

Permeation of Oxygen and Water Vapor Through EVOH Films as Influenced by Relative Humidity

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ABSTRACT: The transport properties of oxygen and water vapor through EVOH films as functions of relative humidity (RH) and temperature were studied. The results of oxygen and water vapor permeation demonstrated that temperature and RH markedly affected barrier properties of these films. In general, the EVOH films had minimal oxygen and water vapor permeabilities at a low RH, attributed to the reduced mobility of the polymer resulting from strong interactions between small water molecules and the polymeric matrix at low RH. Beyond 75% RH, the permeabilities increased considerably. In addition, the barrier performance of the EVOH films was found to be dependent on their ethylene content and orientation. From the experimental data, semiempirical equations describing oxygen transmission rates (O_2TR) as functions of RH and temperature were developed. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1866–1872, 2001

Key words: EVOH; oxygen transmission rate; water vapor transmission rate; permeability

INTRODUCTION

The permeability of polymeric packaging materials is quantified by the amount of the mass exchange between the packaged product and the external environment. The transport of penetrant molecules through polymeric materials is determined by the potential capacity of a polymer matrix to sorb the permeant molecules and by the ability of those molecules to diffuse through the polymeric material. In general, the barrier performance of a particular polymeric material is determined by extrinsic and intrinsic factors. Intrinsic factors are related to the crystallinity, orienta-

tion, chain stiffness, free volume, and cohesive energy density of the polymer, whereas extrinsic factors include temperature and moisture conditions to which the polymer is exposed.^{1,2} As far as moisture is concerned, polymers such as polyethylene and polyethylene terephthalate do not change their barrier resistance when allowed to come into contact with moisture because the hydrophobic polymers do not absorb enough water to plasticize the polymer chains to cause an increase in gas permeability. However, the barrier properties of hydrophilic polymers can be seriously impaired by the presence of organic vapors and liquids that penetrate and plasticize the polymer. Those polymers that contain hydroxyl groups (cellophane) and amide groups (nylon 6, nylon 6,6, etc.) exhibit large permeability increases as the polymers absorb water.^{3–5}

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Ethylene vinyl alcohol (EVOH) copolymers are produced by complete hydrolysis of ethylene vinyl acetate random copolymer, which is commonly produced by solution polymerization. Permeability properties of EVOH are mainly dependent on the copolymerization ratio of ethylene and vinyl alcohol. EVOH with 50 mol % ethylene is not considered as a high barrier. On the other hand, EVOH with 20 mol % ethylene is too hygroscopic and loses its practical applications. EVOH polymers with 25 to 45 mol % ethylene are considered as having superior gas barrier properties. Such limited gas permeation through EVOH is attributed to high intermolecular and intramolecular cohesive energy of the polymers.⁶ However, they are still sensitive to moisture and lose much of their barrier properties at high relative humidities (RH).⁷⁻¹¹ The thermal and mechanical properties of EVOH are also affected by water absorption. It was found that glass-transition temperatures (T_g) of EVOH polymers decreased with increasing RH and their T_g depression resistance depended on ethylene content and orientation. The tensile modulus and yield strength of the EVOH polymers were also found to be influenced by RH, ethylene content, and orientation.^{12,13} It is believed that water molecules absorbed by EVOH at high RH level interact with hydroxyl groups in the polymer matrix and weaken the existing hydrogen bonds between polymer molecules. As a result, the chains' segmental motion is enhanced, thereby changing their transport and mechanical properties.^{6,14,15}

To date, although the effect of RH on oxygen permeation through EVOH has been well known, no efforts have been made to establish mathematical relationships that describe the oxygen transmission rates (O_2TR) of EVOH as influenced by RH and temperature. Evaluation of the water vapor transmission rates (WVTR) of EVOH is also very limited because the polymers are used mainly as oxygen-barrier materials. Therefore, the first objective of this investigation was to determine O_2TR for EVOH at various RH and temperatures and to develop semiempirical equations for calculation of O_2TR based on the observed relationships. The equations may be useful for obtaining oxygen permeation into EVOH-containing packages and the resulting shelf life of oxygen-sensitive foods in the packages. The second objective was to measure the water vapor transmission rates of EVOH. The results may provide a better understanding of the interaction between water and EVOH.

EXPERIMENTAL

Nonoriented and biaxially oriented EVOH films with 32 mol % ethylene (EF-F15 and EF-XL15, respectively) and nonoriented EVOH film with 44 mol % ethylene (EF-E15), each 15 μm thick, were provided by Eval Co. (Lisle, IL).

