

Ethylene Vinyl Alcohol: A Review of Barrier Properties for Packaging Shelf Stable Foods

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Ethylene vinyl alcohol (EVOH) is one of the best known flexible thermoplastic oxygen barrier materials in use today. It is especially important for refrigerated and shelf-stable foods where oxygen deteriorates the quality of packaged products and reduces their shelf life. EVOH accounts for a majority of thermoplastic barrier materials used for rigid or semi-rigid retortable food containers. However, it is of limited use in flexible packages or lid films for rigid trays used for packaging thermally processed shelf-stable low acid foods due to its moisture sensitivity. Nevertheless, current use of other oxygen barrier materials such as polyvinylidene chloride and aluminum foil creates environmental concerns. Innovations in food processing technologies provide opportunities for increased use of EVOH in food packaging. The aim of this review is to give an overview of research on the oxygen barrier properties of EVOH from the perspective of structure-barrier property relationships and the consequences of food processing conditions.

Keywords oxygen transmission, retort processing, moisture sensitivity, crystallinity

INTRODUCTION

Shelf stable, low acid ($\text{pH} > 4.6$) foods are commonly processed in retorts, which involves filling packages with food, sealing, and heating food packages in water or steam at temperatures of $115\text{--}135^\circ\text{C}$ under pressure (May, 2000). Loss of quality of thermally processed foods can occur through lipid oxidation during storage when oxygen enters the package and reacts with food lipids, reducing the product shelf life (Irwin and Hedges, 2004). Maximum oxygen ingress of 1 to 5 ppm is enough to limit the shelf life of canned meats, vegetables, soups, and spaghetti in storage at 25°C to 1 year (Koros, 1990). Packaging materials used for thermally processed foods have evolved over the years. Flexible and semi-rigid containers (pouches, bowls, trays, etc.) made of polymers/plastics are gradually replacing the traditional metal cans and glass jars for packaged shelf-stable foods. Unlike metal cans and glass jars, plastic materials are relatively permeable to gases, water vapor, and other small penetrant molecules. Therefore, polymer materials used for packaging oxygen sensitive foods should possess low oxygen permeability (i.e., high barrier). In addition to the high barrier requirement, materials

for plastic packages should possess various other characteristics such as mechanical strength, heat resistance, puncture resistance, chemical resistance, transparency, gloss, printability, compliance with relevant food contact legislation, etc. (Sidwell, 1992). These requirements are met through use of multilayer structures consisting of different polymers, each contributing certain specific functions. Because of the stringent requirement of withstanding the rigors of high temperatures and pressures, relatively few polymers are suitable for retort applications. The most common retortable plastic containers are thermoformed from co-extruded multilayer structures consisting of polyolefins (e.g., polypropylene (PP) and polyethylene (PE)), high density (HD) at the surfaces, with an internal oxygen barrier layer.

The traditional oxygen barrier material in flexible pouches has been aluminum in the form of sheets of a few micrometers thick and as metallization (Lange and Wyser, 2003). Aluminum foil provides the ultimate gas and moisture barrier in flexible packages when it is used at thickness greater than $25.4\ \mu\text{m}$ (Robertson, 2006). However, when used in smaller thicknesses it is susceptible to the formation of pinholes and other stress induced fractures such as flex crack. Incorporation of foil into the multilayer structure requires multiple lamination steps; this is expensive compared to coextrusion which reduces the process to a single step.

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Additionally, foil-based packaging results in non-recyclable material, generating excess waste. Other limitations of aluminum foil include lack of transparency (product visibility) and microwavability. Therefore, eliminating the foil layer in packages has become an important aspect of package design.

Two most important high barrier polymers for food packaging applications are polyvinylidene chloride (PVDC) and ethylene vinyl alcohol (EVOH). The oxygen permeability of high barrier PVDC is about 0.08 cc.mil/100 in².day.atm at 23°C (Brown, 1986). The gas barrier properties of PVDC are not affected by moisture, and PVDC itself has relatively low water vapor transmission rate. The thickness normalized water vapor transmission rate of saran XU-32024 PVDC is 0.06 g.mil/100 in².day as opposed to 8.0 g.mil/100 in².day for EVOH resin with 27 mol% ethylene (EVAL Americas). However, the use of PVDC is challenged by several issues that include cost, processing difficulties, and environmental concerns. PVDC homopolymer has a melting point of 198–205°C and decomposes at around 210°C, which makes the polymer difficult to process (Valentas et al., 1997). On the other hand, copolymers of PVDC have lower melting points of about 140–175°C, making melt processing feasible. However, because of the fairly narrow range of feasible processing temperatures for PVDC, its coextrusion with polymers that require high processing temperatures such as nylon 6 (260–290°C) and PET (280–310°C), etc., becomes difficult (Massey, 2003). The limited extrusion conditions also make the recovery of mixed waste that contains polymers with high processing temperatures particularly difficult. The use of PVDC has also been seriously questioned in terms of recycling. Among the approaches currently used in designing packages is the selection of materials that do not produce harmful by-products during disposal (Katsura and Sasaki, 2001). PVDC, a copolymer of vinylidene chloride and vinyl chloride, contains chlorine which may give rise to hazardous by-products such as hydrogen chloride during incineration (Hui, 2006). Therefore, PVDC has to be incinerated according to specific established industry standards to avoid creating harmful residues. While PVDC is still being produced and used for packaging, its demand is declining. Annual changes in shipment volumes for Japan showed an overall decrease for PVDC based barrier films while other non-PVDC barriers (including EVOH) were on the rise during the period from 1995 to 1999 (Katsura and Sasaki, 2001).

