

Limonene Transport and Mechanical Properties of EVOH and Nylon 6,6 Films as Influenced by RH

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Received 14 September 2000; accepted 7 April 2000

ABSTRACT: The transport properties of *d*-limonene through ethylene vinyl alcohol copolymers (EVOH) and nylon 6,6 films as functions of relative humidity (RH) and temperature were studied. Permeation properties of these polymers were strongly influenced by temperature and RH. Compared to the EVOH films, the nylon 6,6 film had much greater limonene permeability. Mechanical property studies indicated that both the tensile modulus and yield strength of the EVOH films decreased with an increase in RH. The polymer changed from being stiff and brittle at low RH to being soft and ductile at high RH. In addition, ethylene content and orientation were found to affect the transport and mechanical properties of limonene through EVOH polymers. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1949–1957, 2001

Key words: limonene; permeability; mechanical properties; EVOH; nylon 6,6

INTRODUCTION

Thermoplastic polymers have been used commonly as food packaging films due to their convenience and low cost.^{1–3} However, in comparison to glass and metal food containers, plastic packages are more permeable to gases, water vapor, and aroma compounds. In many cases, the gain or loss of these components may compromise the quality of packaged foods.^{4,5} To overcome this problem, high-barrier polymers such as ethylene vinyl alcohol copolymers (EVOH), polyvinylidene chloride (PVDC), polyacrylonitrile (PAN), polyethylene naphthalate (PEN), and liquid crystal polymers (LCPs) were developed over the past three decades.^{6–8} Among these polymers, EVOH resins have the fastest growing and largest market for

the food packaging industry due to their outstanding gas barrier properties, excellent resistance to solvent, flavor and aroma permeation, moderate cost, and easy processibility.⁹

It is widely recognized that transport properties of small gas molecules (O₂ and CO₂) through EVOH, nylons, and other hydrophilic polymers are affected by the presence of water within the polymer matrix; thus the effects of film hydration on gas permeation have been studied extensively.^{10–15} Compared to O₂ and CO₂, mass transport of flavor and aroma compounds through these packaging materials are relatively scarce. As the exchange of aroma constituents and unwanted odors between the food and packaging system can result in product quality losses, more research has been carried out to address the interaction between flavor/aroma and plastic packaging materials.^{16–20} One research area that has been emphasized recently is the loss of *d*-limonene in citrus juice products due to the scalping effect of

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Journal of Applied Polymer Science, Vol. 79, 1949–1957 (2001)
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polyethylene (PE) liners in barrier packages for aseptically processed juices.^{21–25} A barrier carton laminate material usually contains PE/tie layer/Al foil/tie layer/paperboard/PE. Due to its high barrier properties, EVOH has been proposed for replacing aluminum foil as the aroma barrier layer.²⁶ However, this approach would not prevent the flavor absorption by inner sealable PE layers. Furthermore, *d*-limonene may permeate the EVOH layer at high relative humidity (RH), which could magnify the scalping effect of the package upon the juice product. Alternatively, EVOH could be used as a coating material on the inner layer of barrier packages to decrease the scalping effect of PE. Nevertheless, its effectiveness may be compromised at high RH.

The presence of water molecules in the hydrophilic polymer matrix not only influences the way in which the permeant is sorbed and diffused, but also leads to changes in thermal and mechanical properties of the polymer due to the plasticization effect of water.^{13,14,27,28} Therefore, integrated studies involving the evaluation of mechanical and barrier properties under various RH conditions are necessary to better predict the end-use performance of these polymers.

To date, changes in aroma barrier and mechanical properties of EVOH films due to water absorption have not been completely understood. The first objective of this study was to investigate the effects of RH and temperature on the permeation of limonene through EVOH. The nylon 6,6 film, which is sensitive to RH variation, was also studied for comparison. The second objective was to evaluate the effects of RH on the mechanical properties of EVOH.

Materials and Methods

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). Nylon 6,6 film (25.4 μm thickness) was provided by DuPont Canada Inc. (Whitby, ON).

