thermal and morphological properties in the polymer encountered during PATS processing. However, the thermal properties measured by differential scanning calorimeter (DSC) and the morphology measured by X-ray diffraction (XRD) alone had limitations in providing a clear correlation of gas barrier changes in the (EVOH)-based multilayer polymeric films (Yoo et al., 2009). Thus, techniques like positron annihilation lifetime spectroscopy (PALS) is required in addition to XRD to understand the morphological and free volume modifications taking place in the polymeric film after processing and thus, provide a better understanding on their gas barrier changes.

Inefficient chain packing of the polymer created by folding and molecular architecture of polymer chain segments leads to the formation of free volumes. The extent of free volumes present in a polymer matrix help understand the molecular gas transport through the polymer membrane as the free volumes in a polymer create an easier pathway for the diffusion of solutes through the solid matrix. PALS is a powerful nondestructive versatile technique utilized for detecting and characterizing free volume sizes and their distribution in polymers and vacancy-type defects in crystals with excellent sensitivity. Positrons injected into a solid from a

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radioactive source annihilate with electrons, either from a delocalized state in the bulk or from a trapped state in an open volume such as a lattice vacancy in crystals or an open volume in polymers and porous materials (Awad et al., 2012). Trapping at defects or open volumes leads to an increase in the average positron lifetime. In fair approximation, the positron lifetime varies inversely with the electron density at the annihilation site. Consequently, annihilation in vacancies or open volumes, where electron densities are low, has longer lifetimes. Measured lifetimes are characteristic of the open volume in which the positrons annihilate, and therefore can be used to discriminate among different locations where positrons annihilate. A measured lifetime spectrum  $N(t)$  consists of a sum of components corresponding to each annihilation site:

$$N(t) = \sum_{i=1}^{k+1} \frac{I_i}{\tau_i} \exp\left(\frac{-t}{\tau_i}\right) \quad (1)$$

in which  $k + 1$  is the number of lifetime components in the spectrum, corresponding to annihilation in the bulk and in  $k$  defect types, and in which  $\tau_i$  and  $I_i$  are the lifetime and intensity of the  $i$ th component in the spectrum. Fitted lifetimes give information about defect/open volume sizes and characteristics and the intensities determine defect/open volume concentrations. Therefore, lifetime spectrum provides information about free volumes in polymers and porous materials just as about defects in crystalline solids. Positrons also form positronium in polymers which leads to much longer lifetime (Jean, 1994).

Danch et al. (2007) utilized PALS for studying the influence of low temperature and high pressure on the free volume in polymethylpentene. Temperature rise from 0 to 300 K led to an increase in free volume, whereas, increase in pressure from 0 to 500 MPa led to a decrease in free volume in polymethylpentene. However, no studies have been carried out to study the influence of food processing technologies like PATS on food packaging polymers. Such studies will help gain a fundamental understanding of combined influence of both temperature and pressure on the free volume parameters which in turn could be related to the change in the gas barrier properties after processing.

Thus, the objective of this work is to determine the effect of PATS on two multilayer ethylene–vinyl alcohol (EVOH) based high barrier films to understand the influence of free volume characteristics and film morphology on gas-barrier properties of PATS processed EVOH films.

## 2. Materials and methods

### 2.1. Multilayer EVOH films

Two multilayer polymer films containing a thin barrier layer of EVOH were developed by EVAL Company of America (Houston, TX). Film A is laminated, and composed of an outer layer of 12  $\mu\text{m}$  of biaxially oriented polyethylene terephthalate (PET), a middle layer of 12  $\mu\text{m}$  of EF-XL EVOH resin layer (32 mol% ethylene); and an inner layer of 75  $\mu\text{m}$  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  $\mu\text{m}$  layer of L171 EVOH resin (27 mol% ethylene) sandwiched between 10  $\mu\text{m}$  nylon 6 homopolymer and 50  $\mu\text{m}$  polypropylene homopolymer on both sides. The tie layer in film B was a maleic anhydride acid modified polypropylene. A previous study by Mokwena et al. (2009) gives a detailed description of the structure of the materials. The above films were used to make flexible pouches with dimensions of 6  $\times$  4 in. that were utilized for this study. 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 Corporation, St. Louis, MO). The pouches for the control experiment were not treated with PATS and characterized for their barrier, morphological and free volume properties.

