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Water absorption and oxygen barrier characteristics of ethylene vinyl alcohol films

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ABSTRACT

Oxygen transmission rates (OTR) of two multilayer films containing ethylene vinyl alcohol (EVOH) were analyzed after water absorption at 121 °C. The films, referred to as film A and film B, were laminated film of PET/EVOH/PP and coextruded film of PET/PP/nylon 6/EVOH/nylon 6/PP, respectively. OTR increased with water absorption for both films. Graphical representation of data revealed two apparent linear regions describing the change of OTR with water absorption for both films. At low water contents (up to 4%) OTR were similar for the two films but differed dramatically at higher water contents. Water sorption characteristics of two monolayer EVOH barrier films (biaxially oriented and non-oriented) were determined at 25 °C using standard gravimetric method. Moisture sorption isotherms were analyzed using the Guggenheim-Anderson-de Boer model and the cluster theory of Zimm and Lundberg to evaluate the interactions between water and EVOH.

1. Introduction

Ethylene vinyl alcohol (EVOH) is widely used in food packaging because of its low permeability to oxygen. But the hydrophilic nature of EVOH is well known to compromise its barrier properties in humid environments (Zhang et al., 2001; Muramatsu et al., 2003). EVOH is capable of absorbing more than 10% by weight of moisture at equilibrium in saturated relative humidity (RH) environments or when immersed in water at room conditions (Aucejo et al., 1999). The presence of even small amounts of moisture in EVOH affect the oxygen barrier as well as their mechanical (Gaucher-Miri et al., 2002; Cabedo et al., 2006) and thermal properties (Aucejo et al., 1999; Zhang et al., 2001; Lagaron et al., 2001; Cabedo et al., 2006).

Shelf-stable food products are commonly packaged in rigid, semi-rigid or flexible polymer packaging materials and processed in pressurized steam or water systems (retorts) and heated to 115–125 °C (May, 2000). In order to withstand these processing conditions retortable food packages are invariably multilayer structures consisting of high gas barrier inner layer such as EVOH or polyvinylidene chloride (PVDC) protected by water barrier layers such as polypropylene (PP) (Tung and Britt, 1995). In spite of the protection of outer water barrier layers, the combined influence of high RH, high temperatures and long processing times during retort processing can have an adverse effect on the barrier properties of EVOH containing films when used in flexible pouches or thin lid films for trays. Mokwena et al. (2009) reported increase in oxygen transmission rates (OTR) by over 10 times from 0.16 to 1.75 cc/m^2 day for a multilayer film containing PET/EVOH/PP film and by 47 times for PET/PP/nylon 6/EVOH/nylon 6/PP film after retort treatments at 125 °C for 28 min. Similarly, Lopez-Rubio et al. (2005b) reported an 456 fold increase in oxygen permeability, from initial 0.0197 to 8.99 cm^3 mm/m^2 day atm, for PP/EVOH/PP films after retorting at 121 °C for 20 min. Data from Hernandez and Giacin (1998) also showed an increase in OTR by more than 60 times from 0.3 to 18.8 cc/m^2 day for PET/EVOH/PP film. The effects of moisture on polymer films containing EVOH are mainly attributed to plasticization of the EVOH matrix (Aucejo et al., 1999; Zhang et al., 2001; Muramatsu et al., 2003) and possible changes in polymer crystallinity (Hodge et al., 1996; Lopez-Rubio et al., 2005b). In this study, the effect of water absorbed during simulated retort heating on OTR was evaluated for two multilayer films containing EVOH. Experimental sorption data for two monolayer EVOH films (similar to those used in the multilayer films) was analyzed at 25 °C to determine interactions between water molecules and EVOH.

2. Materials and methods

2.1. Description of films

Two multilayer films, referred to as film A and film B, were evaluated for oxygen transmission rates. Film A was a laminated structure consisting of biaxially oriented EVOH layer sandwiched between oriented polyethylene terephthalate (PET) and cast PP,

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i.e., PET//EVOH//PP (12μ//12μ//75μ). Film B was made using both lamination (denoted by //) and coextrusion (denoted by /) processes in which PET was laminated to a co-extruded structure of PP homopolymer, nylon 6 homopolymerand non-oriented EVOH, i.e., PET//PP/tie/nylon 6/EVOH/nylon 6/tie/PP (12μ//50μ/10μ/15μ/10μ/50μ). A solvent based adhesive was used to bond the laminated layers of both film A and film B, i.e., between all layers of film A and between PET and PP in film B. The tie layer between PP and nylon 6 in film B was Admer Q551, a PP based maleic anhydride modified tie resin. EVOH and nylon 6 have affinity for each other hence no tie or adhesive was used between the two. The EVOH layers in film A and film B were EVAL® resins EF-XL and L171, respectively. EF-XL has an ethylene molar content of 32% and is biaxially oriented; while L171 resin in film B has an ethylene molar content of 27% and is non-oriented. Monolayer films of EF-XL with a thickness of 0.023 mm and L171 with a thickness of 0.071 mm were also evaluated for their water sorption characteristics. At 20 °C and 0% RH, both EF-XL and L171 have oxygen permeability in the order of 0.002 cm^3 mm/m^2 day atm. All films were supplied by EVAL Company of America, Houston, TX.

