

Gas Barrier Changes and Morphological Alterations Induced by Retorting in Ethylene Vinyl Alcohol-Based Food Packaging Structures

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ABSTRACT: Ethylene vinyl alcohol (EVOH)-based packaging structures were analyzed in terms of both barrier properties and morphological alterations after a retorting process and as functions of ethylene content. From the results, it was found that the samples do have a substantial decrease in oxygen barrier properties and that the kinetics of recovery strongly depends on the copolymer ethylene fraction. A morphological deterioration was also observed as a result of retorting, particularly for packaging structures composed of EVOH copolymers of low ethylene contents.

However, the polymer morphology and barrier properties were restored after a dry thermal treatment of the retorted samples. Interestingly, preannealing of copolymers of low ethylene content rendered them more resistant to the retorting process by means of promoting both a more robust crystallinity and a lower water sorption capacity. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2192–2202, 2005

Key words: EVOH copolymers; barrier; food packaging; crystal structures; morphology

INTRODUCTION

Ethylene vinyl alcohol (EVOH) copolymers are excellent gas-barrier semicrystalline materials with very good chemical resistance and, as such, they are widely used in a number of packaging applications. One of the most widely implemented applications is that of an intermediate barrier layer in multilayer structures, to be used in various packaging designs for foodstuffs. The presence of EVOH in the packaging structure is key to food quality and safety because, for instance, it delays the ingress of oxygen, the agent responsible for a number of food deterioration processes.

The excellent barrier properties of EVOH copolymers derive from a high degree of crystallinity and the presence of hydroxyl groups in the polymer structure, which confer them with both high intermolecular and intramolecular cohesive energy and a low fractional free volume between the polymer chains available for the mass exchange of low molecular weight substances. On the other hand, these hydroxyl groups

make the materials highly hydrophilic, so that in the presence of water, their barrier performance is substantially reduced. Water molecules sorbed by EVOH in high relative humidity (RH) environments are believed to hydrogen bond to the hydroxyl groups present in the polymer and reduce the overall polymer self-association. Consequently, segmental mobility becomes greatly activated, thus facilitating diffusion of permeants.¹

As a result of the above, in many food packaging applications, multilayer structures are used that are composed of an intermediate layer of high-barrier EVOH sandwiched between at least two layers of hydrophobic materials such as poly(propylene) (PP), polyethylene (PE), polystyrene (PS), and so forth. These multilayer structures are usually made by coextrusion or coinjection processes.

EVOH is commercially available in various grades with different ratios of ethylene and vinyl alcohol. The copolymers are used in flexible as well as in rigid and semirigid packages. Some of these packaging designs are used to pack O₂-sensitive foods and beverages that undergo processes such as hot filling, aseptic packaging, or sterilization inside the package. During typical industrial sterilization processes, which make use of heated water vapor as the heat-transfer medium, it is believed that some of the pressurized water vapor is

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capable of traversing the external hydrophobic layers, sorb into, and subsequently plasticize the EVOH intermediate layer, leading to a decrease in barrier properties. In this context, many studies have been carried out to ascertain the effects of water sorption²⁻⁴ and retorting⁵⁻⁷ on the permeability and thermal properties of these copolymers. However, a search of the open literature reveals a lack of studies that focus on the potential morphological consequences of water sorption and sterilization for these polymers and their corresponding packaging structures. Over the last few years, several strategies have been devised to reduce the water sensitivity of EVOH, that is, blends of the copolymer with other materials,⁸⁻¹¹ chemical modification,¹² addition of desiccants,¹³ and even incorporation of nanoparticles on its structure.¹⁴ In a more recent paper,¹⁵ it was reported that water sorption at room temperature does lead to a partial melting of defective crystals and, upon retorting of EVOH monolayers, a dramatic deterioration of the copolymer crystallinity was observed by synchrotron X-ray analysis immediately above room temperature, which resulted in earlier melting of the material 83°C below its actual melting point. This deterioration was ascribed to pressurized water vapor sorbed in the amorphous phase, penetrating the crystalline phase through the interphase. It is very important to understand and control morphological alterations because they are also responsible for changes in barrier properties through factors such as crystallinity (impermeable phase to gases), tortuosity (or detour), and chain immobilization factors.¹⁶

In this article, we report and interpret changes in the oxygen permeability of multilayer structures, having EVOH as barrier layer, after different thermal treatments and as a function of the ethylene content. From the results obtained, methodologies are proposed that seek to avoid or reduce the dramatic effects of combined temperature and humidity treatments in typical retortable PP/EVOH/PP packaging structures.