### 2.2. Pressure-assisted thermal sterilization (PATS)

Flexible pouches containing water were first preheated in water to 90  $^{\circ}\text{C}$  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 prior to 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  $^{\circ}\text{C}$  in order to achieve sterilization process conditions. The compression fluid was 5% Houghton Hydrolubic 123B soluble oil/water solution (Houghton & 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.

PATS processing conditions for the EVOH pouches were 680 MPa for 5 min at 100  $^{\circ}\text{C}$ . Fig. 1 shows a typical temperature–pressure profile during processing at 680 MPa for 5 min holding time at 100  $^{\circ}\text{C}$ . Once the PATS processing was complete, the water was drained and the pouches were air dried and stored at ambient conditions ( $\sim 23$   $^{\circ}\text{C}$  and 60% RH). All the following analysis was done within a week of PATS treatment.

### 2.3. Oxygen transmission rate

Oxygen transmission rates (OTRs) were measured according to the ASTM standard method D 3985. A Mocon Ox-Tran 2/21 MH permeability instrument (Modern Control, Minneapolis, MN) was utilized to conduct the measurements at 23  $^{\circ}\text{C}$ , 55  $\pm$  1% RH, and 1 atm. The OTR measurement characterizes the ease in which oxygen gas passes through the films when a gradient in partial pressure of oxygen is present across the films. Film specimens of

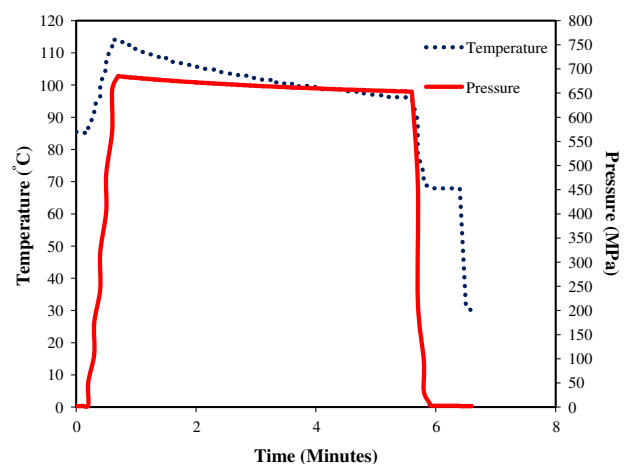


Fig. 1. Representative temperature (●) and pressure (—) profile during PATS. The processing condition is 680 MPa for 5 min at 100  $^{\circ}\text{C}$ .

surface area 50 cm<sup>2</sup> were cut from the polymeric pouches and mounted inside the testing chambers and readings were measured with the help of a coulometric sensor that was fitted in the equipment. The OTR of the control (untreated) and PATS processed pouches were measured in replicates.

#### 2.4. Water vapor transmission rate

Water vapor transmission rates (WVTRs) were measured according to the ASTM standard method F 372-99. A Mocon Permatran 3/33 tester (Modern Control, Minneapolis, MN) utilizing an infrared detector was used to characterize the water vapor transmission rate (WVTR) of the packaging materials at 100% RH and 38 °C. Film specimens of surface area 50 cm<sup>2</sup> were cut from the polymeric pouches and mounted inside the testing chambers. The WVTR of the control (untreated) and PATS processed pouches were measured in replicates.

#### 2.5. X-ray diffraction

A Siemens D-500 diffractometer (Bruker, Karlsruhe, Germany) was utilized to obtain the X-ray diffraction patterns for the two untreated (control) and processed films A and B. The diffractometer uses a copper target tube which provides a wavelength ( $\lambda$ ) of 0.15 nm and the copper tube was operated at 35 kV and 30 mA. The dimensions of the multilayer EVOH sample required for recording the diffraction patterns were 2 in.  $\times$  2 in. The intensity of diffraction was recorded as a function of increasing scattering angle from 8 to 35° ( $2\theta$ ) with a step angle of 0.05° and scan time of 3 s per step. The crystallinity percentage and crystalline size were estimated from the XRD patterns. The ratio of area under the peaks (crystalline region) to the area of the amorphous region in the diffraction patterns helped estimate the overall crystallinity. The Scherrer equation was used to determine the crystal size ( $D$ ) as follows (Yoo et al., 2009):

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (2)$$

where  $\beta$  is the full-width at half maximum and  $\theta$  is the angle between the incident rays which were obtained from the XRD peaks. The initial profiles were refined and processed using the peak fitting program JADE (Materials Data, Inc., Livemore, CA) for accurate computation.