Oxygen Permeation

The O_2TR values of the three EVOH films were measured using a MOCON Oxtran-2/20 instrument (Modern Controls, Minneapolis, MN), following the ASTM Standard Method D 3985.¹⁶ Three temperatures (15, 25, and 35°C) and eight levels of RH ranging from 0 to 94% were used for O_2TR measurements. Saturated salt solutions of known a_w were used to calibrate the RH sensors. Duplicate samples of each EVOH film were used at each experimental treatment. During the conditioning period, a film sample was placed between the two halves of the permeability cell and flushed with nitrogen carrier gas to remove traces of oxygen from the cell and the film. Oxygen was then introduced to one surface of the sample at atmospheric pressure. Permeated oxygen was carried away from the downstream surface of the film sample by the carrier gas to a coulometric sensor, to quantify O_2TR .

Water Vapor Permeation

The WVTR values of the three EVOH films were measured at 15, 25, and 35°C and five levels of RH ranging from 30 to 90%, following ASTM method F-1249,¹⁷ and using a MOCON PERMAT-RAN-W 3/31 instrument (Modern Controls). The calibration of the instrument for WVTR measurements was performed using polyester standard films provided by MOCON. The RH sensors were calibrated using saturated salt solutions. During testing, water vapor that permeated through the film sample was carried by dry nitrogen gas to an infrared detector. Duplicate samples were used for each treatment.

RESULTS AND DISCUSSION

Oxygen Permeation

O_2TR of the EVOH films decreased over the range of 0 to 35% RH at all three temperature levels, but increased at higher temperatures (Figs. 1, 2,

and 3). Above 35% RH the O_2TR tended to increase as RH increased. The RH at which O_2TR regained dry condition levels varied over a range from approximately 50 to 80% RH as the testing temperature decreased from 35 to 15°C. Moreover, after reaching O_2TR values comparable to dry condition levels, O_2TR increased strongly with an increase in RH, most notably at 35°C. A similar behavior was reported for nylon 6, EVOH-containing multilayer films, and nylon 6,6.^{5,18,19}

The decrease in O_2TR with low RH and the increase at high RH may be explained by mixed permeant analyses.^{20,21} Water molecules were more strongly adsorbed than oxygen molecules by the polymer, and occupied free volume that would otherwise be available for oxygen. Exclusion of oxygen by water from free volume within a polymer matrix reduced the available diffusive pathways for the oxygen. As a result, oxygen permeation decreased as the RH increased up to an intermediate RH. Concurrently, however, adsorbed water molecules interacted with polar hydroxyl groups of the polymer and weakened the intermolecular and intramolecular hydrogen bonding, thereby facilitating segmental motion and oxygen diffusion. At high RH, this bonding effect was more pronounced than the reduction of absorption sites because the polymer was increasingly plasticized by the sorbed water, resulting in the large increase in O_2TR observed.

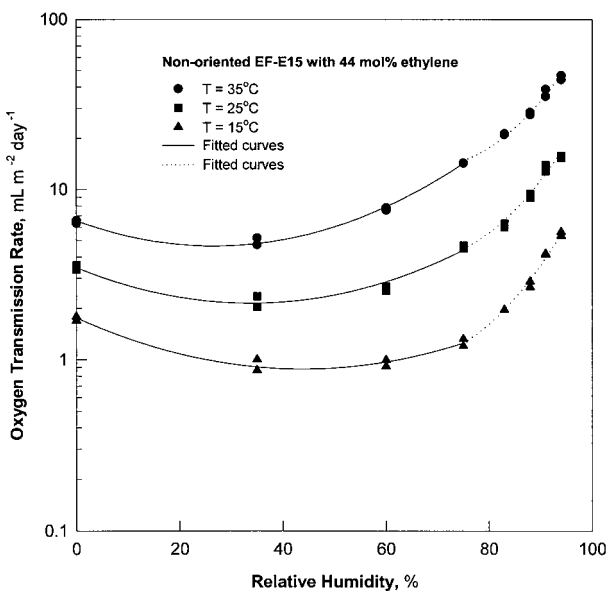


Figure 1 Experimental and fitted values for O_2TR of nonoriented EVOH film with 44 mol % ethylene content (EF-E15) at 1 atm oxygen. Predicted values are based on equations from Table I.