EXPERIMENTAL

Materials

Six different grades of commercial ethylene vinyl alcohol (Soarnol[®]) copolymer, supplied by The Nippon Synthetic Chemical Industry Co., Ltd. (Nippon Gohsei, Japan), were analyzed: EVOH26, EVOH29, EVOH32, EVOH38, EVOH44, and EVOH48, where the numbers indicate the mole percentage of ethylene in the copolymer composition.

Films (~ 10 μm thick) of these EVOH materials were coextruded between poly(propylene) layers both with adhesive (typical commercial retortable multilayer structures, termed PP//EVOH//PP) and without adhesive (for easy delamination of the high-bar-

rier layer, termed PP/EVOH/PP). Unless otherwise stated, all samples were dried at 70°C for 1 week in a vacuum oven. Structures of the tested multilayer films were PP/EVOH/PP = 100/10/100 μm and PP//EVOH//PP = 90/10/10/10/90.

Thermal treatments

The materials were thermally treated under dry and humid conditions in a conventional oven (annealing) and in a sterilization autoclave (retorting), respectively. The standard treatment given to the samples, both in the oven and in the autoclave, was 120°C for 20 min. Other thermal conditions applied are specifically cited throughout the article.

Oxygen transmission rate

Oxygen transmission rate (O_2TR) measurements were performed in an OX-TRAN[®] 2/20 (Mocon Inc., Minneapolis, MN) at a temperature of 45°C and 0% RH. High-temperature assays were carried out to increase the permeability of the EVOH films and thus to measure it with higher certainty, given the very high barrier character of the materials with lower ethylene contents. O_2TR values are given instead of permeability coefficients because many of the samples measured were multilayer structures (PP//EVOH//PP). Because the thickness of the samples (always cut from the middle of the coextruded rolls section) was checked to be constant, the O_2TR values of the different specimens of the various samples were directly compared.

FTIR experiments

Transmission FTIR experiments were recorded within a N_2 -purged environment using model Tensor 37 equipment (Bruker, Darmstadt, Germany) with a resolution of 1 cm^{-1} .

SEM observation

For scanning electron microscopy (SEM) observation, the samples were fractured in liquid nitrogen and mounted on a sample holder. The fracture surface of the different samples was sputtered with Au/Pd in a vacuum. The SEM microphotographs (S4100, Hitachi, Osaka, Japan) were taken with an accelerating voltage of 10 keV on the sample thickness.

DSC experiments

DSC experiments were carried out using a Perkin-Elmer DSC-7 calorimeter (Perkin-Elmer Cetus Instruments, Norwalk, CT). The rate of both heating and cooling for the runs was 10°C/min, where a typical