Limonene Permeation

Limonene (>97% pure *d*-limonene) obtained from Sigma Chemical Co. (St. Louis, MO) was used to evaluate the aroma barrier properties of the EVOH and nylon 6,6 films. The permeation of limonene was measured by using a permeability

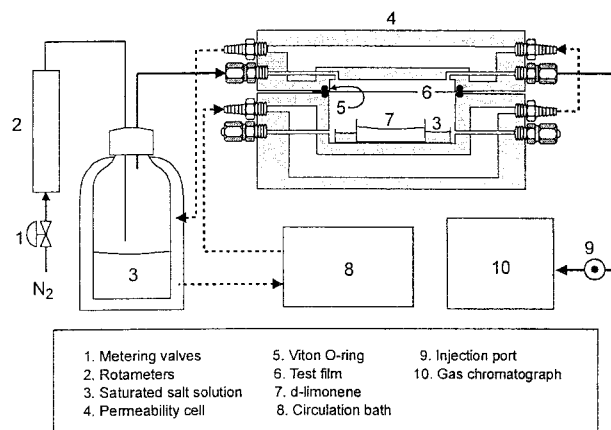


Figure 1 The experimental setup for measuring limonene permeability through plastic films by using a dynamic quasi-isostatic method.

testing cell as described by Lim and Tung.²⁹ Figure 1 shows the test apparatus which allows continuous gathering of permeation data from the initial time zero to steady state conditions, following a dynamic quasi-isostatic procedure. The cell comprised upper and lower stream (high- and low-permeant concentration, respectively) chambers separated by the test film. Hermetic separation of the two chambers was achieved by compressing two Viton O-rings on the sample film along the periphery of the chambers. Cell temperature was maintained by circulating a temperature-controlled fluid through jackets of the permeability cell chambers. Stainless steel tubing was wound with heating tape to avoid condensation of limonene and/or water vapor in the carrier gas. Saturated salt slushes or distilled water were used to provide a constant RH condition in the bottom chamber. The RH in the top chamber was adjusted by passing N_2 carrier gas (30 mL/min) through a temperature-controlled glass jar containing salt slushes or distilled water.

During permeability testing, the lower stream chamber was purged constantly with a stream of N_2 carrier gas. The increase in limonene concentration in the carrier gas was determined continuously by using a gas chromatograph (GC; HP6890, Hewlett-Packard Co., Wilmington, DE) until steady state conditions were attained. The GC was equipped with a flame ionization detector and fitted with an empty stainless steel column (3.18 mm o.d.). The GC operating conditions were as follows: oven temperature, 180°C; detector temperature, 260°C; N_2 flow rate, 30 mL/min; air flow rate, 240 mL/min. GC calibration was carried

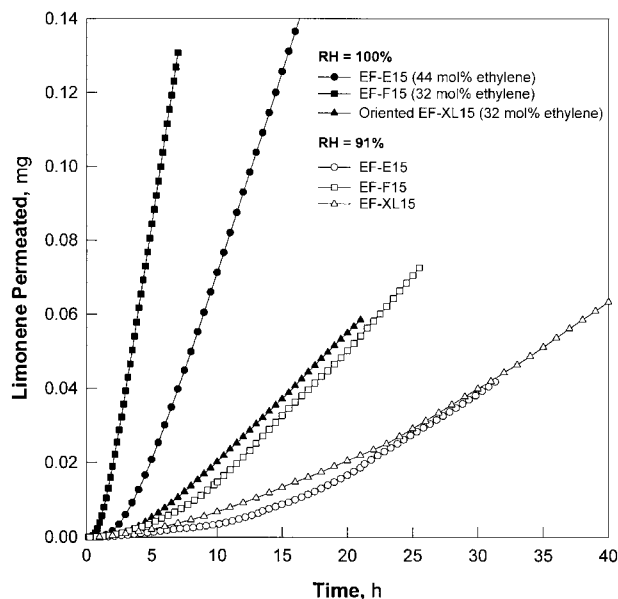


Figure 2 Permeation curves for limonene permeation through EVOH films at 35°C.

out from a standard curve of response versus penetrant concentration.

Limonene permeation through the three EVOH films, as well as nylon 6,6 film, was measured. The latter was included in this study for comparison. Before permeability measurements, the test film was conditioned to the test RH in a glass jar for more than 12 h and then secured on the surface of the top chamber with masking tape. Limonene permeation was measured at 25, 35, and 45°C under 75, 83, 91, and 100% RH conditions. Films were further conditioned for 2 h at the testing conditions. This was achieved by positioning aluminum foil between the test film and the upper stream chamber, shielding the film from limonene vapor. To initiate a test, the aluminum foil was withdrawn and the two chambers of the cell were fasten immediately. Duplicate samples of each film were evaluated for limonene permeation.