2.2. Determination of water absorption at 121 °C

Water uptake was measured at 121 °C to simulate retort heating conditions. Prior to testing, film specimens approximately 5 cm in diameter were dried in a vacuum oven (60 cm Hg vacuum) at 70 °C for 2–3 days. Initial (dry) weight was taken before each water uptake measurement using an analytical balance with a resolution of 0.0001 g (Analytical Plus, OHAUS). A custom made aluminum test cell, shown in Fig. 1, was used for measurement of water uptake at 121 °C. The circular test cell consisted of two main parts – the base and top – and a screw cap closure. The two parts were opened and closed along machined threads. The top had an opening for adding water on the upper side of the tested film sample. In order to obtain a hermetic seal the test cell was fitted with *O*-rings at all closures (i.e., at the sealing faces between the base and the top, and on the screw cap closure). A 0.032 inch type T thermocouple (Omega Inc.) was inserted through the screw cap closure for monitoring temperature inside the test cell. To prepare for testing, the bottom part was filled with water and a film sample was placed on the sealing surface. The top part was then screwed in place, filled with water through the opening and sealed with the screw cap closure. The two *O*-rings on the sealing surfaces between the base and top parts also ensure that there was no water absorption at the cut film edges. The test cell with a sample inside was then immersed in an oil bath (HAAKE W13, Thermo Electron Corporation) with ethylene glycol (JT Baker) set at 121 °C. Predetermined heating times that varied between 5 and 60 min were selected to cover a range of conditions used in microwave assisted sterilization processes and conventional thermal retorting operations for single meal sized trays or pouches (Tang et al., 2008; Guan et al., 2003). At the end of heating, the test cell was removed from the oil bath and immediately cooled in ice/water mixture. Film samples were removed from the test cells; the film surfaces were wiped with a paper towel to remove surface water and weighed immediately to obtain the wet weight. Triplicate measurements were done for each retort heating time. The percentage of water uptake was calculated as follows:

$$\%\,\text{water uptake} = \frac{W_t - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \tag{1}$$

where W_t is the weight of sample after time t (wet weight) and W_{dry} is the dry (or initial) weight of sample.

2.3. Oxygen transmission rates of multilayer EVOH films

OTR was measured for film A and film B samples immediately following retort heating at 121 °C and on untreated films as control. OTR represents the ease with which oxygen gas passes through films when submitted to a partial pressure gradient across

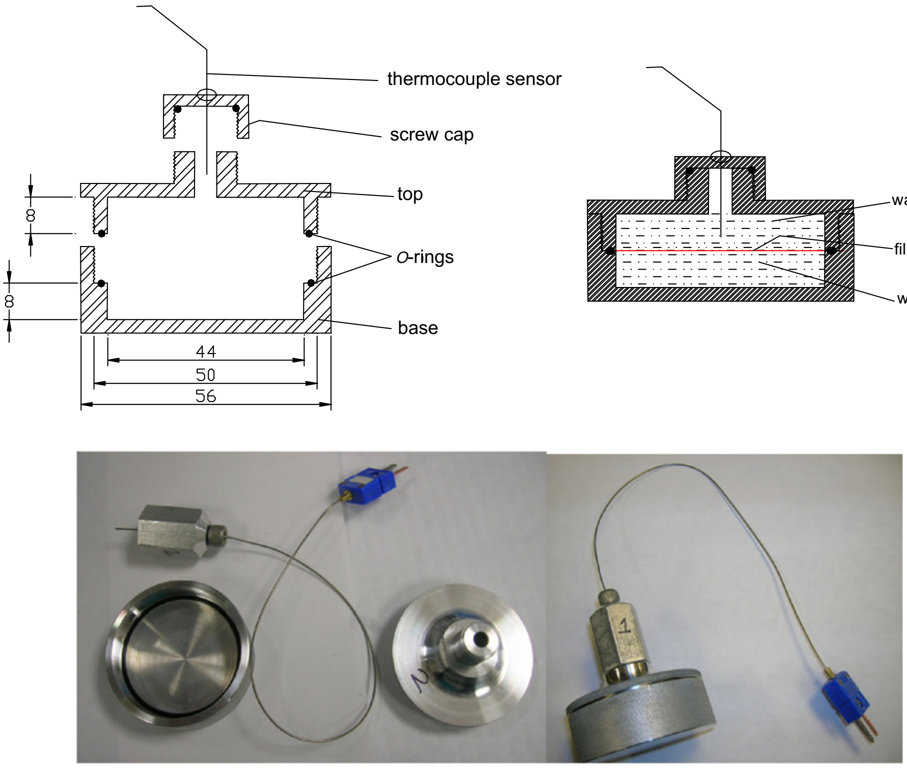

Fig. 1. Schematic diagram and picture of test cells. Dimensions shown are in mm.

the films. It is expressed as the quantity (Q) of oxygen molecules passing through a film of surface area (Q) during time (t) at steady state under a partial pressure difference (Δp) in oxygen between the two surfaces of the sample (Massey, 2003):

$$\mathrm{OTR} = \frac{Q}{At\Delta p} \tag{2}$$

OTR was measured using MOCON OX-TRAN 2/20 instruments (MOCON, Inc., Minneapolis, MN) operating according to ASTM standard method D3985-95 which is a procedure for determining steady-state rate of transmission of oxygen gas through films, sheets, laminates, coextrusions, or plastic-coated papers or fabrics (ASTM, 1995).