#### 2.6. Positron annihilation lifetime spectroscopy (PALS)

PALS is a powerful nondestructive versatile technique utilized for detecting and characterizing free volume sizes and their distribution in polymers with good sensitivity at the atomic- and nano-scale. The free volume characterization of polymers is possible because of the capability of positronium (bound state of electron and positron) to preferentially localize in regions of low electron density such as pores, free volume, interfaces, and holes (Choudalakis and Gotsis 2009; Awad et al., 2012; Ramya et al., 2012).

Here, positron lifetimes were measured using a conventional fast-fast time coincidence spectrometer with two BaF<sub>2</sub> gamma-ray detectors mounted on photomultiplier tubes. The spectrometer has been described in detail by Selim et al. (2013). A positron source was made by depositing <sup>22</sup>NaCl activity on an 8- $\mu$ m thick kapton foil that was then folded and sandwiched between two identical samples. PAL spectra were recorded at room temperature with a time resolution of  $\sim$ 200 ps. Several million counts were accumulated in each lifetime spectrum for good statistical precision. LT9 program was employed for analyzing the lifetime distribution after applying the source correction term (Kansy, 1996).

MELT program was used to verify the lifetime values obtained from LT9 and to attain the lifetime distributions (Shukla et al., 1993). The measured spectra were resolved into three components ( $\tau_1$ ,  $\tau_2$ , and  $\tau_3$ ) with their respective intensities ( $I_1$ ,  $I_2$ , and  $I_3$ ) for finite-term lifetime analysis. Spectra were fit to the best  $\chi^2$  with the lowest standard deviation.

The shortest lifetime ( $\tau_1$ ) could be attributed to the self-annihilation of *para*-positronium (*p*-Ps) whereas, the intermediate lifetime ( $\tau_2$ ) could be related to the free positron annihilation. The third mean lifetime ( $\tau_3$ ) is due to the *ortho* positronium (*o*-Ps) pick-off annihilation in free-volume holes of amorphous region. A semi-empirical equation given by the following relation along with the *o*-Ps lifetime ( $\tau_3$ ) could be used to obtain the mean free-volume hole radius ( $R$ ).

$$(\tau_3)^{-1} = 2 \left[ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R_0} \right) \right] \text{ns}^{-1} \quad (3)$$

where  $\tau_3$  and  $R$  are expressed in the units of ns and Å, respectively.  $R_0$  equals  $R + \Delta R$  where  $\Delta R$  is the fitted empirical electron layer thickness with a value of 1.66 Å. Relative fractional free volume (%) or the number of free volume content ( $f_v$ ) is expressed as follows

$$f_v = \left( \frac{4\pi R^3}{3} \right) I_3 \quad (4)$$

where  $I_3$  (%) is the *o*-Ps intensity and  $C$  is a constant.

The chain folding and molecular architecture of the polymer chains and its segments lead to formation of free volume holes of varying sizes. Therefore, a distribution of sizes could be characterized from the measured *o*-Ps lifetime. MELT program (Shukla et al., 1993) was employed in this study to measure the free volume distribution of both films A and B before (control) and after PATP (Cheng et al., 2009; Ramya et al., 2012).

#### 2.7. Data analysis of OTR and WVTR

The OTR and WVTR data for the two films before and after PATS 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).

### 3. Results and discussion

The gas barrier, morphological and free volume changes underwent by the two multilayer EVOH films immediately after PATP will be discussed in this section.

#### 3.1. Oxygen transmission rate (OTR)

Table 1 shows the OTR of the two films before (control) thermal treatment and immediately after treatment by PATS. The OTR of

**Table 1**  
Oxygen transmission rate (OTR) and Water vapor transmission rate (WVTR) for the films A and B, untreated (control), and after pressure-assisted thermal sterilization (PATP).