EVOH has a far better oxygen barrier than PVDC when dry, that is, at 0% relative humidity (RH). Data from EVAL Americas (Houston, TX) indicates that oxygen permeability of EVOH (EVAL[®] resin with 27 mol% ethylene) is about 0.006 cc.mil/100 in².day.atm at 23°C and 0% RH. However, the most significant issue concerning the use of EVOH as barrier material is its moisture sensitivity. EVOH is hydrophilic, absorbing a significant amount of moisture when directly exposed to humid conditions, leading to an increase in its oxygen permeability. Thus the performance of EVOH as a barrier material in food packages depends upon the processing and storage conditions to which the packages are exposed. The most severe conditions

are encountered during retort processing due to the conditions of high moisture and high temperature involved. Despite the problems of moisture sensitivity, EVOH is still a preferred barrier material for various packaging applications, accounting for about 70–75% of barrier resin used for retortable rigid containers (Burke, 1990). In recent years, there has been significant research on the mechanisms and effects of water absorption by EVOH containing films leading to a better understanding of its performance in various food processing environments. Innovations in food processing and polymer film technologies present end users with opportunities to reinvent EVOH barrier packaging to drive new business. For example, advanced food processing technologies such as microwave sterilization and high pressure processing provide processing conditions that are less stringent than those of the conventional retort heating. In a recent study Mokwena et al. (2009) compared the oxygen barrier performance of multilayer EVOH films after microwave sterilization and hot water retort. The results showed that oxygen transmission rates of PET/EVOH/PP films increased from 0.16 cc/m².day to 0.79 cc/m².day after microwave sterilization, while the transmission rates for films processed by retort increased by more than 10 times to a value of 1.75 cc/m².day. Similarly, oxygen transmission rates for a film of PET/PP/nylon 6/EVOH/nylon 6/PP increased by 16 times after microwave heating, and by over 47 times after retort heating.

The issues discussed above, plus the compatibility of EVOH in coextrusion with a wide range of other polymers, ease of recycling, etc., make EVOH an important barrier polymer. The main objective of this article was to present an overview of research on oxygen barrier properties of EVOH copolymers in relation to its use in food packaging applications. The review will provide a general discussion on EVOH synthesis and morphological/structural characteristics that determine its inherent high gas barrier property. The influence of high relative humidity conditions such as those in retort processing on oxygen barrier of EVOH will be evaluated.

OVERVIEW OF OXYGEN BARRIER PROPERTIES OF EVOH

EVOH has one of the lowest oxygen permeability reported among polymers commonly used in packaging. Figure 1 compares oxygen permeability of EVOH with that of other common polymers. Only polyvinyl alcohol (PVOH) has oxygen permeability lower than that of EVOH. However, PVOH is soluble in water and difficult to process by melt extrusion because its melting point is close to its heat degradation temperature. The melting point of PVOH is about 180–190°C, while it thermally degrades at temperatures around 150°C (Holland and Hay, 2001). Therefore PVOH has limited use in food packaging. PVDC, nylon 6, and PET all have oxygen permeability that is 1–2 orders of magnitude higher than that of EVOH. Nonpolar polymers such as PP, PE, and polystyrene exhibit oxygen permeabilities over 4 orders of magnitude higher than that of EVOH.

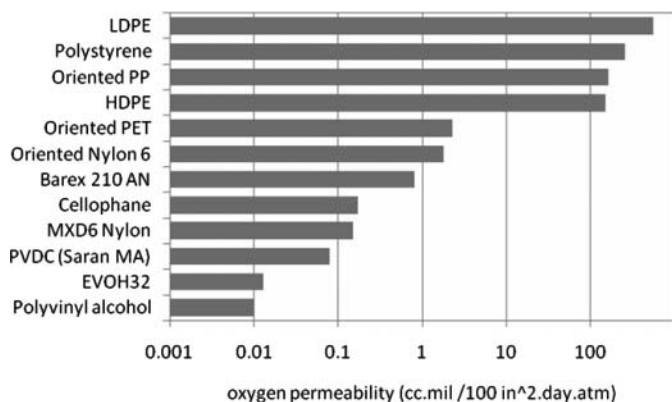
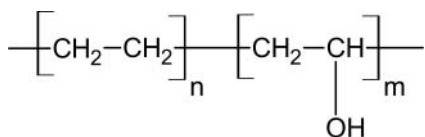


Figure 1 Oxygen permeability of selected polymers at 23°C and 0% relative humidity. EVOH32 is EVOH with 32 mol% ethylene; MXD6 is a copolymer of meta-xylylene diamine and adipic acid; Barex 210 is acrylonitrile-methyl acrylate copolymer. (Data from EVAL Americas).

The differences in oxygen barrier properties depend in most part on the chemical composition and molecular structure of the polymers. However, there exists a complex interdependence of polymer factors with environmental conditions. The different factors that influence the oxygen permeability of EVOH are discussed in the next sections.

EVOH SYNTHESIS

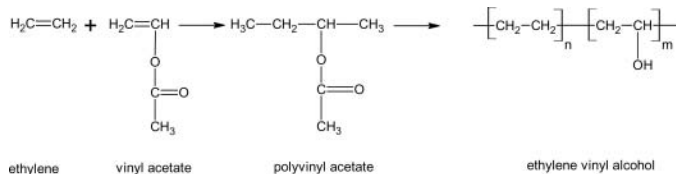
EVOH is a semi-crystalline copolymer of ethylene and vinyl alcohol monomer units (Iwanami and Hirai, 1983). The repeating unit of EVOH has the following chemical structure:



Copolymerization is widely used to provide an opportunity to adjust properties of the resulting resins to meet specific needs in utility of polymers that would otherwise be of limited use. As mentioned earlier, PVOH, one of the monomer units in EVOH, has exceptional gas barrier properties, but it is water soluble and difficult to process. PE, the other parent monomer, has good water resistance, but also has one of the poorest gas barrier properties. Copolymerization of monomer units based on PVOH and PE results in EVOH copolymers which have improved properties in terms of gas barrier, processability, and sensitivity to moisture (Robertson, 2006).