Film samples were masked with aluminum foil masks to expose a measurement area of 5 cm^2 and mounted between two chambers in a 'diffusion cell' at ambient atmospheric pressure. Masking provides support and a uniform area of measurement for small sample sizes such as those used in this study. One hundred percentage oxygen was continuously admitted to the outer chamber of the diffusion cell (i.e., the PET side of film both film A and film B) and a carrier gas which was a mixture of 98% nitrogen and 2% hydrogen was continuously admitted to the inner half (i.e., on the PP side). As oxygen permeates through the film sample, it was picked up by the carrier gas and carried through a coulometric oxygen sensor. The OX/TRAN 2/20 uses a COULOX® sensor which generates an electrical current proportional to the amount of oxygen passing through when exposed to oxygen. The environmental test conditions used in the diffusion cells of the instrument were 65% RH and 20 °C. The testing time for OTR measurement for duplicate samples (in each of the two diffusion cells of the instrument) was about 14 days. Duplicate samples were analyzed for each retort heating time.

2.4. Differential scanning calorimetry (DSC) analysis

Similar to OTR analysis, DSC measurements were done on film samples immediately following treatments at 121 °C for heating times ranging between 5 and 60 min. Non-treated samples were used as control. T2920 DSC cell (TA Instruments) operated with nitrogen flow was used to determine phase transitions of film samples. Prior to the tests, standard non-hermetic aluminum sample pans and lids were weighed. The sample pans were filled with about 10 mg of film sample by piling up several circular pieces cut using a cork borer. The sample pan was then sealed and weighed. The sample pan and an empty references pan were loaded into the DSC sample holder. The pans were cooled from room temperature to −50 °C at 10 °C/min, held for 1 min and then heated from −50 to 300 °C at a rate of 10 °C/min. DSC thermograms were evaluated using thermal analysis software (Universal Analysis, TA Instruments). The enthalpy of melting was determined from the area under the melting endotherm. Duplicate measurements were performed for each retort heating time.

2.5. Determination of sorption isotherms of monolayer EVOH barrier films

Two types of EVAL® EVOH oxygen barrier films, i.e., EF-XL and L171, were evaluated. Samples of these films (approximately 5 cm in diameter) were initially dried in a vacuum oven set at 60 cm Hg vacuum and 70 °C for 2–3 days. The samples were weighed to get the initial, dry weight, and then directly exposed to various humid environments maintained with saturated salt solutions inside hermetically sealed glass jars at 25 °C. The salts used were lithium chloride ($a_w = 0.11$), potassium acetate ($a_w = 0.23$), magnesium chloride ($a_w = 0.33$), potassium carbonate ($a_w = 0.43$), magnesium nitrate (0.53), sodium chloride ($a_w = 0.75$), potassium chloride ($a_w = 0.84$), and potassium nitrate ($a_w = 0.94$). The samples were then weighed periodically as they absorbed moisture over a period of 2 weeks until constant weights were attained. Equilibrium water content (M_e, %) was determined according to the following equation:

$$M_e = \frac{W_{\mathrm{final}} - W_{\mathrm{dry}}}{W_{\mathrm{dry}}} \times 100 \tag{3}$$

where W_{final} is the final weight of the sample, i.e., at the end of equilibration period and W_{dry} is the dry weight of the sample. The final weight was determined as an average of several consecutive measurements that showed no appreciable weight changes (i.e. about three measurements). The experimental isotherm data was fitted with the Guggenheim-Anderson-de Boer model.

3. Results and discussion

3.1. Performance evaluation of test cell

During water uptake experiments the immersion water inside the test cell required some time to reach the desired temperature of 121 °C. This heating up period should be as short as possible to minimize absorption of water by film samples during the non-steady heating period and to provide isothermal conditions for the duration of a heat treatment. Therefore the selection of final test cell dimensions was based on the shortest heating up time possible. Another factor considered for design of the test cell was to have film samples with sufficient dimensions to fit in the diffusion chamber of MOCON OX/TRAN instruments used for OTR analysis. The standard sample size required for MOCON OX/TRAN instruments is 10.16 cm × 10.16 cm. However, smaller samples of no less than 5 cm^2 can be used with aluminum foil masks. After evaluating several test cell sizes, the final design chosen had an inner diameter of 4.4 cm to provide sufficient sample size for measurement and also allow ease of handling. The cell had an inner depth of 1.6 cm (0.8 cm each of the top and bottom parts) and wall thickness of about 0.3 cm. Evaluation of time–temperature data indicated that water temperature inside the test cells reached within 0.5 °C of 121 °C after 2½ min of heating. Typical experimental data of temperature history in a test cell is shown in Fig. 2. Data from the three test cells used in the study showed good consistency.