Film <sup>a</sup>	OTR (cc/m <sup>2</sup> -day)		WVTR (g/m <sup>2</sup> -day)	
	Control	PATS	Control	PATS
A	0.24 $\pm$ 0.03	1.1 $\pm$ 0.09	0.73 $\pm$ 0.02	1.27 $\pm$ 0.03
B	0.11 $\pm$ 0.01	0.43 $\pm$ 0.07	0.61 $\pm$ 0.01	0.71 $\pm$ 0.01

<sup>a</sup> Film A: PET/EVOH/PP; Film B: PP/tie/Nylon6/EVOH/ Nylon6/tie/PP.

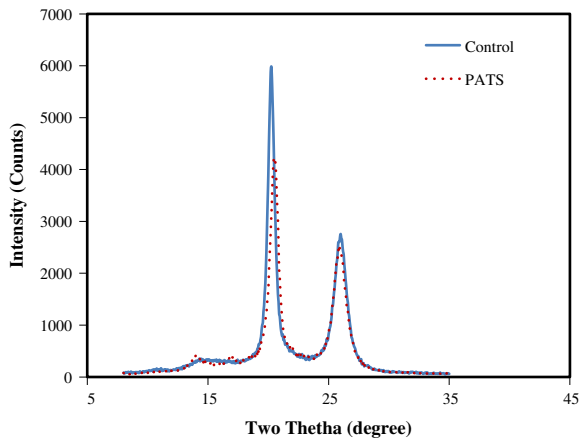


Fig. 2. X-ray diffraction patterns for film A before and after the PATS treatments.

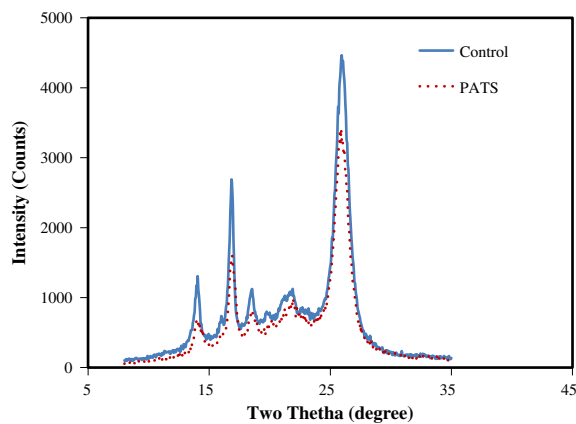


Fig. 3. X-ray diffraction patterns for film B before and after the PATS treatments.

the control films A and B were 0.24 and 0.11 cc/m<sup>2</sup> day, respectively. The PATP process led to a nearly 5-fold increase in the OTR of film A to a final value of 1.1 cc/m<sup>2</sup> day. On the other hand, the OTR for film B increased nearly by 4 times to a final value of 0.43 cc/m<sup>2</sup> day after PATP. Thus, the PATP process significantly increased ( $P < 0.05$ ) the OTR values of films A and B. It has been previously observed that monolayer EVOH copolymer with lower ethylene content showed slightly higher barrier properties after high pressure processing (López-Rubio et al., 2005a). Similar results were obtained in our study as film B with 28 mol% ethylene showed superior oxygen barrier property compared to 32 mol% ethylene in film A. Additionally, the EVOH layer in film B is better protected by the individual polymer layers compared to that of film A.

The deterioration of oxygen barrier properties of EVOH containing films A and B could be related to the plasticization of the hydrophilic EVOH copolymer in a higher moisture environment. Such a high moisture environment is exhibited by the preheating step

which exposes the films to 90 °C for 10 min. Similar results of deterioration in oxygen barrier properties of biaxial nylon/coextruded EVOH during the preheating step of PATS was found in another study by Koutchma et al. (2009). It has also been hypothesized that the plasticization of the EVOH layer could lead to a decrease in the polymer chain-to-chain interactions, resulting in an increase in the free volume (López-Rubio et al., 2003). Thus, this study further investigated the influence of processing on the morphological and free volume properties of the films A and B.