Mechanical Testing

Tensile properties of EVOH films were evaluated at room temperature by using an Instron Universal Testing Machine (Instron Co., Canton, MA) in accordance with ASTM D 882–95a test protocols.³⁰ Tests were carried out on the transverse direction (TD) and the machine direction (MD) of the samples to study the effect of film forming processes on the structural homogeneity of the

polymer. From the stress–strain curves, the following properties were determined: tensile modulus, yield strength, elongation at failure, and tensile strength. Initial gauge length was 50 mm, and crosshead speeds of 50 and 500 mm/min were used for tensile modulus and tensile strength measurements, respectively. Razor blades were used to cut EVOH films into rectangular strips (15 × 150 mm). The samples were dried in a vacuum oven overnight at 85°C for 6 h to remove the moisture that was present initially in the polymer matrix. Rehumidification of samples were carried out at room temperature (22 ± 1°C) for 24 h at the RH range of 0 to 94% using desiccant and saturated salt slushes. At each RH level, five and eight samples of each EVOH film were used for tensile modulus and tensile strength measurements, respectively.

RESULTS AND DISCUSSION

Permeation of Limonene in EVOH and Nylon 6,6 Films

Permeation curves of limonene through the EVOH and nylon 6,6 films at 35°C exhibited a typical initial induction, nonsteady state, and steady state periods (Figs. 2 and 3). The induction period tended to decrease with RH, whereas steady state transmission rates increased as RH

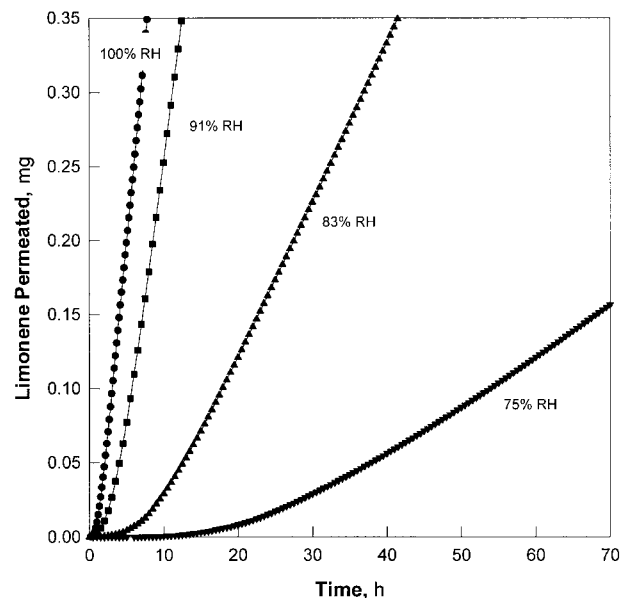


Figure 3 Permeation curves for limonene permeation through nylon 6,6 film at 35°C.

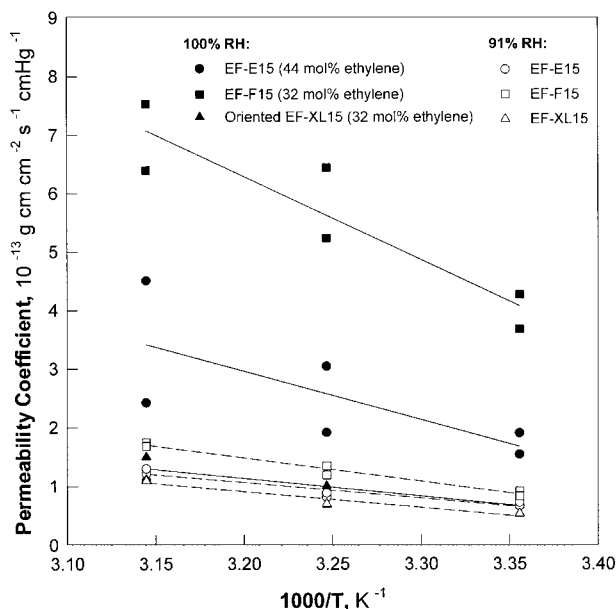


Figure 4 Permeability coefficient of limonene for EVOH films as a function of the reciprocal of absolute temperature (K^{-1}).

increased. The increased permeation of limonene through these films at high RH was attributed to moisture sorption in the polymer matrix.