Another essential design criterion for the test cell was to ensure that no water absorption occurs through the cut film edges. Commonly, thin films (in which thickness is much smaller than

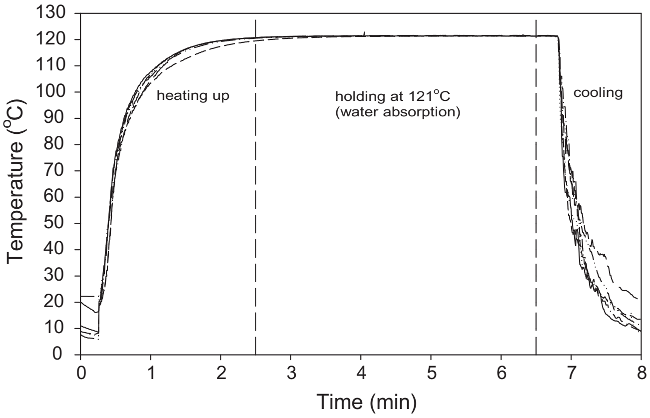

Fig. 2. Temperature history inside test cells showing heating and cooling. Graph shows six curves obtained using three test cells.

diameter) are used without any edge sealing as it is assumed that water absorption through edges is small and can be neglected. However, under high temperature conditions water absorption into unprotected EVOH film at the cut edges may be significant. Barrer et al. (1962) showed that errors arising from neglecting edge effects may lead to large differences in transport coefficients determined using different methods. In the test cell method used in this study, edges were sealed by holding film samples between *O*-rings on the sealing surfaces of test cells. Proper sealing of cut edges was evaluated from visual observations of film samples after heat treatments. A good seal was demonstrated by a clear ring along the edge of the films where there was direct contact with the *O*-rings. It was assumed that no water was absorbed in these clear areas as opposed to an opaque area observed on the rest of the film surface as shown in Fig. 5. Film samples from test cells which were not sealed properly did not show these clear regions and their weight gain was much higher after retort treatments, indicating that more water entered through the cut edges.

3.2. Effect of water absorption at retort conditions on oxygen transmission

The results of the effect of water absorption at 121 °C on OTR of film A and film B are presented in Table 1. Film A absorbed slightly more water than film B at the same retort processing conditions. It is assumed that the hydrophilic EVOH layers in the multilayer films have a great influence of the amount of water absorbed and barrier properties of the films. However, film A contains the less hydrophilic EF-XL and film B contains the more hydrophilic L171 and nylon 6 layers. This disparity could be the result of the thicker outer protective layers in film B limiting the amount of water reaching the EVOH and nylon 6 layers. Retort treatment of individual PP, PET and nylon 6 films showed that PP absorbed about 0.5% of moisture by weight, PET absorbed about 0.8% and nylon 6 absorbed about 10% at equilibrium, which was reached in less than 10 min for PP and PET and almost instantaneously for nylon 6. The amount absorbed by EVOH films could not be determined as EVOH without moisture protection cannot withstand retort conditions. For these reason the data in Table 1 is used to assess the general trends of influence of water absorption on OTR rather than the actual contribution of the EVOH layers in the films.

The general trends of OTR as a function of water absorption for film A and film B are illustrated in Fig. 3. OTR increased with increasing amount of water absorbed by both films. Film A and film B initially showed comparable OTR up to water uptake of approximately 4%, suggesting that water absorption might have a similar mechanism in the effects on the two films. Above 4% water uptake, the OTR of film B increased sharply, while that of film A continued to increase in a gradual manner. Close observation of Fig. 3 reveals that there might be two distinct stages describing the change of OTR with water uptake for both film A and film B. The points at which the break in the trend of OTR changes occurred at approximately 6% water uptake for film A and at 4% for film B. Linear fits of these two apparent stages yielded fairly high R^2 values as indicated on Fig. 3. The R^2 value of the second stage for film A was not shown because only two data points were available.

Table 1
Water absorption at 121 °C and oxygen transmission data for film A and film B immediately after the heat treatments.

Heating time (min)	% Water absorption		OTR (cc/m^2 day)	
	Film A	Film B	Film A	Film B*
0	0	0	0.16 ± 0.006	0.096 ± 0.005
5	3.3 ± 0.01	2.2 ± 0.02	4.57 ± 0.46	–
10	4.3 ± 0.14	2.9 ± 0.02	6.33 ± 0.29	2.86 ± 0.19
20	5.7 ± 0.05	4.1 ± 0.46	6.77 ± 0.69	7.34 ± 0.65
30	6.2 ± 0.12	4.7 ± 0.22	7.20 ± 0.49	17.28 ± 0.50
60	7.3 ± 0.05	5.3 ± 0.40	13.99 ± 1.41	25.25 ± 1.93

* OTR data for film B at 5 min retort time not available.