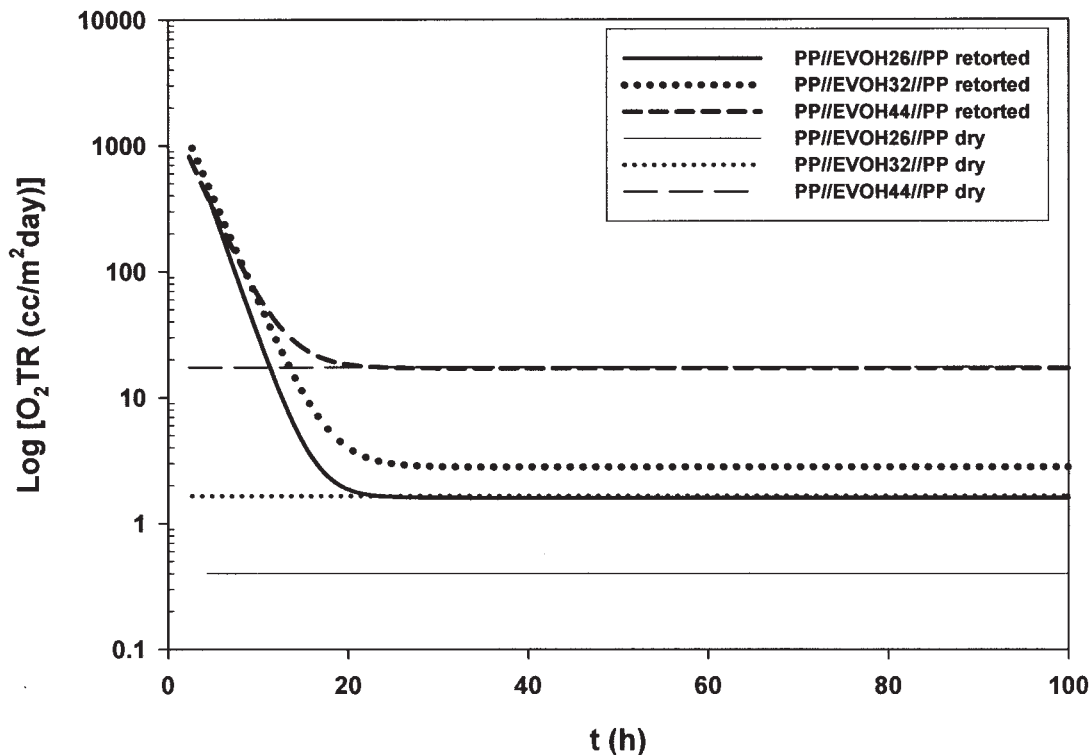


Figure 1 Oxygen transmission rate of retorted multilayer structures (PP//EVOH//PP) versus time after retorting and O_2TR of the dry analogous structures.

sample weight was around 8 mg. Calibration was performed using an indium sample. All tests were carried out, at least, in duplicate.

RESULTS AND DISCUSSION

Oxygen transmission rate

Figure 1 shows, as an example, the O_2TR evolution after retorting of three of the six multilayer materials analyzed versus the O_2TR values of the dry analogue. From this figure, it can be first seen that the dry O_2TR of EVOH increases with increasing ethylene content in the copolymer, as expected and in agreement with previous understanding of these materials. In this figure, it can also be observed that the barrier properties of the different EVOH materials, irrespective of their ethylene content, are substantially deteriorated immediately after retorting. From the results, however, it appears that, after approximately 30 h of testing, a considerably low O_2TR value was reached for the materials, even though it was also expected that the kinetics of recovery would clearly have been slower had the experiments been carried out at room temperature. From the previous rationalization of this phenomenon, it is considered that water vapor penetrates the PP layers and plasticizes the intermediate EVOH barrier layer with a subsequent depletion in the overall barrier properties of the packaging structures. After

sterilization, sorbed water is progressively eliminated from the copolymer structure; this phenomenon is reflected by observation of a continuous decrease in permeability with time. This process of barrier recovery can be properly fitted to a simple exponential decay equation, expressed as

$$OTR(t) = OTR_{\infty} + a e^{(-bt)}$$

where a is approximately the transmission rate value of a freshly retorted sample and OTR_{∞} is that reached by the retorted sample at equilibrium. The parameter b is related to the kinetics of the OTR recovery: the lower the value, the slower the process. The parameters of the equation for the curves shown in Figure 1 are presented in Table I. As can be seen in Table I, the values of those parameters are, as expected, related to the ethylene content of the copolymers. With increas-

TABLE I
Curve-Fitting Parameters for the Permeability Recovery Data of the Multilayer Structures PP/EVOH26/PP, PP/EVOH32/PP, and PP/EVOH44/PP to Eq. (1)

Blend	OTR_{∞}	OTR_0	b	R^2
PP//EVOH26//PP	1.6	3222.28	0.4706	0.9863
PP//EVOH32//PP	2.8	2681.87	0.3866	0.9809
PP//EVOH44//PP	17	1885.14	0.3676	0.9755

TABLE II
Oxygen Transmission Rate ($\text{cm}^3 \text{m}^{-2} \text{day}^{-1}$) of the Various EVOH Grades
After Different Treatments Measured at 45°C

Specimen	EVOH26	EVOH29	EVOH32	EVOH38	EVOH44	EVOH48
EVOH dry	0.45	0.82	1.97	5.35	17.55	32.00
EVOH retorted and dry	0.43	0.62	1.65	4.00	11.40	22.00
PP//EVOH//PP dry	0.40	0.70	1.65	5.00	17.37	34.30
PP//EVOH//PP retorted and dry	0.35	0.73	1.60	3.50	12.95	29.00
PP//EVOH//PP oven	0.37	0.60	1.57	5.32	18.45	35.50
PP//EVOH//PP ret (150 h) ^a	1.62	1.68	2.80	4.96	17.00	28.55

^a O₂TR of multilayer structures after 150 h after retorting.

ing ethylene content, the values of *a* and *b* decrease, whereas OTR_∞ values increase.