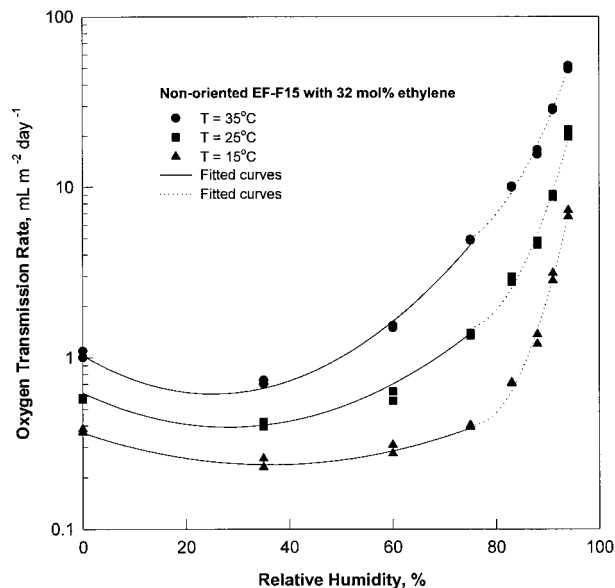


Figure 2 Experimental and fitted values for O_2TR of nonoriented EVOH film with 32 mol % ethylene content (EF-F15) at 1 atm oxygen. Predicted values are based on equations from Table I.

Compared to the EF-F15 film, the EF-E15 film had a higher O_2TR at a constant temperature and a relatively lower RH resulting from its higher ethylene content. Under dry conditions, the O_2TR values of the EF-E15 film were four to sixfold higher than those of the EF-F15 film. However, these differences were reduced with an increase in RH and finally a reverse situation was observed beyond 90% RH (Figs. 1 and 2). The lower water resistance of the EF-F15 film compared with that of the EF-E15 film would likely have resulted in itself being more extensively plasticized by the absorbed moisture at a higher RH. The biaxially oriented EF-XL15 film had an oxygen-barrier property similar to that of the EF-F15 film at low RH, but had double the barrier property at 90% RH (Figs. 2 and 3), which would be attributed to increased tortuosity and stress-induced crystallization resulting from polymer stretching and molecular alignment during biaxial orientation.

Semiempirical Model for Oxygen Permeation

The O_2TR of a polymeric material is commonly defined as:²²

$$O_2TR = \frac{Q}{At} \quad (1)$$

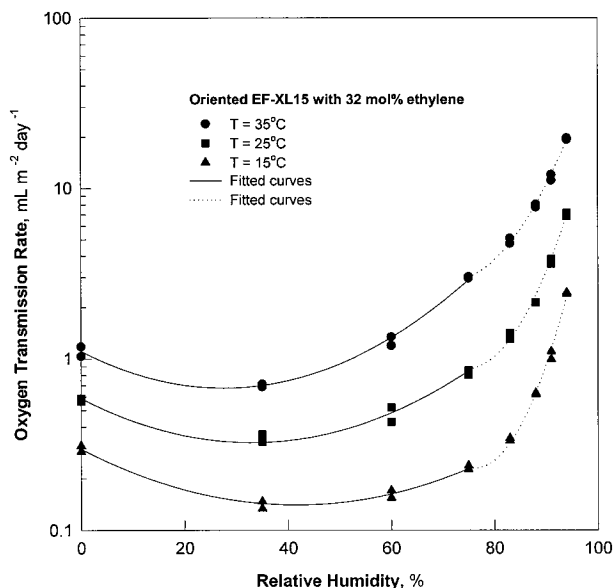


Figure 3 Experimental and fitted values for O_2TR of biaxially oriented EVOH film with 32 mol % ethylene content (EF-XL15) at 1 atm oxygen. Predicted values are based on equations from Table I.

where Q is the volume of oxygen permeated through the polymer film, t is time, and A is the surface area of the film. When using O_2TR , the oxygen partial pressure difference between the two sides of the film, the temperature, the material thickness, and type of film must be clearly specified. Temperature dependence of O_2TR can be described by the Arrhenius equation over a certain range of temperature:²²

$$O_2TR = (O_2TR)_0 \exp\left(\frac{-E_p}{RT}\right) \quad (2)$$

where $(O_2TR)_0$ is the preexponential factor and E_p is the activation energy of the penetrant.