The permeability coefficients of limonene through the EVOH and nylon 6,6 films were calculated as⁵:

$$P = \frac{Qx}{At\Delta p}$$

where Q is the total amount of limonene permeated through area A during time t during steady state permeation; x is the thickness of the film; and Δp is the vapor pressure difference crossing the film sample. The limonene vapor pressures reported by Boublik et al.³¹ were used to calculate permeability coefficients.

Linear relationships between limonene permeability and the reciprocal of absolute temperature were observed (Figs. 4 and 5). In addition, RH had a substantial effect on the limonene permeabilities of the films. The EF-F15 film was expected to exhibit better aroma barrier properties at low RH than the EF-E15 film due to the lower ethylene content of the EF-F15 film. Conversely, an opposite trend was anticipated under high RH conditions due to the lower water resistance of the EF-F15 film. As expected, Figure 4 demonstrated the higher limonene permeability of the EF-F15

film in comparison with the EF-E15 film beyond 90% RH, indicating that the EF-F15 film was more sensitive to variations in RH. The biaxially oriented EF-XL15 film appeared to provide the best limonene barrier performance of the three EVOH films. Limonene permeation through the EVOH films was not detected after 10 days of continuous testing at 35°C under 75 and 83% RH conditions (data not shown). The excellent barrier to limonene of the EVOH films at this RH range may be due to reduced diffusivity below 80–85% RH.

Figure 5 indicated that the nylon 6,6 film was much more permeable to limonene than the EVOH films at the same RH. At 45°C and 100% RH test conditions, the permeability coefficient of the nylon 6,6 film was approximately $28 \times 10^{-13} \text{ g cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$, which was four times higher than that ($7 \times 10^{-13} \text{ g cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$) of the EF-F15 film (Fig. 4). In addition, the permeation of limonene through the nylon 6,6 film was measurable at 75% RH.

In general, the permeation of organic vapors through hydrophilic films is concentration-dependent (i.e., the permeability increases as the vapor pressure increases) due to the strong interaction between penetrant molecules and the polymer. When the EVOH and nylon 6,6 films are exposed to food products containing a normally low limonene concentration (ppm level), the aroma per-

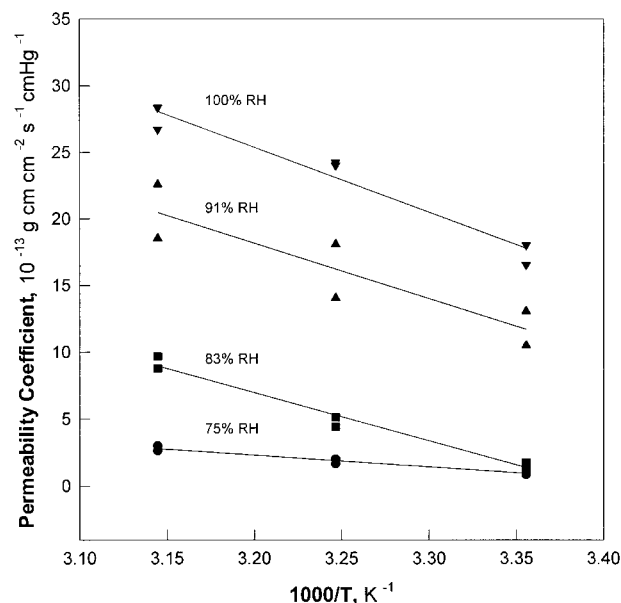


Figure 5 Permeability coefficient of limonene for nylon 6,6 film as a function of the reciprocal of absolute temperature (K^{-1}).

meability would be much lower compared to the permeabilities obtained by using the saturation vapor pressure of liquid limonene. Therefore, the limonene vapor transmission rates extrapolated to low concentrations using the permeability results obtained from this study will likely overestimate the limonene permeation through these films. Nevertheless, knowledge of the limonene barrier properties of these polymeric packaging materials, as influenced by RH and temperature, can aid in designing and/or selecting a barrier structure for packaging a specific food product where the scalping and permeation of limonene are concerns.