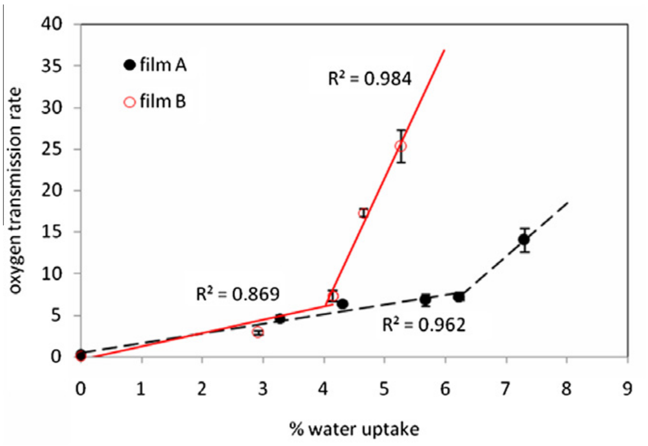

Fig. 3. Effect of water absorption on oxygen transmission rates (cc/m^2 day) of film A and film B.

The effect of water absorption on OTR has been attributed to various factors such as plasticization of polymer matrix, changes in polymer crystallinity, delamination of adjacent polymer layers, formation of voids and cracks, formation of water clusters, etc. Plasticization is said to occur when water is dissolved in a polymer matrix leading to possible weakening or breaking of bonds between polymer chains and increased free volume (Levine and Slade, 1988; Hodge et al., 1996). Water plasticization is particularly important in hydrophilic polymers such as EVOH and nylon 6 because of strong interactions between water molecules and the polar groups of the polymers. This is expected to promote a great deal of polymer chain mobility that enhances permeation of oxygen through the polymer. Yamamoto et al. (2009) correlated higher oxygen permeabilities with increased molecular mobility of EVOH chains after water absorption using nuclear magnetic resonance. Plasticization has been reported to be a strong function of the amount of water absorbed (Hodge et al., 1996), which might explain the increase in OTR with amount of water absorbed by film A and film B.

Plasticization of polymers by water is also generally characterized by depression of T_g, hence an attempt was made in this study to determine the T_g values of EVOH layers in film A and film B using DSC. However, very weak or no glass transition regions were observed for the EVOH layers because of the very small contribution of EF-XL and L171 to the total sample size used in the DSC measurements. For example, of the 10 mg sample of film A used for DSC determinations, only about 1% or 0.1 mg of this was EF-XL. The glass transition of highly crystalline polymers such as EVOH is also generally weak since only the amorphous part (which is already small in such polymers) contributes to the transition. In spite of this, it is well known that the T_g values of EVOH films are well below room temperature when saturated with water (Matsui et al., 1996; Cabedo et al., 2006). It is interesting to note that the change in slope observed in Fig. 3 is similar in behavior to change in slope at T_g typically observed in graphical representation of effect of temperature on specific volume of polymers (Ferry, 1980). Levine and Slade (1988) have noted that the primary plasticizing effect of increasing moisture content at constant temperature is equivalent to the effect of increasing temperature at constant moisture content. Based on this similarity, it can be speculated that the inflection points in Fig. 3 might be related to changes in T_g of EVOH in film A and film B, leading to increased segmental motion of chains and free volume at higher water contents. One would indeed expect that the free volume and thus OTR have a lower dependence on moisture uptake in the glassy region (i.e., below T_g) while in the rubbery region the increased free volume should induce a higher temperature dependence on OTR. This is the trend observed in the two linear regions identified in Fig. 3.

The large difference in oxygen transmission behavior of film A and film B observed at water uptake levels higher than 4% (Fig. 3) can be explained in terms of the crystallinity of EF-XL and L171 films in film A and film B, respectively. It has been proposed that during retort pressurized water at elevated temperatures may penetrate into, melt and disrupt some crystalline regions of semi-crystalline polymers as a result of swelling stresses imposed by the severe conditions (Hodge et al., 1996; Lopez-Rubio et al., 2005a). This decreased crystallinity leads to an increase in oxygen permeability. Possible changes in crystallinity were evaluated from DSC measurements by integrating the area under melting peaks of the different components of film A and film B. In general, crystallinity is calculated by dividing the enthalpy of melting calculated from the endothermic peak by a reference value that represents the enthalpy of melting of a 100% crystalline material (Reading et al., 2001). Because the calculated enthalpy values were based on total sample weight of the films (rather than weights of individual film layers) percentage crystallinity was not calculated and the data of enthalpy of melting was used only as a general indication of possible changes in crystallinity. Fig. 4 shows the enthalpy of melting for EF-XL in film A and L171 in film B. In general there was a decrease in enthalpy of EVOH layers as more water was absorbed by the films. Statistical analysis of the data for EF-XL layer revealed that only the enthalpy value for the dry film (i.e. 0% water uptake) was significantly different from the other values. Hence, the data implies that enthalpy decreased and remained basically constant after 3.8% of water uptake. For L171 layer, enthalpy values for the first three water content levels of 0%, 3.8% and 4.2% were statistically similar. Similarly the enthalpy values for the last three water content levels of 4.9%, 5.5% and 6% were statistically comparable. Hence, for L171 layer there was not much change in enthalpy until a water content of 4.2%. The general decrease in melting enthalpy might be due to reduction in crystallinity of the EVOH layers in film A and film B.