To develop semiempirical equations describing the influence of temperature and RH on the O_2TR values of three EVOH films, the Arrhenius equation was used to correlate the O_2TR of the EF-E15 film to the reciprocal of absolute temperature at 0 and 91% RH (Fig. 4). A good linear relationship was observed at both RH levels. RH was found to affect the preexponential factor and the activation energy. A similar observation was observed for the other two EVOH films (data not shown). The calculated preexponential factor and the activation energy of oxygen diffusion through the EF-E15 film were plotted versus RH (Fig. 5). Activation energy values increased from 48 kJ/

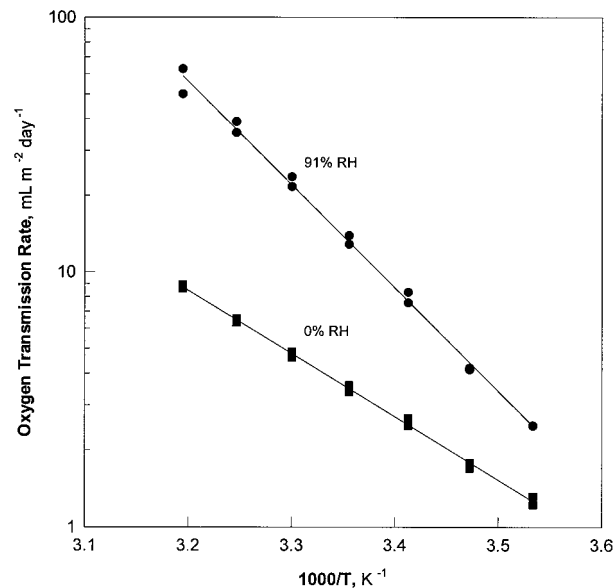


Figure 4 Relationship between the O_2TR of nonoriented EVOH film (EF-E15) and the reciprocal of absolute temperature (K^{-1}) at 1 atm oxygen. Seven temperatures ranging from 10 to 40°C were used for O_2TR measurements per RH value.

mol at 0% RH up to approximately 89 kJ/mol at 75% RH, and then decreased to 78 kJ/mol at 94% RH. The initial increase in the activation energy

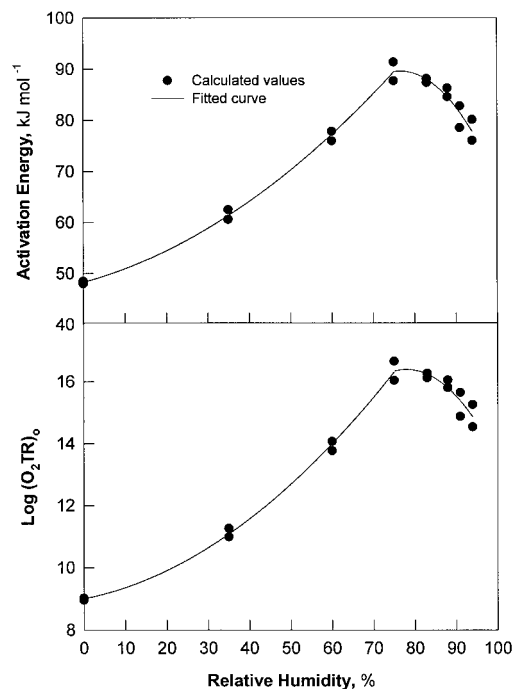


Figure 5 Activation energy and preexponential factor in the Arrhenius equation describing O_2TR of non-oriented EVOH film (EF-E15) as a function of RH.

Table I Fitted Semiempirical Equations for O₂TR (mL m⁻² day⁻¹) of Three EVOH Films Over Two RH Ranges Using SAS Analysis (Y = O₂TR^a)

0 to 75% RH	
EF-E15:	$\ln Y = 19.876 + 0.19027RH + 0.000422RH^2 - (5552.9 + 65.191RH)/T$
EF-F15:	$\ln Y = 15.028 - 0.29231RH + 0.007804RH^2 - (4619.3 - 77.343RH + 2.1533RH^2)/T$
EF-XL15:	$\ln Y = 17.411 + 0.20181RH + 0.000543RH^2 - (5348.0 + 70.832RH)/T$
75 to 94% RH	
EF-E15:	$\ln Y = 64.789 - 0.49637RH + 0.001910RH^2 - (16390 - 72.293RH)/T$
EF-F15:	$\ln Y = -369.15 + 9.9697RH - 0.06062RH^2 - (-119690 + 3232.1RH - 19.845RH^2)/T$
EF-XL15:	$\ln Y = -297.67 + 8.2307RH - 0.05009RH^2 - (-97650 + 2694.0RH - 16.546RH^2)/T$

^a O₂TR values were calculated at 1 atm oxygen.

may indicate that the tortuosity of the diffusing path for the oxygen molecules increased as RH increased. It is most likely that the sorption of water at active sites of the polymer and formation of water clusters are responsible for this trend. The decrease in activation energy beyond 75% RH may reflect the dominating plasticization effect of water molecules absorbed by the polymer. The plot of the preexponential factor showed a similar influence by RH (Fig. 5).