It may be reasonable to conclude that the use of EVOH-containing multilayer flexible films to package liquid foods containing low concentrations of limonene may provide excellent limonene barrier properties at normal storage conditions. This conclusion is based on an EVOH layer coextruded in the middle of the package, resulting in a low-equilibrium RH (<85%) in the EVOH layer during storage. In considering barrier containers for aseptically packaged juices, EVOH may be used to replace aluminum foil as an aroma barrier without compromising the quality of the product because of limited aroma permeation through the EVOH. Further, EVOH could be used as a coating material on the surface of the inner polyolefin layer, thereby avoiding the effect of flavor scalping by these polyolefin materials. Because the EVOH would be in direct contact with liquid foods with approximately 100% RH, use of the high-ethylene-content EVOH as the coating material may provide better protection of the packaged foods. The lower moisture sensitivity of this polymer would be expected to result in low aroma solubility and diffusivity.

Values for the diffusion coefficient (D) of limonene in the EVOH and nylon 6,6 films were calculated according to the expression^{32,33}:

$$D = \frac{x^2}{6l}$$

where l is the lag time which was derived as the intercept on the time-axis from straight line extrapolation of the steady state portion of the each limonene permeation curve (Figs. 2 and 3). Values for D were not calculated for EVOH films below 90% RH because limonene diffusion was not detectable at the lower RH levels studied. Figure 6 demonstrated that the diffusion coeffi-

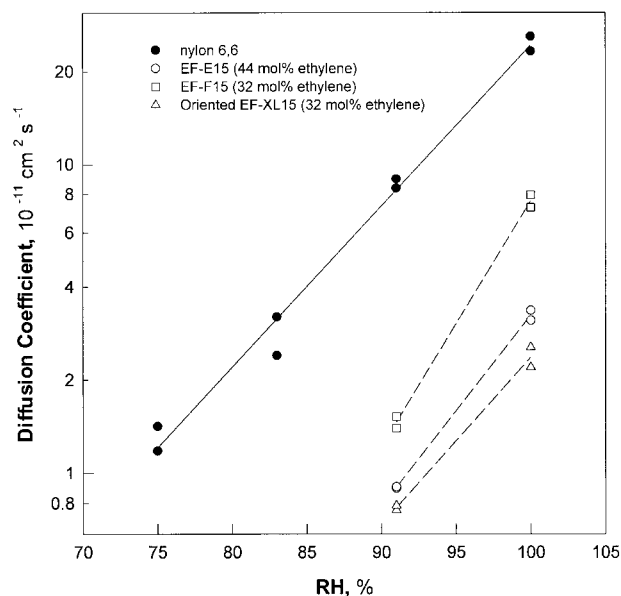


Figure 6 Diffusion coefficient of limonene for EVOH and nylon 6,6 films as a function of relative humidity at 35°C.

cients for the nylon 6,6 film were approximately 3 to 10 times higher than those calculated for the EVOH films over the 91 to 100% RH range. For instance, the diffusion coefficient of the nylon 6,6 film was approximately $24 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ at 35°C and 100% RH. At the same conditions, the diffusion coefficients for the EF-E15, EF-F15, and oriented EF-XL15 films were 3.2, 7.5, and $2.4 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, respectively. Moreover, the diffusion coefficient of limonene increased exponentially with RH for the nylon 6,6 film. Increases in D for the EF-E15, EF-F15, and oriented EF-XL15 films were 3.6, 5.2, and 3.0 times, respectively, as RH increased from 91 to 100%.

Among the EVOH films, the diffusion coefficient of limonene in the EF-F15 film was the greatest at any given RH, and this film also exhibited the strongest RH influence in terms of limonene diffusion. The oriented EF-XL15 film was found to have substantially lower diffusion coefficients than the comparable nonoriented EF-F15 film. This could be attributed to the increased tortuosity of the path taken by the permeant molecules, stress-induced crystallization, and rearranged amorphous phase in the polymer resulting from stretching or drawing of the polymer during orientation. These observations, in combination with the aforementioned permeability results, suggested that the presence of moisture in the EVOH and nylon 6,6 hydrophilic polymers de-