The considerable differences in OTR of film A and film B after 4% water content observed in Fig. 3 can also be attributed to some physical damage induced by water absorption at high temperatures. Fig. 5 shows typical damage observed for film A after 30 min of retort heating and film B after retort heating for more than 20 min. Visual observations showed that samples of film A turned opaque after retort heating at 121 °C for periods longer than 30 min. However, the opacity faded away within a relatively short time when films were air dried at room conditions. On the other hand, Film B showed blisters and wrinkles after heating at 121 °C for over 20 min. The damage in film B may have been caused by development of voids or crazes, or delamination of adjacent layers during water absorption. These voids remained on film B samples when air dried for prolonged periods. Film B structure has PP layers on both sides of EVOH layer and this could have contributed to resistance to drying of the film hence the continued presence of observed damage. Table 1 shows that the 30 min duration for film A and 20 min for film B corresponds with the inflection points observed in Fig. 3. The voids formed on film B could have created an easier pathway for oxygen to diffuse through the film than for film A. Fan et al. (2008) noted that the simultaneous action of thermal stresses and internal water vapor pressure generated during heating can result in damage such as interfacial delamination and formation of blisters.

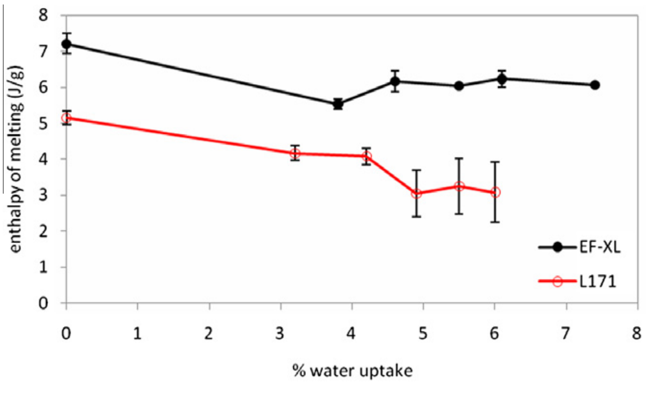

Fig. 4. Enthalpy of melting as a function of water absorption for EF-XL and L171. Enthalpy data is based on total film mass.

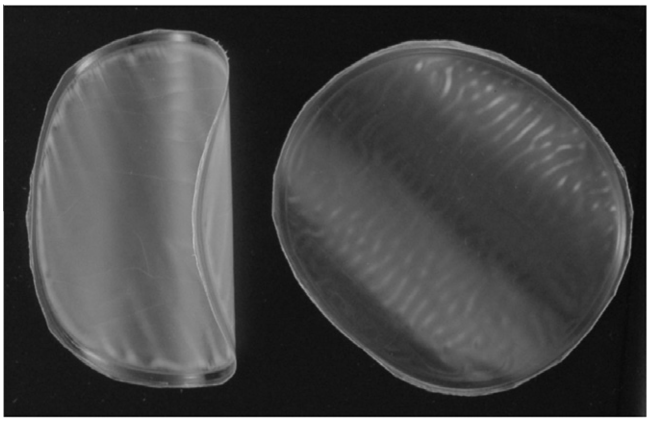

Fig. 5. Visible damage on film A (left) and film B (right) after 60 min heating in water at 121 °C.

3.3. Analysis of sorption isotherms of EVOH films at 25 °C

Water sorption isotherms of EVOH barrier films can provide information on the interaction between water molecules and polymer chains. These interactions are dependent on both the polymer structure and its thermodynamic compatibility with water. Sorption isotherms of monolayer films of EF-XL and L171 films were evaluated at 25 °C. Fig. 6 shows that the isotherms were sigmoid in shape, a behavior which is typical in hydrophilic materials which corresponds to type II isotherm according to the classification by Brunauer et al. (1940). The sigmoid shape is presumably due to existence of different strengths of binding between water molecules and polymer chains. At low water activities, site-specific hydrogen bonding occurs between water molecules and the polar groups of the polymer chains (Starkweather, 1980). Thus, the absorbed water molecules engage in strong localized interactions with hydroxyl sites in EVOH as explained by Hodge et al. (1996) and Aucejo et al. (2000). The sorption isotherms of EF-XL and L171 seem to be overlapping at water activity below 0.23, and the difference between the two copolymers is only accentuated at higher water activities. Water absorption by these two EVOH films is influenced by contributions from both copolymer composition and orientation. The vinyl alcohol content of EF-XL is 68 mol% while that of L171 is 73 mol%. EF-XL is also biaxially oriented while L171 is non-oriented. This combination of properties may explain the higher amount of water absorbed by L171 at high water activities. The slightly higher content of vinyl alcohol in L171 implies more hydroxyl sorption sites and hence more water absorption. It is also generally accepted that water molecules interact only

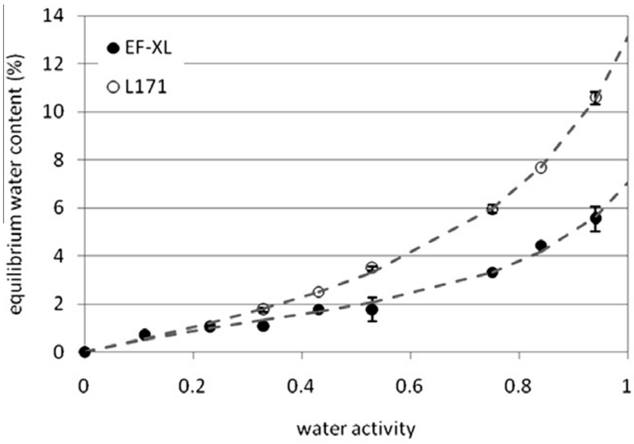

Fig. 6. Water sorption isotherms at 25 °C for L171 (○) and EF-XL (●). Dashed lines represent Guggenheim-Anderson-de Boer model fit.

with polar groups in non-crystalline regions of a polymer; hence interaction of water molecules with hydroxyl groups is expected to be less in EF-XL because of biaxial orientation.