Based on the above-described observations, it is reasonable to divide the RH effect on O₂TR into two ranges of relative humidity, from 0 to 75% and from 75 to 94%, to better fit the Arrhenius equation to the experimental data. Assuming that the preexponential and activation energy terms can be expressed as quadratic functions of RH in each of these ranges, eq. (2) can be written as:

$$\ln O_2TR = (\alpha_0 + \alpha_1RH + \alpha_2RH^2) - (\beta_0 + \beta_1RH + \beta_2RH^2) \frac{1}{T} \quad (3)$$

The coefficient of each parameter in eq. (3) was determined for three EVOH films using PROC GLM of the Statistical Analysis System software²³ and only significant terms ($p < 0.01$) were used to fit the model to the experimental data. The fitted equations for three EVOH films are presented in Table I. Close agreement was found between values obtained using these equations and the experimental O₂TR values shown in Figures 1, 2, and 3. These fitted equations, therefore, make it possible to calculate the O₂TR of the EVOH films or resins at any given temperature and RH.

Water Vapor Permeation

The change in WVTR of the EVOH films as a function of upstream RH was slow at a low RH range (30 to 60% RH; Fig. 6). Beyond 75% RH, a more pronounced increase in WVTR with increasing RH was observed for the EVOH films. The

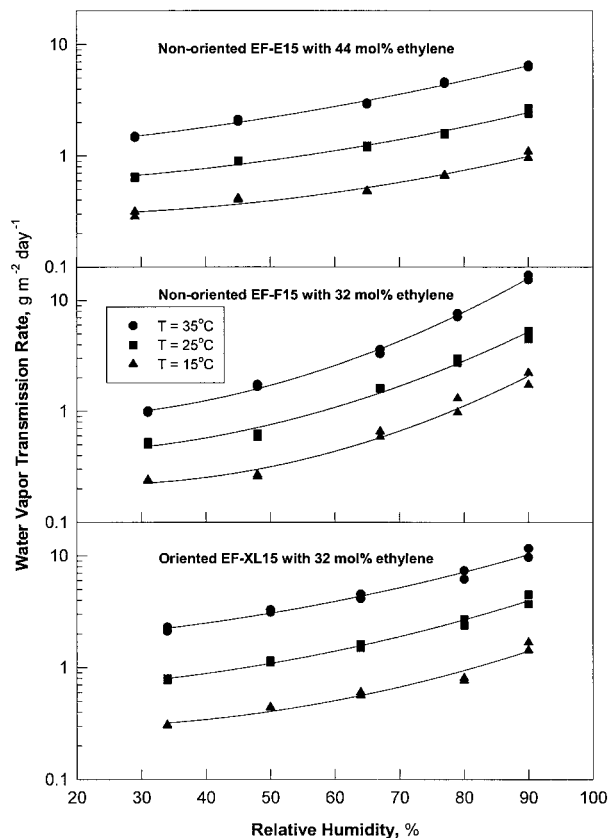


Figure 6 Water vapor transmission rates of three EVOH films as functions of RH.

nonoriented EVOH film with 44 mol % ethylene (EF-E15) had a greater WVTR at low RH than that of the nonoriented EVOH film with 32 mol % ethylene (EF-F15) because of the greater polymer chain motion of the higher ethylene EF-E15 film. However, as RH increased beyond 75%, the EF-F15 film had greater WVTR values compared to those of the EF-E15 film, indicating that the plasticization effect of water was more pronounced on the lower ethylene EF-F15 film. The biaxially oriented EVOH film (EF-XL15) did not demonstrate better water vapor-barrier properties than those of the nonoriented EF-F15 film at low RH. However, at high RH levels, the water vapor transmission rates of the EF-XL15 film were found to be lower. Therefore, the influence of orientation, resulting in better water-barrier properties of the EF-XL15 film, occurred only at high RH as a result of the decreased water sorption by the oriented EVOH film, and thus less plasticization effect by water at high RH.

The permeability coefficients of the EVOH films to water at 15, 25, and 35°C as a function of upstream RH are presented in Figure 7. At low RH, permeability coefficients decreased slightly with increasing RH for all EVOH films. However, after permeability coefficient values reached minimal levels, they increased with increasing RH; the degree of increase was the greatest for the EF-F15 film.