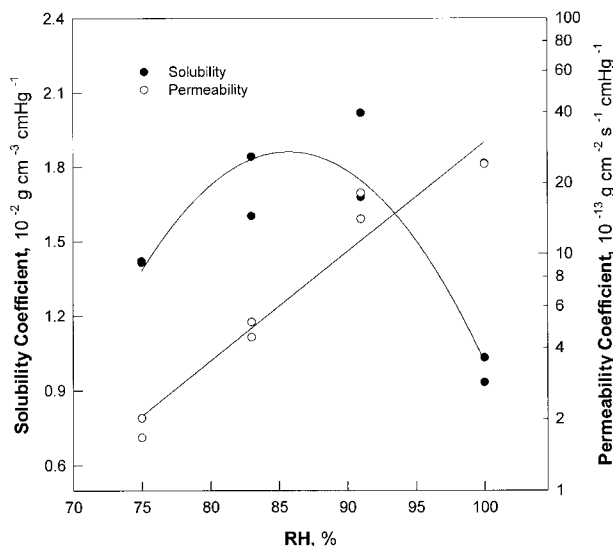


Figure 7 Solubility and permeability coefficients of limonene for nylon 6,6 film as a function of relative humidity at 35°C.

creased cohesive forces among polymer chains and resulted in an increase in polymer chain segmental mobility, which permitted increased limonene diffusion. The limonene permeability of the tested films as influenced by RH was dictated mainly by the diffusion coefficient rather than by the solubility coefficient in the polymers. This was further substantiated by plotting the solubility and permeability coefficients of limonene in the nylon film against RH (Fig. 7). The solubility coefficient of limonene in the nylon 6,6 film (S) was calculated from the equation of $S = P/D$.³³ Figure 7 indicated that the solubility coefficient of limonene increased with the increase in RH from 75 to 91% and then decreased with increasing RH, whereas the permeability coefficient increased exponentially as RH increased. The decreased solubility of limonene demonstrated at 100% RH may be due to the displacement of limonene from the severely plasticized polymeric matrix by water. A study of allyl isothiocyanate (AIT) sorption in nylon 6,6 film³⁴ showed that the sorption of AIT in the nylon 6,6 film also decreased at high RH, and this decrease was attributed to displacement of the aromatic compound by water.

Mechanical Properties

Tensile Modulus and Yield Strength

The modulus of EVOH decreased strongly at elevated RH, but the effect of RH on the modulus

was less pronounced at low RH (Fig. 8). For the nonoriented EF-E15 and EF-F15 films, there were no significant differences in the moduli in the two directions of the polymer at each level of RH ($p > 0.05$). In contrast, for the biaxially oriented EF-XL15 film, the modulus in the MD was significantly higher than that in the TD at a given RH ($p < 0.05$). The higher modulus in the machine direction may be attributed to the relatively higher stretching ratio of the film as compared to that in the transverse direction. Therefore, the biaxially oriented EVOH film appeared to be anisotropic based on the tensile moduli measurements.

The ethylene content of EVOH films was found to affect the modulus. The higher the ethylene content, the lower the modulus over the RH range of 0 to 75%. With differences in ethylene content, the cohesive energy density of the copolymer, which is dictated mainly by the intermolecular hydrogen bonds, is believed to change, thereby influencing the flexibility of the polymer chains. The EF-F15 film, with a lower ethylene content than the EF-E15 film, has a greater cohesive energy density, resulting in lowered film flexibility, as reflected by the higher tensile modulus below 75% RH. Above 75% RH, the modulus of the EF-F15 film decreased strongly and was lower than that of the EF-E15 film. Therefore, it may be concluded that the EF-F15 film is likely more

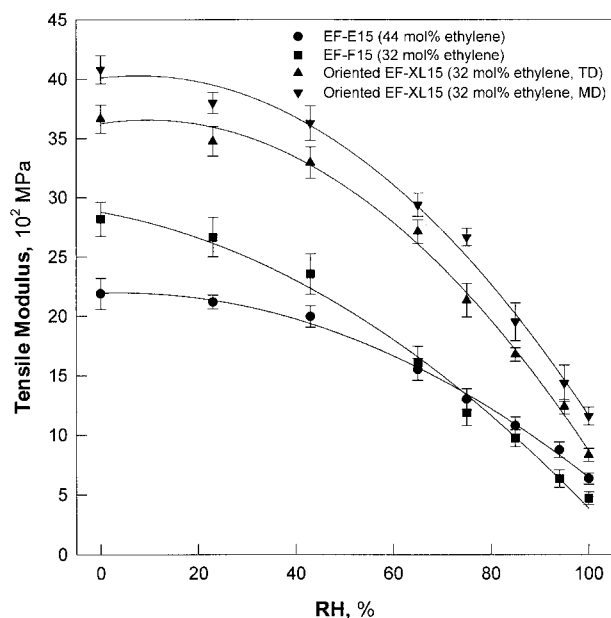


Figure 8 Tensile modulus for three EVOH films as functions of relative humidity.