Commercial production of EVOH is generally a two-step process involving free radical polymerization followed by saponification (Iwanami and Hirai, 1983). Vinyl alcohol is unstable and cannot be isolated into a free state, hence the polymerization process utilizes ethylene and vinyl acetate instead (Blackwell, 1986). The acetate functional groups in polyvinyl acetate copolymer are converted into alcohol (hydroxyl) groups during

a saponification process according to the reaction scheme shown below:



The copolymer composition (i.e., relative amounts of ethylene and vinyl alcohol) affects properties of EVOH copolymers such as gas barrier, mechanical properties, water vapor transmission, etc., and hence influences EVOH processing and end-use applications. EVOH resins are commercially available in a range of compositions, most commonly encompassing vinyl alcohol contents of about 52–76 mol%. Generally, copolymers of higher vinyl alcohol content have properties resembling those of PVOH. Similarly, those with higher ethylene contents resemble properties of PE. For instance, EVOH copolymers with lower ethylene contents have better gas barrier properties than those with higher ethylene contents. Data from Kuraray America Inc. (Houston, TX) show that EVOH with 27 mol% ethylene offers ten times more oxygen barrier than one with 44 mol% ethylene (as shown in Fig. 2). Zhang et al. (2001) reported oxygen transmission rates 4 to 6 times higher for an EVOH copolymer with 44 mol% when compared to a film containing 32 mol% ethylene. An exponential increase in oxygen transmission rates of EVOH with ethylene content was reported by Ito et al. (2001). Copolymer composition also affects water absorption and transmission by EVOH copolymers. Copolymers with low ethylene contents absorb more water than those with higher ethylene (Zhang et al., 1999, Cava et al., 2006). For example, the normalized water vapor transmission rate of EVAL[®] EVOH resin with 27 mol% is 8 g.mil/100 in².day while that of a resin with 48 mol% ethylene is only 1.4 g.mil/100 in².day. Since water absorption takes place by water molecules hydrogen bonding preferentially to the vinyl alcohol groups present in the polymer, an increase in the number of vinyl alcohol groups leads to an increase in

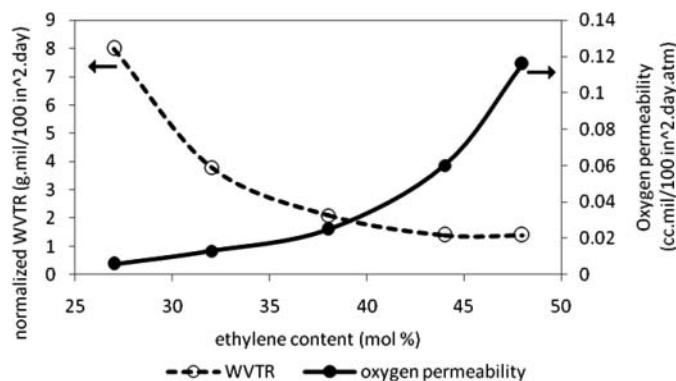


Figure 2 Oxygen permeability and thickness normalized water vapor transmission (WVTR) as a function of ethylene content for EVOH copolymers. (Data from EVAL Americas).

the number of water molecules sorbed to the polymer (Lagaron et al., 2003).

DEGREE OF CRYSTALLINITY

At a microscopic scale, semi-crystalline polymers are heterogeneous materials typically represented as crystalline domains dispersed in an amorphous matrix (Ezquerro et al., 2002). The crystalline phase contains segments that are organized into three-dimensional arrays characterized by the existence of long range order with respect to molecular arrangement, while the amorphous regions consist of disordered chain segments (Gestoso and Brisson, 2001). Properties of semi-crystalline polymers are related not only to the degree of crystallinity, which indicates the relative proportions of the crystalline and non-crystalline phases, but also to the crystalline features such as the size and the perfection of the crystals (Ezquerro et al., 2002). The good barrier properties of EVOH copolymers are largely attributed to their inherent high degree of crystallinity. The benefits of a higher degree of crystallinity include improved barrier to gases and moisture. Oxygen permeability becomes lower as the degree of crystallinity increases as shown in Table 1 for EVOH and other polymers. For example, the oxygen permeability of EVOH samples (with 32 mol% ethylene) decreased by almost 5 times when the crystallinity of samples increased from 58% to 70%. It is suggested that the permeation of most low molecular weight substances such as non-condensable gases occurs mainly through the amorphous regions (Michaels et al., 1963a; 1963b). These authors showed that solubilization of gases such as oxygen, carbon dioxide, etc., occurs only in the amorphous phase of PET and that crystallinity impedes the diffusion of such gases. Thus, the presence of large amounts of impermeable crystalline regions in polymers with high degree of crystallinity such as EVOH reduces gas permeability by creating a more irregular tortuous diffusive path for penetrant molecules and by decreasing the volume of polymer available for solution to occur (Lagaron et al., 2004).

Table 1 Effect of crystallinity on oxygen permeability of polymers

Polymer	Morphology	Oxygen Permeability (cc.mil/100 in ² .day.atm)
EVOH ^a	58% crystallinity (non-oriented)	0.71
	68% crystallinity (uniaxial orientation)	0.25
	70% crystallinity (biaxial orientation)	0.15
LDPE ^b	50% crystalline	480
	75% crystalline	110
PET ^b	10% crystalline	10
	50% crystalline	5
PP ^b	Atactic (low crystallinity)	250
	Isotactic (higher crystallinity)	150

^a Data from Armstrong (2002), oxygen permeability measured at 20°C, 100% RH for EVOH with 32 mol% ethylene.

^b Data from Salame (1986), oxygen permeability measured at 23°C, 50% RH.

Crystallization of EVOH

Thermoplastic polymers will crystallize to varying extents when the molten polymer is cooled below the melting point of the crystalline phase (Young and Lovell, 1991). Crystallization occurs when polymer chains aggregate to form crystals, which possess a high degree of order in comparison with the amorphous phase. Whether or not crystallization occurs depends on the thermodynamics of the crystallization process, the chemical microstructure and geometrical structure of the polymer. The rate and extent to which crystallization occurs is also controlled by the physical conditions (temperature, time, strain), quenching rate, orientation, aging, etc., under which crystallization occurs. EVOH has an extremely rapid crystallization rate compared to other thermoplastic polymers which can cause difficulties in controlling the degree of crystallinity during cooling of the polymer from the molten state (Armstrong, 2008).