The influence of RH on changes in vapor permeabilities through glassy polymers has been commonly observed.²⁴⁻²⁶ The reduced permeabilities to water at low RH may be ascribed to the strong interaction of sorbed water molecules with the polymeric matrix, which is in a glassy state at low RH. Less mobility of sorbed water molecules at active sites, resulting from the strong interaction between the sorbed penetrant and the polymer, may have caused the decreased diffusion coefficient of water through the polymer and reduced water permeability. Because active sites were occupied and saturated by water molecules at increasing RH up to an intermediate level, the diffusion coefficient was less affected by the presence of the sites and reached an asymptotic low limit. As RH increased further, more water was absorbed in the polymer and weakened the strength of intermolecular bonds. Above approximately 75% RH, the polymer was increasingly plasticized by the sorbed water, resulting in the increased water permeability.

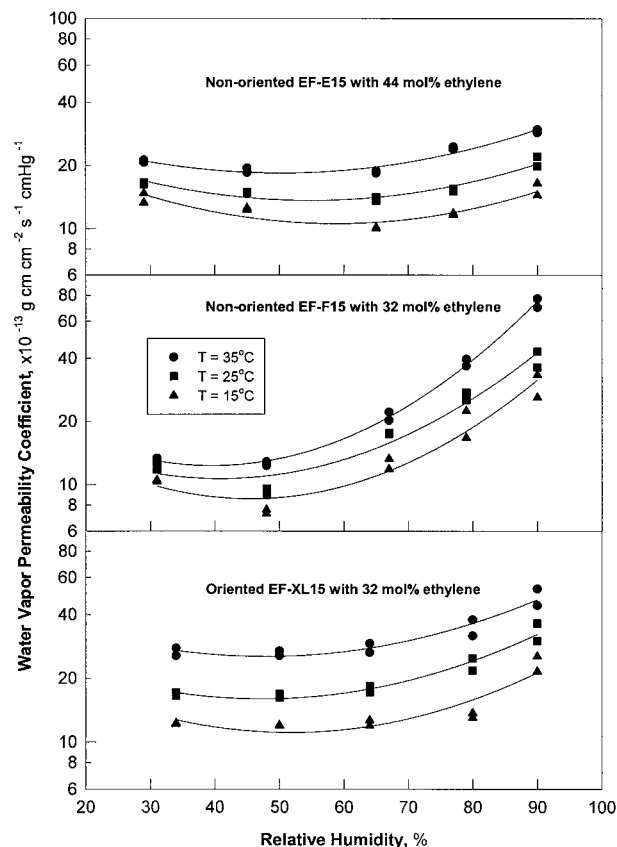


Figure 7 Water vapor permeability coefficients of three EVOH films as functions of RH.

CONCLUSIONS

The O_2 TR and WVTR of three EVOH films (EF-E15, EF-F15, and EF-XL15) were determined using permeability testing equipment at 15, 25, and 35°C and various levels of RH ranging from 0 to 94%. Overall, RH and temperature markedly affected oxygen- and water vapor-barrier properties of the EVOH films. From 0 to 75% RH, the O_2 TR and WVTR of EVOH were dependent mainly on the ethylene content of the polymer; the higher the ethylene concentration, the greater the O_2 TR and WVTR. However, above 75% RH, differences in O_2 TR and WVTR among the films became much smaller and finally a reverse situation was observed beyond 90% RH. The biaxially oriented film (EF-XL15) had improved oxygen- and water vapor-barrier properties. Moreover, at an intermediate RH, minimal O_2 TR and water vapor permeability coefficients for the EVOH films were found, possibly attributable to the strong interaction of sorbed water with the active sites of the polymer under its glassy state.

Based on the experimental data, semiempirical equations were developed to estimate O_2TR of the EVOH films at various RH and temperatures. These equations may be useful for calculations of oxygen permeation into EVOH-containing packages as influenced by moisture and temperature, and to obtain estimates of shelf life for oxygen-sensitive foods, provided that the maximum allowable permeation of oxygen in the package is known. Additional applications of the equations may be to help evaluate the barrier performance of EVOH-containing packages, identify barrier insufficiency, or eliminate unnecessary overpacking. A similar approach of developing semiempirical equations for predicting WVTR of the films affected by RH and temperature was not attempted because the EVOH polymers are not commonly used to provide a water vapor barrier.

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