The Guggenheim-Anderson-de Boer (GAB) model was used to fit the data. This model is believed to be valid over a wide range of water activities (Zhang et al., 1999; Rahman and Labuza, 1999; Sun, 2002). The GAB model is a three-parameter equation which is based on the assumptions that water molecules are first sorbed into primary sorption sites (forming a monolayer), and subsequently into identical multilayers of much more loosely held water (Quirins et al., 2005a). The GAB model is expressed as follows (Sun, 2002):

$$M_e = \frac{M_m C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)} \tag{4}$$

where M_e is the water content at equilibrium (%, dry basis) as calculated by Eq. (3), a_w is the water activity, M_m is the monolayer water content (%, dry basis), C is a parameter related to the monolayer enthalpy of sorption (i.e. the energy difference between water molecules of the first sorption layer and those absorbed in successive layers), and K is a constant related to the multilayer heat of sorption (i.e. the energy difference between water molecules absorbed in the second and successive layers and the free water molecules of the surrounding environment). The GAB model fit for EF-XL and L171 films is shown as solid lines in Fig. 6 and the values of parameters derived from the fitting process are presented in Table 2. There is a noticeable difference in the values of M_m for EF-XL and L171. The monolayer value for L171 was higher than that of EF-XL, indicating the possibility of more sorption sites on L171 than on EF-XL. Two inflection points are generally observed in sigmoid isotherms and the inflection at the lower water activity is attributed to the monolayer water content. The upper inflection point is generally associated with formation of water clusters, which will be discussed later. An expression to determine the water activity level where the first inflection point occurs (i.e., monolayer value) was given by Lewicki (1997) as follows:

Table 2
Parameters of GAB equation for EF-XL and L171 films at 25 °C.

Parameter	EF-XL	L171
M_m(%)	1.52	3.58
C	4.975	3.828
K	0.796	0.766
R^2	0.990	0.994

R^2 is the correlation coefficient.

$$a_W = \frac{(C-1)^{2/3} - 1}{K[(C-1) + (C-1)^{2/3}]} \tag{5}$$

Using this expression, the amount of water that would occupy available sorption sites was estimated to occur at water activity of 0.29 for EF-XL film and 0.25 for L171 film.

Quirins et al. (2005a) stated that the parameter C is enthalpic in nature, and is a measure of the strength of binding water to the hydrophilic sorption sites. A larger value of C indicates monolayers of water molecules which are strongly bound to the polymer. Since C is lower for L171 film, the water molecules are less strongly bound to the polymer than with EF-XL film. Akbarov (2004) noted that the enthalpy factor dominates for highly crystalline polymers (such as EF-XL) for which the coefficient of molecular packing is also high. Values of K approaching 1 imply that there is almost no distinction between multilayer molecules and bulk liquid molecules implying that the water molecules beyond the monolayer are not structured in multilayers, but instead have characteristics similar to those in the bulk liquid (Quirins et al., 2005a). Blahovec and Yanniotis (2008) noted that theoretically parameter C has values higher than zero, and K has values in the range between 0 and 1 and mathematical analysis of the GAB equation by Lewicki (1997) have shown that a relatively good sigmoidal type isotherms is obtained when parameters C and K fall in the regions $5.67 \leqslant C \leqslant \infty$ and $0.24 \leqslant K \leqslant 1$. Lewicki (1997) asserted that keeping these values within the suggested ranges assures that the calculated monolayer values differ by not more than 15.5% from the true value. The values of K in Table 2 fall within the suggested range while values of C fall slightly lower than the minimum of the suggested range. The accuracy of parameter C obtained might have been affected by the lack of enough sorption data at low water activity. As noted by Quirins et al. (2005b), parameter C mainly represents the thermodynamic difference in enthalpy between water in the monolayer and multilayers. Since monolayer water exists at low water activity, lack of enough data at low water activity will lead to inaccurate estimation of this parameter. Nevertheless, the correlation coefficients for fitting the GAB model were very good ($R^2 > 0.99$) for isotherms of both EF-XL and L171 films.