A polymer must possess some degree of chemical, geometrical, and spatial regularity for crystallization to occur. Naturally copolymers are known to lack the necessary chemical regularity along their chains. In addition, geometrical regularity in those copolymers produced by free radical polymerization occurs only infrequently (Vaughan and Bassett, 1989). EVOH chains are known to be atactic, having spatially disordered configurations (Takahashi et al., 1999). X-ray diffraction studies have shown that vinyl alcohol and ethylene monomer units in EVOH are distributed randomly along the polymer chains in a planar zigzag conformation. Despite the lack of stereoregularity, it has been established that EVOH copolymers can crystallize at all copolymer compositions (Nakamae, et al., 1979; Takahashi et al., 1999). This has been attributed to the fact that the size of the hydroxyl groups on the polymer chains is small enough relative to the space available in the crystal structure such that the symmetry of the polymer is not significantly affected. Therefore, the atactic nature of EVOH chains does not affect the ability of EVOH copolymers to crystallize. Significant cohesion between adjacent polymer chains is also necessary for polymer molecules to aggregate together into a crystalline solid. The large number of hydroxyl groups in EVOH copolymers results in high intermolecular and intramolecular forces and hence a high cohesive energy (Lagaron et al., 2004). Both intermolecular and intramolecular hydrogen bond strength decrease with an increase in ethylene content (Ketels, 1989). Thus, in EVOH with a higher content of the vinyl alcohol unit, chain mobility in the amorphous region is more restricted by intermolecular hydrogen-bonding interactions (Zhang et al., 2000). A comparison of the cohesive energy of EVOH with that of other common polymers is shown in Fig. 3.

Crystal Structure of EVOH Copolymers

It is generally recognized that the type of structure of EVOH crystals depends on the relative proportions of ethylene and vinyl alcohol in the copolymer. Three crystal structures were

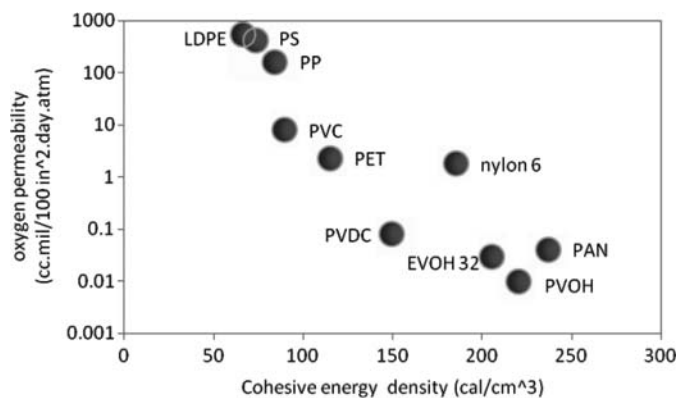


Figure 3 Relationship between oxygen permeability (measured at 23°C and 0% RH) and cohesive energy density of some polymers. PVC is polyvinyl chloride, PS is polystyrene, PAN is polyacrylonitrile. (Cohesive energy data from van Krevelen (1990) and Brandrup and Immergut (1989); Oxygen permeability data from EVAL Americas and Salame (1986)).

proposed for EVOH, depending on the proportions of ethylene and vinyl alcohol in the copolymer. Nakamae et al. (1979) identified an orthorhombic crystal structure similar to that of PE for copolymers with a vinyl alcohol composition range below 20 mol%, a pseudo-hexagonal structure for the range of 20–60 mol%, and a monoclinic structure similar to that of PVOH above 60 mol%. Similarly Cerrada et al. (1998) studied crystal structure of copolymers with 56, 68, and 71 mol% vinyl alcohol. These authors reported monoclinic lattice for vinyl alcohol contents of 68 and 71 mol%, and an orthorhombic lattice for the copolymer with 56 mol% vinyl alcohol. Takahashi et al. (1999) reported a similar general trend albeit with different margins of vinyl alcohol content between the different crystal structures. According to these authors, EVOH copolymers with vinyl alcohol contents of 6–14 mol% were reported to resemble the orthorhombic crystal structure of PE, while those between 27–100 mol% resemble the monoclinic structure of PVOH. An intermediate hexagonal structure was observed at vinyl alcohol contents between 14–27 mol%.

Cerrada et al. (1998) observed that the existence of different crystalline structures with EVOH copolymer composition was influenced not only by the copolymer composition, but also by the crystallization conditions. The control of temperature during cooling in the final stage of a crystallization process usually determines the development of a specific morphology, which influences the final properties of the material. The cooling rate can therefore be adjusted to control the level of crystallinity and the crystal morphology of the polymer. Cerrada et al. (1998) determined that while slowly cooled samples showed the types of crystal structure reported by the different researchers, fast cooling or quenching (e.g., at 100°C/min) exhibited only the orthorhombic structure for all copolymer compositions. The ethylene content of EVOH copolymer also affects the degree of crystallinity. Alvarez et al. (2003) noted that higher ethylene content in the chain of EVOH copolymers decreases molecular mobility, requiring large activation energy for polymer chains to diffuse into the crystalline lattice. This leads to lower crys-

tallization rates resulting in the formation of larger quantity of crystals and more perfect crystalline structure.

Orientation

Orientation is a common industrial technique used to enhance crystallinity and hence the mechanical and barrier properties of polymers. During orientation polymer chains are drawn or stretched in specific directions (Peacock, 2000). If a polymer is subjected to an external stress immediately after crystallization the polymer chains align preferentially in the direction of stress since the intrinsic properties of a polymer chain are strongly directionally dependent (Gedde, 1999). Stretching is usually performed at a temperature slightly below the melting point when crystals are partially melted, and the desired shape is maintained during cooling. Orientation can be uniaxial, in which the material is stretched or drawn in one direction only (i.e., machine direction), or biaxial, in which the material is stretched in two orthogonal directions (machine direction and transverse direction).