### 3.2. Water vapor transmission rate (WVTR)

Table 1 shows the WVTR of the two films before (control) thermal treatment and immediately after treatment by PATS. There was a significant increase ( $P < 0.05$ ) in the WVTR of the two films after processing. However, the deterioration in water vapor barrier property was higher in film A as compared to film B. The WVTR of film A increased by 74% from 0.73 to 1.27 g/m<sup>2</sup> day after PATP processing. On the other hand, there was only a 16% increase in the WVTR of film B after PATS from 0.61 to 0.71 g/m<sup>2</sup> day. It is possible that the better protection of the EVOH layer by hydrophobic polyolefins polymers in film B could be responsible for the lesser deterioration of the polymeric chain morphology, compared to that of film A. Similar to oxygen barrier properties, the WVTR of the polypropylene layer in the two films could have been compromised due to the structural changes taking place in the films during preheating and the high pressure processing step. This advocates the need for material science studies to understand the mechanism of gas transport through the films.

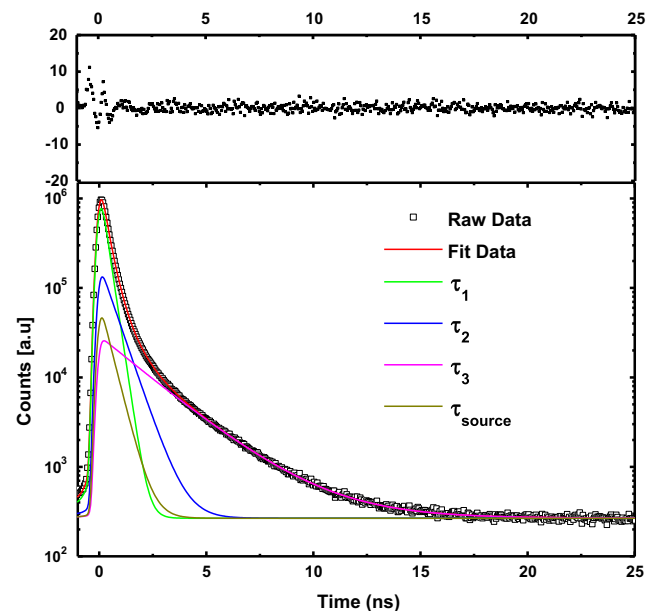


Fig. 4. An example of the fitting of PALS spectrum of film A after PATS using LT program.

Table 2

*o*-Ps parameters from the Positron annihilation lifetime spectroscopy study for the films A and B, untreated (control), and after pressure-assisted thermal sterilization (PATS).

Film <sup>a</sup>	Treatment	<i>o</i> -Ps lifetime, $\tau_3$ (ns)	<i>o</i> -Ps intensity, $I_3$ (%)	Free volume radius (Å)	Free volume fraction ( $F_V$ )
A	Control	2.34	9.5	3.15	2.24
	PATS	2.22	9.4	3.06	2.03
B	Control	2.10	8.9	2.94	1.71
	PATS	2.25	9.6	3.08	2.11

<sup>a</sup> Film A: PET/EVOH/PP; Film B: PP/tie/Nylon6/EVOH/Nylon6/tie/PP.

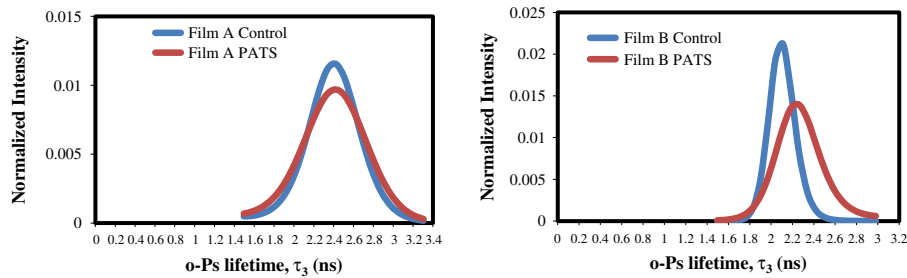


Fig. 5. *o*-Ps lifetime distribution of films A and B before and after the two thermal sterilization treatments.