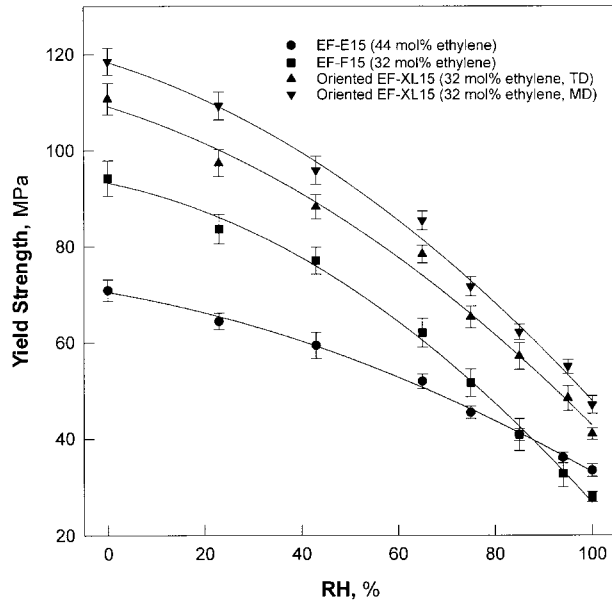


Figure 9 Yield strength for three EVOH films as functions of relative humidity.

sensitive to moisture and, possibly, was more severely plasticized under high RH conditions.

The modulus of glassy polymers can be greatly enhanced by molecular orientation of the polymer chains due to stress-induced crystallization during film stretching.³⁵ Figure 8 indicates that the biaxially oriented EF-XL15 film had a higher modulus in both transverse and machine directions than the nonoriented EVOH films. Yield strength of the three EVOH films shows a similar trend influenced by RH, ethylene content, and orientation (Fig. 9).

The substantial influence of RH on tensile moduli and yield strength of the polymer was attributed to depression of glass transition temperatures (T_g) resulting from the uptake of water by the polymer. The T_g values of EVOH films were found to be approximately 60°C at dry conditions but were depressed to below room temperatures when exposed to >75% RH.³⁶ This was the main contributor to the large decreases in tensile moduli and yield strength.

Elongation at Failure

For the nonoriented EF-E15 and EF-F15 films, different profiles of the elongation in the two directions were observed [Fig. 10(a) and (b)]. In the transverse direction, the polymer was very brittle at dry conditions and the samples broke immedi-

ately during film stretching. As RH increased, elongation increased rapidly and the films became more ductile. In the machine direction, although elongation increased as RH increased, the RH influence was less pronounced than in the TD. Moreover, at low RH, the elongation in the machine direction was higher than that in the TD. Beyond 70%, a reverse situation was observed. For the biaxially oriented EF-XL15 film, elongation in both directions increased linearly as RH increased. Through the entire range of RH from 0 to 100%, the elongation in the machine direction was always lower than that in the TD at a given RH, most likely due to a higher stretching ratio of the film in the machine direction during the orientation processes. As compared to the nonoriented EVOH films, the biaxially oriented EVOH film had lower elongation [Fig. 10(c)].