In general, uniaxial orientation of EVOH is fairly easy. Biaxial orientation is not easy to control, requiring optimized conditions to achieve the simultaneous orientation. Unlike PP and PE which can be easily biaxially oriented at temperatures close to their melting points, EVOH display poor capability for biaxial drawing (Djezzar et al., 1998; Matsui et al., 2003). EVOH displays a sheet-like structure due to the strong intermolecular and intramolecular hydrogen bonding interactions in its polymer chains, which is an obstacle to biaxial orientation at temperatures close to the melting point. Seguela et al. (1998) noted that the planar distribution of hydrogen bonds in the stable monoclinic crystalline form involves strong mechanical anisotropy that causes cracking/splitting and prejudices biaxial drawing. However, it has been reported that both simultaneous and sequential biaxial drawing of EVOH copolymers are possible at low draw temperatures (50–100°C) due to a strain induced phase change of the stable monoclinic form into a mesomorphic state (Okaya and Ikari, 1992).

Although not always easy to achieve in practice, biaxial orientation is known to produce significant improvements in properties of EVOH copolymers, including the oxygen barrier. As shown in Table 1, biaxial orientation of EVOH resulted in 70% crystallinity and oxygen permeability of 0.15 cc.mil/100 in².day.atm, in comparison with 58% crystallinity and 0.71 cc.mil/100 in².day.atm for non-oriented material (Armstrong, 2002). On the other hand, uniaxial orientation resulted in 68% crystallinity and oxygen permeability of only 0.25 cc.mil/100 in².day.atm.

GLASS TRANSITION AND FREE VOLUME CONCEPTS

The glass transition is a characteristic phenomenon in amorphous and semi-crystalline polymers. The glass transition

temperature (T_g) defines the temperature at which the polymer structure transitions from the “rubbery” state to the “glassy” state in response to changes in external variables such as temperature (Aharoni, 1998). It is believed that the cooperative movement of both gas molecules and polymer chain segments is required for mobility of gas molecules through the polymer matrix (Adam and Gibbs, 1965; Eyring, 1936). Therefore, the concepts of free volume (Cohen and Turnbull, 1959) and cooperative motion (Adam and Gibbs, 1965) are useful for explaining aspects of chain mobility and gas permeability of polymers. Free volume characterizes the amount of space in a polymer matrix that is not occupied by the constituent atoms of the polymer (Freeman and Hill, 1998). The permeation of gas molecules requires sufficient free volume into which the molecules can move. T_g is usually visualized as the onset of large-scale cooperative motion of chain segments (Ebewele, 2000). As temperature increases above T_g there is enough thermal energy to overcome the intramolecular and intermolecular forces holding together chain segments, the chains undergo viscous flow and experience rotational and translational motions (Bicerano, 1993; Aharoni, 1998). Sufficient free volume is created that allows polymer chains to move relative to one another and gas molecules to easily move through. As temperature is decreased the density of the polymer increases and free volume decreases. Movement of polymer chain segments is negligible in the glassy state, and it becomes increasingly difficult for gas molecules to find sufficient free volume for motion to occur on a reasonable time scale (Cohen and Turnbull, 1959).

EVOH copolymers show high glass transition points and are typical glassy polymers when dry, hence the low oxygen permeability values. The T_g values of EVOH copolymers vary depending on the copolymer composition, decreasing as ethylene content increases. Product data from EVAL Americas show that T_g values of EVOH copolymers with 27, 32, and 48 mol% ethylene are 60°C, 57°C, and 49°C, respectively. Local free volume arises due to irregular and inefficient packing of disordered chains. This implies that free volume exists mainly in the amorphous regions; hence polymers with a high degree of crystallinity such as EVOH would generally have less free volume (Ito et al., 2003). Ito et al. (2001) observed that the free volume size of EVOH copolymers increases significantly at ethylene contents above 30 mol%. That is, the free volume size for EVOH copolymer with 30 mol% ethylene or less was found to be 0.04 nm³ as compared to a value of 0.18 nm³ for PE. This increase in free volume size was related to reduction of hydrogen bonding interactions at higher ethylene contents, allowing polymer chains greater flexibility. The relationship between oxygen permeability and free volume hole size in an EVOH copolymers was studied by Ito et al. (2003) and Muramatsu et al. (2003). A correlation coefficient of 0.99 was observed between oxygen permeability and free volume hole size for EVOH (with 29 mol% ethylene) at different temperatures and RH (Muramatsu et al., 2003).

EVOH SENSITIVITY TO MOISTURE

The major limitation for EVOH is its inherent sensitivity to moisture which poses a negative effect on its oxygen barrier and other properties. When exposed to humid conditions, EVOH absorbs significant amounts of moisture. Lagaron et al. (2001) reported equilibrium water uptake of about 9% by EVOH films with 32 mol% ethylene in saturated RH conditions at 21°C. Aucejo et al. (1999) reported water absorption of up to 13%, while Zhang et al. (1999) reported equilibrium water sorption values of 8.4% for EVOH films with 32 mol%. The moisture sensitivity of the permeability of EVOH is also a function of degree of crystallinity. For example, Zhang et al. (1999) reported only 6.8% uptake for biaxially oriented film (with 32 mol% ethylene) as compared to 8.4% for non-oriented film.

The degree to which moisture affects oxygen permeability of EVOH copolymers depends on the RH of the environment. Zhang et al. (2001) and Muramatsu et al. (2003) studied the effect of a wide range of RH levels on oxygen permeability of EVOH films and reported a general trend similar to that shown in Fig. 4. Oxygen permeability initially declined at low RH (i.e., from 0 and 25–35%) followed by a gradual increase at RH above 25–35%. Oxygen permeability increased sharply at RH above 75–80%. Similar trends for change in oxygen permeability as a function of RH/water activity were reported for other hydrophilic polymer such as nylon 6, cellophanes, edible films, etc., (Hernandez, 1994; Gontard et al., 1996).