Although the equation that describes this process appears to fit well every multilayer material studied, substantial differences are observed with respect to the final O₂TR value achieved. Whereas for the case of the EVOH44 the permeability value of the dry sample was reached after nearly 20 h after retorting, for the other copolymers with higher content in vinyl alcohol, even after 300 h of continuous testing at 45°C in the transmission rate instrument analyzer, the barrier properties were not fully recovered. Moreover, the lower the ethylene content of the EVOH sample, the higher the gap left (see Fig. 1) between the untreated and the retorted specimens. Most of the works reporting about oxygen permeability changes attributed to retorting treatments were carried out in EVOH32 (the most widely used commercial composition) and, as such, the behavior of other EVOH grades was not previously reported in published research articles. From experiments in all samples, it was found (see Table II) that the permeability plateau value reached after retorting appears to differ from that of the untreated specimens for samples with ethylene contents < 38%, although it does lead to an improved barrier property, by 20 h after retorting, for EVOH44 and EVOH48.

In subsequent experiments, all samples, PP//EVOH//PP and PP/EVOH//PP, were retorted and then dried at 70°C for 1 week in a vacuum oven. The O₂TR results measured on these retorted and dry samples are shown in Table II, together with the oxygen transmission rate of dry and sterilized multilayer structures after 150 h in the O₂TR instrument. In the case of the PP/EVOH//PP structures, the specimens were delaminated after retorting and only the EVOH layer was tested. Fortunately, the multilayer samples were well able to withstand the retorting process without delamination throughout the treatment. Samples that were accidentally delaminated during or before the treatment were severely damaged during retorting and were consequently discarded. Results on the effect of temperature and humidity on the structure of bare EVOH monolayers were reported in an earlier work.¹⁵

Surprisingly, the O₂TR values of the retorted and then dried samples were found to be superior to those of the untreated ones, where this improvement was more pronounced for those copolymers with higher ethylene content. Also not entirely expected was the general observation that the samples with higher ethylene contents (EVOH38, EVOH44, and EVOH48), which were annealed in the oven at 120°C for 20 min, did not show improved performance compared to that of samples retorted at 120°C and then vacuum dried. From the above results, there appear to be additional factors that influence barrier properties than that of just the well-reported water-induced plasticization process.

Morphological characterization

In a novel approach to the study of the retorting effects on EVOH copolymers, it was thought that potential structural modifications promoted by the humid thermal treatment could play a role in these permeability changes. This was further justified by observations from a previous investigation, in which the combination of temperature and humidity factors was found to discernibly deteriorate the structure of these materials upon direct exposure. From this latter work, it was also amply shown that the FTIR spectroscopy technique is an appropriate tool to study morphological alterations in these materials because of its high sensitivity to detect both crystallinity alterations through the use of the 1140 cm^{-1} band and the presence of humidity in the sample through observation of the OH in-plane bending band at 1650 cm^{-1} . The 1140 cm^{-1} band is likely attributable to C—O—C stretching or to C—C stretching coupled with a C—O stretching mode. The absorbance of this band (divided by that of the internal standard at 1333 cm^{-1}) can thus give us an indication of potential alterations in crystallinity after the various treatments, irrespective of differences in optical path and of minor thickness variations between different specimens.

As an example of the sensitivity of this band in determining crystallinity changes on the samples, Figure 2 shows the effect of a stepwise annealing process on the infrared spectrum of an EVOH26 sample. To