When the amount of water absorbed is greater than the amount that can be bound to hydrophilic groups of the polymer, water molecules begin to form hydrogen bonds with one another, leading to formation of water clusters (Starkweather, 1980; Hernandez and Gavara, 1994). Water clustering in EF-XL and L171 films was evaluated using the cluster function developed by Zimm and Lundberg (1956). The function has been used extensively to predict water cluster formation in various polymers including EVOH (Zhang et al., 1999; Aucejo et al., 2000). The cluster function for two-component systems (such as water in polymers) is written as follows:

$$\frac{G_{11}}{V_1} = (1 - \varphi_1)\left[\frac{\partial \frac{a_w}{\varphi_1}}{\partial a_w}\right] - 1 \tag{6}$$

Where $\frac{G_{11}}{V_1}$ is the cluster function; V_1 is the molar volume of water; φ_1 is the volume fraction of water in the polymer film; and a_w is the water activity. The quantity $\frac{G_{11}}{V_1}$ denotes the water-water interaction as a function of water content and indicates the tendency of water molecules to form clusters. For ideal solutions the activity coefficient $\frac{a_w}{\varphi_1}$ does not vary with concentration and $\frac{G_{11}}{V_1}$ is equal to -1. When the activity coefficient decreases with increasing φ_1, $\frac{G_{11}}{V_1}$ becomes greater than -1. Therefore, the extent of clustering is indicated by the extent to which $\frac{G_{11}}{V_1}$ exceeds -1. To determine the water activity at which cluster formation occurs the GAB equation was applied to the Zimm and Lundberg cluster function according to a procedure by Sun (2002). The gravimetric equilibrium water content (M_e) was first converted to volume fractions using the densities of

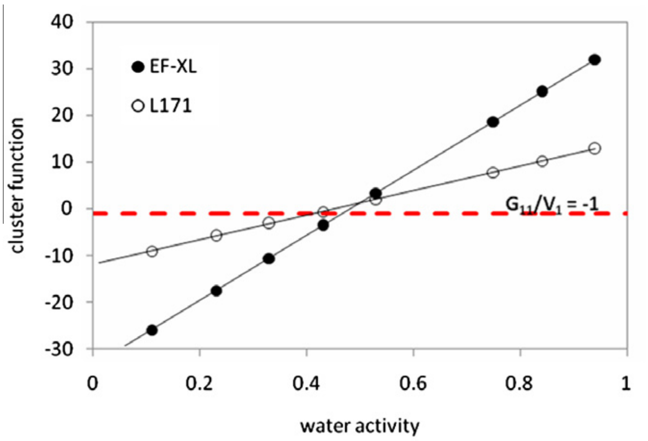

Fig. 7. Cluster function for EF-XL and L171 versus water activity at 25 °C.

water and polymer, i.e., $M_e = \frac{\varphi_1\rho_1}{\varphi_2\rho_2}$ and Eq. (4) is re-written as follows:

$$\frac{a_w}{\varphi_1} = \frac{(1-Ka_w)(1-Ka_w+CKa_w)\rho_1}{M_m CK\rho_2(1-\varphi_1)} \tag{7}$$

Where φ_1 and $\varphi_2 = 1-\varphi_1$ are the volume fractions of water and polymer at equilibrium, respectively, and ρ_1 and ρ_2 are the densities of water (assumed to be 1 g/cm^3) and polymer, respectively. The density of both EF-XL and L171 was taken to be 1.2 g/cm^3. Eq. (7) is then substituted into Eq. (6) to get the following form of the cluster function (Sun, 2002):

$$\frac{G_{11}}{V_1} = \frac{(2K - CK - M_m CK) + (2CK^2 - 2K^2)a_w}{M_m CK\rho_2} \tag{8}$$

The values of $\frac{G_{11}}{V_1}$ are obtained by substituting the GAB parameters (i.e., M_m, C, and K) from Table 2 into Eq. (8). The plot of $\frac{G_{11}}{V_1}$ as function of water activity is presented in Fig. 7. From the analysis of Zimm and Lundberg function, values of $\frac{G_{11}}{V_1}$ reached -1 at water activity of 0.42 for L171 and 0.47 for EF-XL, indicating the beginning of water cluster formation. Aucejo et al. (2000) reported that water clustering occurred at water activity of 0.38 for various EVOH films ranging in ethylene content from 29 to 44 mol% ethylene. Some authors have suggested that water cluster formation is related to permeability properties of hydrophilic films. Lieberman and Gilbert (1972) asserted that the formation of water clusters in a polymer matrix lead to increase in available free volume and hence the permeability of gases through the polymer matrix. It is well known that oxygen permeability of hydrophilic films such as EVOH increases dramatically at high water activity, which can be partly explained by effects of water clustering (Zhang et al., 2001). From the results obtained here, water clusters begin to form at a lower water activity for L171 film compared to EF-XL film, which corresponds with higher oxygen permeability expected in the non-oriented L171 film.

4. Conclusions

Oxygen transmission rates of two multilayer EVOH films were found to increase with increasing water absorption at retort temperatures. Two distinct regions were observed when oxygen transmission rate was plotted against water absorption with change of slope at 6% water content for film A and 4% for film B. The effect of water uptake at retort temperatures is attributed to various factors such as plasticization, changes in crystallinity and possible damage such as formation of voids in polymer matrices or delamination of film layers. Analysis of sorption data of two EVOH films using the GAB model showed sigmoid isotherms that are generally expected for hydrophilic films. The monolayer value for L171 film was found to be higher than that of EF-XL film, which implies that there are more sorption sites available on L171 films. Analysis with the Zimm and Lundberg cluster integral indicates water clusters forming at a lower water activity for L171 film compared to EF-XL film.

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