Interactions between EVOH and Water Molecules

The hydroxyl group that confers EVOH with the good oxygen barrier is also the main cause for its moisture sensitivity as a

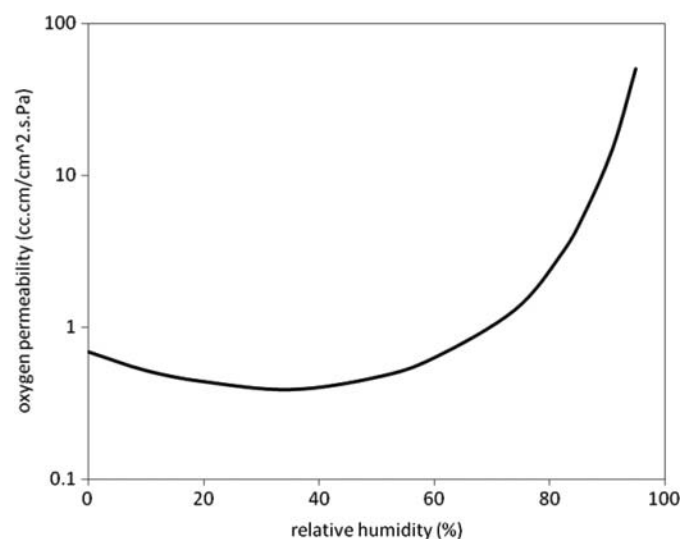


Figure 4 Effect of relative humidity on oxygen permeability of EVOH films (adapted from Muramatsu et al. (2003)).

result of specific associations between water molecules and the polar hydroxyl groups in EVOH. Due to the small size of the water molecule, water is easily incorporated into the supermolecular structure of the polymer, resulting in plasticization (Soles and Yee, 2000). The first water molecules absorbed form hydrogen bonding networks with the surrounding hydroxyl groups in EVOH chains (Zhang et al., 1999). Hydroxyl groups in EVOH are not totally self associated, but are partly isolated in the hydrophobic matrix (Iwamoto et al., 2001). It is believed that water molecules in EVOH are hydrogen bonded one-to-one to isolated hydroxyl groups in EVOH (Iwamoto et al., 2006). At molecular level, plasticization leads to an increase in the distance between neighboring chains in the polymer chain (i.e., increase in free volume) due to swelling. This decreases the energy of polymer-polymer interactions which may involve weakening or breaking of hydrogen bonds between polymer chains (Levine and Slade, 1988; Hodge et al. 1996). An increase in free volume cavity size during water absorption was demonstrated for PVOH. Hodge et al. (1996) observed large scale rotation about C-C covalent bonds (i.e., macromolecular mobility) above 30% water absorption by PVOH which was concurrent with disruption of the vast majority of hydrogen bonds. These authors concluded that water that engages in hydrogen bonding with the hydroxyl groups is believed to be the most effective plasticizing water for the polymer. When hydroxyl groups are fully occupied, subsequent water molecules start bonding with each other, forming water clusters.

It is well established that plasticization by water affects the glass transition by depressing the T_g of the polymer matrix. Figure 5 shows the effect of RH on T_g of two EVOH copolymers. The data used in the figure (from Soarnol®) indicate that as RH increased from 0 to 100%, T_g decreased from 60°C to 3°C for EVOH with 32 mol% ethylene, and decreased from 55°C to 8°C for EVOH with 44 mol% ethylene. Zhang et al. (1999) reported a 24°C drop in T_g for similar EVOH films when RH increased from 0 to 43%, and T_g value that was below room temperature when RH was above 75%. Aucejo et al. (1999) reported a T_g drop from 50°C to -60°C for EVOH films (29 mol% ethylene content) containing 13% moisture. Similarly,

Lagaron et al. (2001) reported depression of T_g by about 80°C (from about 62°C to -18°C) for EVOH films (32 mol% ethylene content) with about 9% moisture. T_g depression can be related simply to an increase of the volume or to the re-distribution of hydrogen bonds in the polymer. The critical effect of plasticization leads to increased mobility and chain flexibility in the dynamically constrained amorphous component of the polymer brought about by the dilution of the main chain by water (Levine and Slade, 1988).

Moisture Effect on Polymer Morphology

While plasticization of hydrophilic polymer matrices by water is largely recognized, the effect of water on the crystalline phase of semi-crystalline polymers is not implicit. It has been suggested that water penetrates only the amorphous regions of a polymer and not the crystalline phase. At room temperature it is expected that only the non-associated hydroxyl groups, which makes up the amorphous region of the semi-crystalline EVOH copolymer, would be associated with water (Min et al., 1994). As recognized, the crystalline phase is made of associated hydroxyl groups, that is, those hydroxyl groups attracted to and associated with their closest hydroxyl groups along the EVOH chains. However, some researchers reported that crystalline regions are also affected by excess quantities of water, an effect more pronounced at high temperatures and pressures used in re-tort processing (Hodge et al., 1996; Lopez-Rubio et al., 2005). Disruption of the crystalline regions may occur in the polymer due to the swelling stresses imposed by increased water uptake thus increasing the effective number of free volume sites available for oxygen permeation (Hodge et al., 1996).