### 3.3. X-ray diffraction

The diffraction patterns for film A before and after PATS are presented in Fig. 2. There was a decrease in peak intensities of the film A after processing leading to a decrease in its overall crystallinity. Additionally, there was a slight increase in peak width which is an indication of the disruption of the crystalline structure caused by crystal fractionation (López-Rubio et al., 2005b). The decrease in crystallinity of the film could lead to a reduced orderliness in the polymeric chains causing an easier path for the gas to travel through the polymer matrix and thus, leading to a reduced oxygen and water vapor barrier property and eventually quality deterioration of the food (Yoo et al., 2009; Lopez-Rubio et al., 2006). The crystal size estimated from the Scherrer equation showed that PATP led to a decrease in size from 133 to 113 Å for the major peak at 20° for film A corresponding to EVOH (López-Rubio et al., 2003; Lagaron et al., 2001). Furthermore, there was a slight decrease in peak intensity for the other two peaks corresponding to PET and PP layer as well. Hence, there was clear change in the crystalline morphology of the polymeric film A after PATS treatment.

On the other hand, Fig. 3 represents the XRD patterns for film B for the PATS treatment. The sterilization operation caused a decrease in the peak intensities for all the characteristic peaks in film B including EVOH at  $2\theta$  value of 20° indicating change in the overall crystallinity of the film. However, unlike film A, there was a slight decrease in the peak width corresponding to the EVOH, Nylon 6, PET, and PP layers indicating lesser distortion to the crystalline morphology. Also, there was an increase in crystal size from 45 to 57 Å for the peak at approximately 26° corresponding to Nylon 6 (Rabiej et al., 1997). Hence, an improvement in crystal size and reduced distortion of the crystalline morphology could be responsible for the lesser increase in gas transmission through film B with compared to film A.

### 3.4. Free volume analysis by PALS

Table 2 summarizes the *o*-Ps parameters measured by PALS for the two films before and after PATS treatment. The PALS raw data were fitted into lifetime distribution using LT9 program and Fig. 4 illustrates an example of the fitting of PALS spectrum of film A after PATP. It should be noted that in our study, the free volume parameters analyzed are an overall influence of the entire multilayer polymeric film. The sterilization treatment led to a decrease in the *o*-Ps lifetime for film A from 3.151 to 3.055 Å, whereas, there was an increase in *o*-Ps lifetime for film B from 2.945 to 3.077 Å after PATS. Additionally, free volume fraction ( $F_v$ ) decreased by 9% for film A and increased by 23% for film B after PATS treatment. This opposing behavior for the two films could have resulted from the fact that increase in pressure leads to a decrease in free volume and a temperature increase causes an increase in thermally induced free volume of polymers (Danch et al., 2007). Thus, the varying effects of the two factors involved in PATS on the free volume could be responsible for this opposing behavior.

Fig. 5 illustrates that there was no change in the peak width of the *o*-Ps lifetime distribution for film A, whereas, there was a broadening in the free volume distribution for film B after PATS. The broader positron lifetime distribution and the increase in positron lifetime of film B after PATS suggest that there could be overlapping of free volumes leading to gas being trapped in the overlapped free volumes. The overlapping of free volumes leads to an increase in the tortuous path of gas flow through the polymer membrane. Hence, the relative increase in OTR and WVTR of film B is less than that of film A.

In addition, overall crystallinity observed from X-ray diffraction indicated that the level of amorphous region in both films varied which may influence the level of changes in film morphology and gas-barrier properties. Thus, the XRD and PALS analysis together help in providing a clear picture of the polymer morphology and free volume properties in relation to the gas barrier properties of the polymer food packaging films.

## 4. Conclusions

PATS had a significant influence ( $p < 0.05$ ) on the oxygen and water vapor barrier properties of the two multilayer EVOH-based films. However, the increase in gas barrier properties of film A was much larger compared to film B which can be understood from the change in overall crystallinity measured by X-ray diffraction, and free volume distributions measured by positron lifetime. PALS is a suitable tool to characterize the free volume properties of multilayer EVOH-based food packaging films before and after PATS. A broader positron lifetime distribution and an increase in positron lifetime of film B after PATS suggests that there could be overlapping of free volumes leading to gas being trapped in the overlapped free volumes and hence, the relative increase in gas-barrier properties of B is lesser than A. This work suggests that X-ray diffraction and PALS are powerful techniques to investigate film morphology and free volume characteristics which helps understanding the gas barrier changes after food sterilization operations.

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