Ultimate Tensile Strength

Different patterns of ultimate tensile strength were observed for the nonoriented EF-E15 and EF-F15 films in the two directions [Fig. 11 (a) and

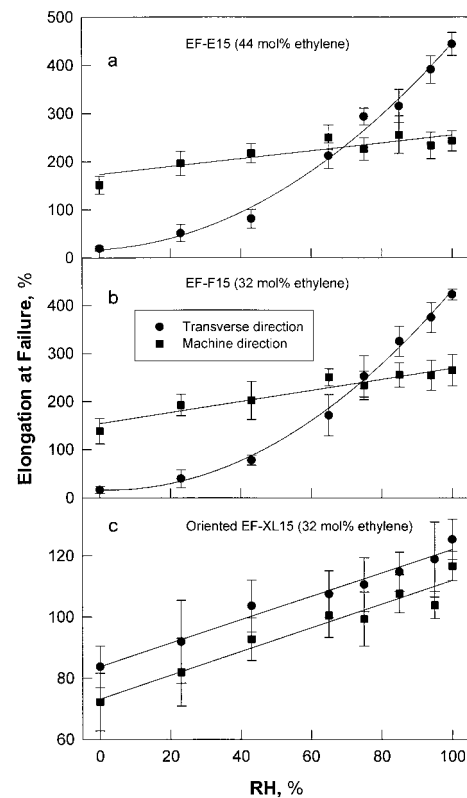


Figure 10 Elongation at failure of three EVOH films as a function of relative humidity.

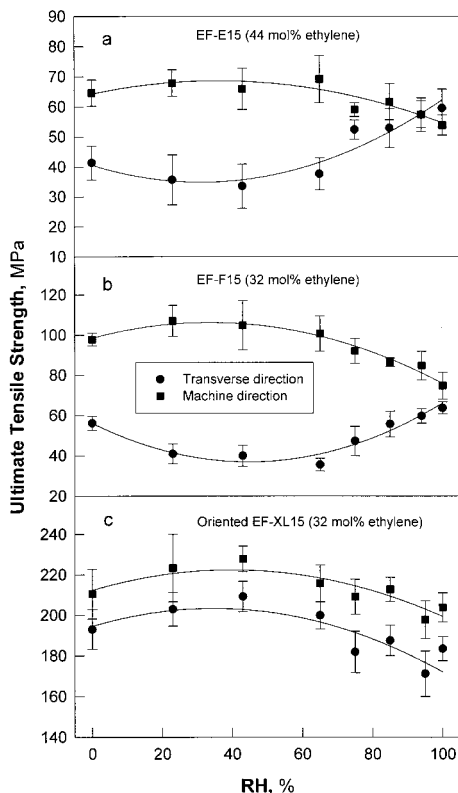


Figure 11 Ultimate tensile strength of three EVOH films as a function of relative humidity.

(b)]. In the transverse direction, ultimate tensile strength decreased as RH increased from 0 to 50% but increased with increasing RH above 50% RH conditions. In contrast, curves for the machine direction were concave to the RH axis. Different ultimate tensile strength profiles in the machine direction and in the transverse direction also indicated that the nonoriented EVOH films had an anisotropic structure.

The ultimate tensile strength of the biaxially oriented EF-XL15 film increased with the increase in RH from 0 to 40% and then decreased with increasing RH up to 100% [Fig. 11(c)]. The curves in the transverse and machine directions had a similar shape which was concave to the RH axis. Moreover, although the elongation at failure in the machine direction was less than in the transverse direction at a given RH [Fig. 10(c)], ultimate tensile strength was higher than in the transverse direction. A high-stretching ratio in the machine direction of the biaxially oriented film may have resulted in the enhanced tensile strength. Compared to the nonoriented EVOH films, the biaxially oriented EVOH film had much higher ultimate tensile strength than the nonori-

ented EVOH films, which is likely due to the greater molecular orientation of the oriented EVOH film.

CONCLUSION

The limonene vapor transmission rates of the EVOH and nylon 6,6 films were affected markedly by temperature and RH. In addition, the higher the ethylene content in the EVOH film, the lower the limonene permeation at high RH. Orientation of EVOH resulted in an improved barrier performance against limonene vapor. The nylon 6,6 film had much greater permeability coefficients for limonene than the EVOH films. Increasing RH resulted in substantial increases in the diffusion coefficients of limonene in EVOH and nylon 6,6 films, as determined at 35°C.

The tensile modulus and yield strength of the EVOH films decreased with increasing RH. This was attributed to the plasticization effect of water on the polymer. As RH increased, the T_g values of the EVOH films were depressed to lower temperatures and consequently the tensile modulus and yield strength at normal ambient temperatures were profoundly decreased. The polymer was relatively stiff and brittle at low RH conditions. However, when RH increased, the polymer became soft and ductile, resulting in high elongation at failure.

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