EVOH USE IN PACKAGES FOR HEAT PROCESSED SHELF STABLE FOODS

Because of the moisture sensitivity of EVOH, its use in food packaging is invariably in the form of multilayer structures where an EVOH film is protected by water resistant polymers. The most commonly water resistant polymers for multilayer packages used for thermally processed foods is PP. The normalized water vapor transmission rates of oriented PP measured at 40°C and 90% RH is 0.38 g.mil/100 in².day compared to 1.4–8.0 g.mil/100 in².day for EVOH copolymers (EVAL Americas). PP also provides good mechanical properties (strength, rigidity, abrasion resistance, etc.) and strong heat seals. PET is also commonly used as an outer layer in multilayer structures due to its strength, abrasion resistance and good printability. Nylon 6 is usually incorporated in multilayer structures because of its thermal stability, toughness, and resistance to cracking and puncture (Massey, 2003). Biaxially oriented nylon 6 has improved strength, oxygen barrier properties, impact and pinhole resistances, and the films are more flexible. Special adhesives (generally polyesters, copolymers of ethylene, polyurethanes,

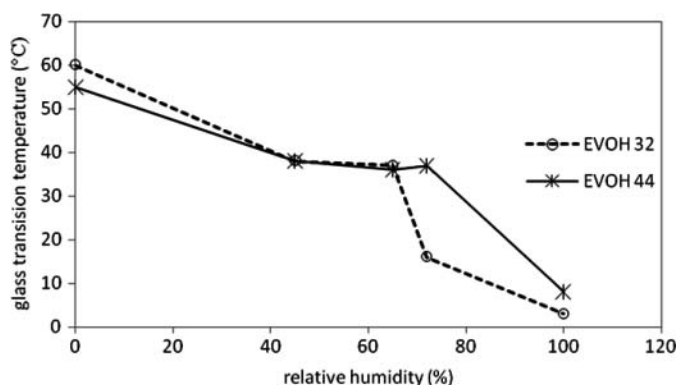


Figure 5 Effect of relative humidity on T_g of EVOH copolymers (Data from Soarnol®).

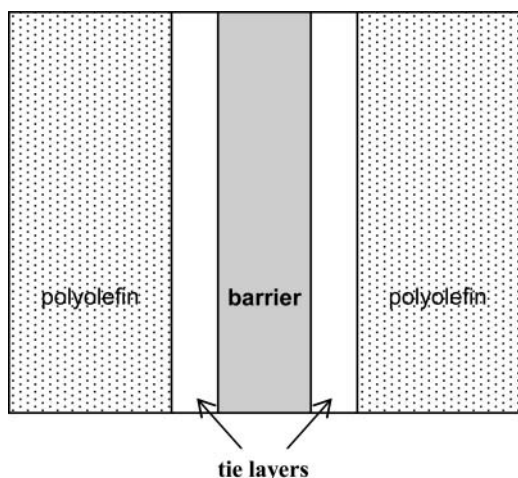


Figure 6 Illustration of a multilayer structure.

or acrylics) known as tie layers may be used to bond adjacent layers to avoid delamination (Osborn and Jenkins, 1992). For example, EVOH can be coextruded with nylon 6 without the use of adhesives, but coextrusion with PP, PE, PET, etc., requires the use of suitable adhesives (Sidwell, 1992).

With the wide range of polymers available, there are many possible combinations of multilayer structures to meet specific needs. Rigid and semi-rigid containers such as bottles, tubs, trays, bowls and tubes are formed by thermoforming, vacuum and pressure molding. Examples of commercial packaging using EVOH in retorted rigid containers include Campbells soup, Dinty Moore MRE and dinner trays, retorted pet food containers such as those for Meow Mix and Beneful. To meet the customized needs of a broad variety of applications, multilayer configurations can be either symmetrical (as shown in Fig. 6) or asymmetrical.

EFFECT OF RETORTING ON OXYGEN BARRIER PROPERTIES

Several investigations on the effect of retorting on the oxygen barrier of packages containing EVOH have yielded results that showed a significant deterioration due to retort processes. Tsai and Jenkins (1988) found 100 times increase in oxygen permeability immediately after retorting at 121.1°C for 120 min for rigid containers consisting of EVOH and an unspecified polyolefin. Similarly, Lopez-Rubio et al. (2005) reported an increase in oxygen permeability from 0.0197 cc.mm/m².day.atm before retort to 8.99 cc.mm/m².day.atm after retort for PP/EVOH/PP films immediately after retorting at 121°C for 20 min. Mokwena et al. (2009) carried out studies comparing the effect of retort processing and combined microwave-hot water sterilization of the oxygen barrier of two multilayer films containing EVOH which were used as lidstock for rigid trays containing mashed potato. An increase in oxygen transmission rate of more than 10 times was reported for a film of PET/EVOH/PP and about

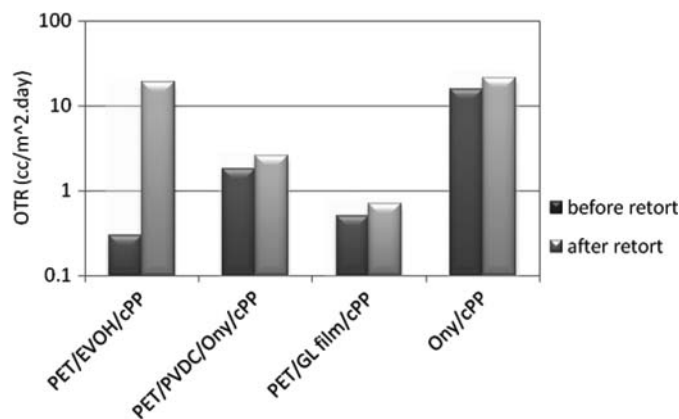


Figure 7 Oxygen transmission rate (OTR) of multilayer films before and after retort at 125°C for 20 min. OTR was measured at 25°C and 70% RH. cPP is cast polypropylene; GL film is silica deposited laminated film (Toppan Printing Co. Ltd); Ony is oriented nylon. (Data from Hernandez and Giacini (1998)).

47 times for PET/PP/nylon 6/EVOH/nylon 6/PP after retorting for 28 minutes at 125°C. Figure 7 shows oxygen transmission rates before and after retort for EVOH containing film and other barrier materials typically used in food packaging. A large increase in the oxygen transmission rate was observed for EVOH containing film than for other barrier materials such as PVDC. The oxygen transmission rate increased by more than 60 times for EVOH containing film, compared to only 1.4 times for silica deposited laminated film and PVDC films under similar retort conditions. The effect of retort processing has been explained on the basis of both plasticization of the polymer matrix and alteration in polymer morphology (Mokwena et al., 2011). Lopez-Rubio and coworkers (2003; 2005; 2005) evaluated changes in crystallinity of EVOH after retort treatments of PP/EVOH/PP films. The authors concluded that an irreversible partial dissolution of EVOH crystalline regions occurred due to pressurized heated water entering the polymer and disrupting the intermolecular hydrogen bonding between EVOH chains.

In general, part of the oxygen barrier of films lost during retort treatments is recovered during long term storage. Mokwena et al. (2009) evaluated oxygen transmission rates of multilayer EVOH films following thermal processing and during storage at ambient conditions (approximately 20°C and 65% RH). The oxygen barrier of the multilayer films decreased considerably during the first 2 months of storage and remained relatively constant for the rest of the storage period (up to 12 months) as shown in Fig. 8. The pre-processing oxygen transmission values were not reached during the entire storage period. At steady state (i.e., after 2 months) the oxygen transmission rate for PET/EVOH/PP film was about four times that of the initial pre-processing value, while that of PET/PP/nylon 6/EVOH/nylon 6/PP film was about eight times the initial pre-processing value. The oxygen transmission rates for both films processed by combined microwave-hot water processing remained below the 2 cc/m².day over the 12 months of storage, a value which is comparable to commercially available PVDC laminated films currently used in the USA as lidstock film for shelf-stable products. Tsai and Jenkins (1988)

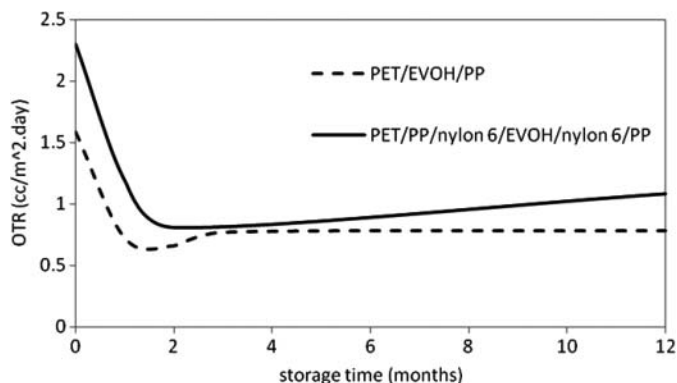


Figure 8 Change of oxygen transmission rates of multilayer films after a short time microwave-hot water sterilization process to $F_0 = 6$ min lethality. Processed packages containing mashed potato were and stored at ambient conditions (20°C and 65% RH) (Adapted from Mokwena et al., 2009).

studied oxygen permeability during long term storage for rigid containers of polyolefin/tie/EVOH/tie/polyolefin. The authors found that at steady state, which was reached after 200 days of storage, oxygen permeability was four times higher than the pre-processing value. Axelson-Larsson (1992) reported that oxygen permeability of PP/EVOH/PP films was still 50–100 times the pre-processing value three days after retort at 121°C for 40 min. On the other hand, Lopez-Rubio (2005) revealed that oxygen transmission rate was only four times the initial value six days after retorting at 121°C for 20 min. In practical applications, the lack of full barrier recovery during storage can lead to substantial additional oxygen permeating into the package resulting in possible deterioration of oxygen sensitive foods, especially during the first few weeks of storage.

CONCLUSIONS AND FUTURE OUTLOOK

There is no doubt that the oxygen barrier properties of EVOH are compromised when exposed to high moisture conditions. But EVOH still serves as an effective oxygen barrier in rigid retort packages such as thermoformed trays and blow molded bottles when used in combination with water resistant polymers such as PP. For thin film structures (< 10 mils) EVOH is vulnerable to the effects of high moisture and high temperature conditions encountered during retort. Therefore, some thin film structures may not provide sufficient oxygen barrier during thermal processing and later in storage. Hence a properly designed package that incorporates both good material selection and their positioning in the multilayer structure is essential to achieve the optimal oxygen barrier. Efforts to deal with issues of moisture sensitivity of EVOH in food packaging are being addressed from both the food industry and package industry perspective. Food scientists and engineers are continuously investigating novel thermal sterilization processes which shorten process times, thereby reducing the severity of thermal processes on both the food and the package. In 2009, the Food and Drug Administration (FDA) accepted petitions for the commercial use

of pressure assisted thermal sterilization of mashed potato in a retort pouch (Somerville and Balasubramaniam, 2009), and microwave sterilization of mashed potato in a single serve polytray (Higgins, 2010). Pressure assisted thermal sterilization utilizes a combination of high pressure and moderate temperatures over a short time to produce shelf stable foods. The microwave sterilization process involves submerging food packages in pressurized hot water while concurrently heating it with microwaves (Chen et al., 2007). Both processes shorten processing times, thereby providing alternatives to the traditional retort processing. Packaging scientists are also working on developing solutions to the moisture sensitivity problem. The use of oxygen scavenging packaging technology, incorporation of desiccants in the layers surrounding EVOH to reduce the amount of moisture reaching the EVOH layer, blending of EVOH with other materials to improve properties, use of nanocomposites, etc., are just a few examples. Although investigations of alternative packaging technologies are promising, much of the activity is still in the research and development stages.

In recent years there has been increased production capacity by the main EVOH producing companies, which might be taken as demonstration of continued confidence and expectation about future growth of EVOH markets worldwide. According to the 2000 annual report for Nippon Gohsei the world demand for EVOH was at 54,000 tonnes per year and expected to grow at an annual rate of 10% (Nippon Gohsei, 2000). In preparation for this anticipated growth, Nippon Gohsei increased its total production capacity at its US plant to 30,000 tonnes per year in 1999, started production of about 15,000 tonnes per year in the UK in 2003, in addition to the 10,000 tonnes per year produced in Japan. Likewise, Kuraray Co. increased its total production from 43,000 tonnes per year in 2001 to over 80,000 tonnes per year from their facilities in Europe, US and Japan (Kuraray Co., 2006).

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