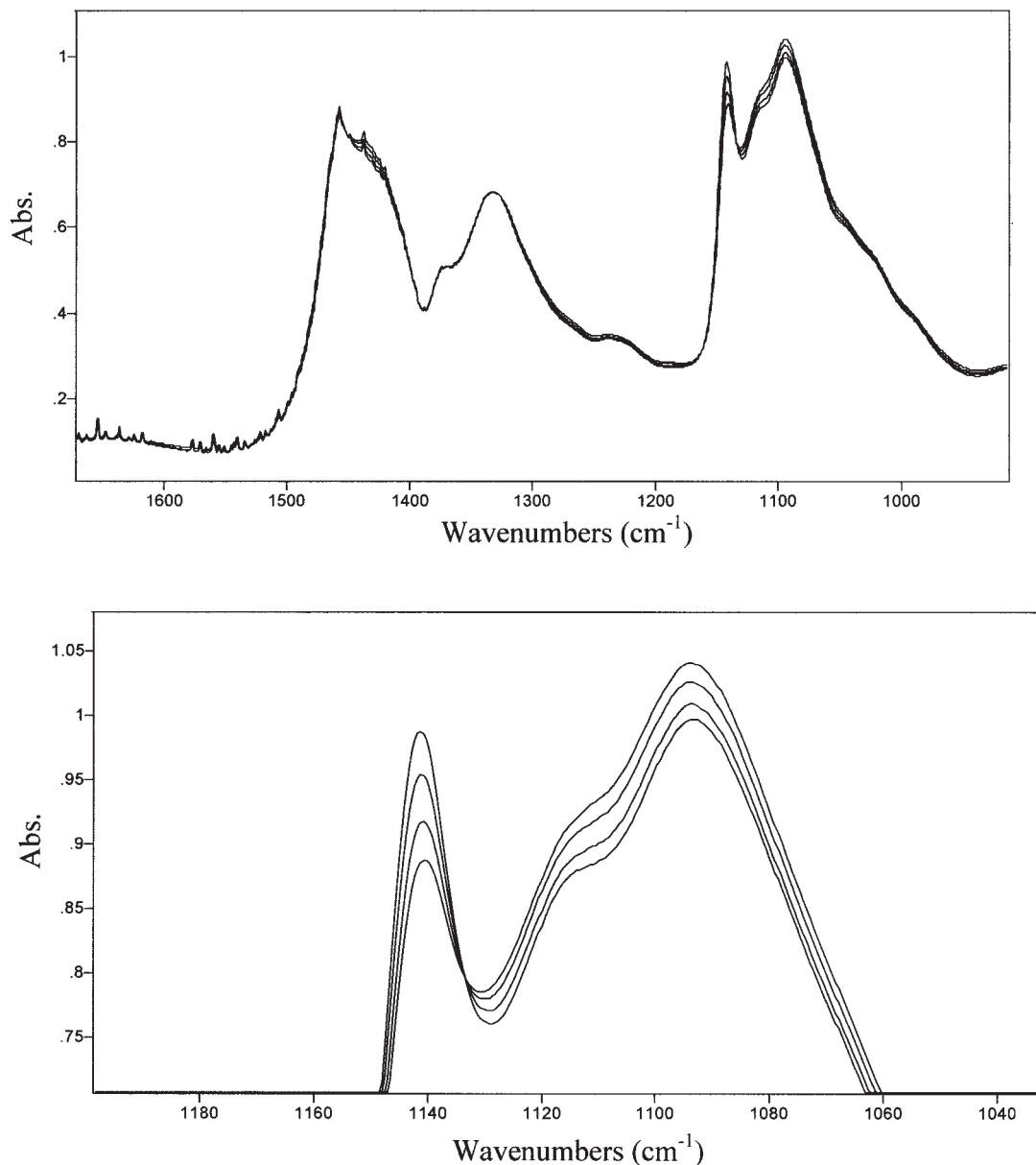


Figure 2 FTIR spectra of an EVOH26 specimens annealed at various temperatures (top) and magnification of the range of the crystallinity band at 1140 cm^{-1} .

obtain this figure, a single specimen of the polymer was cumulatively annealed at 100, 120, 140, and 160°C for 20 min directly onto the FTIR sample holder (to avoid changes in sample thickness or optical path) and, between annealing steps, it was taken out of the oven and FTIR recorded. It is well known that the application of a thermal treatment below the melting point of semicrystalline polymeric materials—particularly above the α -relaxation of the material—favors the mobility of chain segments at the crystals' interphase and within the crystals toward the development of a more stable and thicker crystalline morphology, a phenomenon known as annealing. Therefore, this phenomenon leads to the elimination of defects through

partial melting and recrystallization of the most ill defined (less metastable) crystals, generating a more regular stacking of the lamellae and higher crystallinity. As a result, in Figure 2 it is observed that, as the annealing temperature increases, the crystallinity of the sample also increases and this is represented by the increase of the 1140 cm^{-1} band of the FTIR spectrum.

Figure 3 shows, as an example, FTIR spectra obtained for dry, retorted, and retorted and dried PP/EVOH32/PP specimens. In agreement with the previous understanding of the retorting effects, it is now unmistakably seen that, as stated before, during the retorting process some moisture traverses the PP lay-

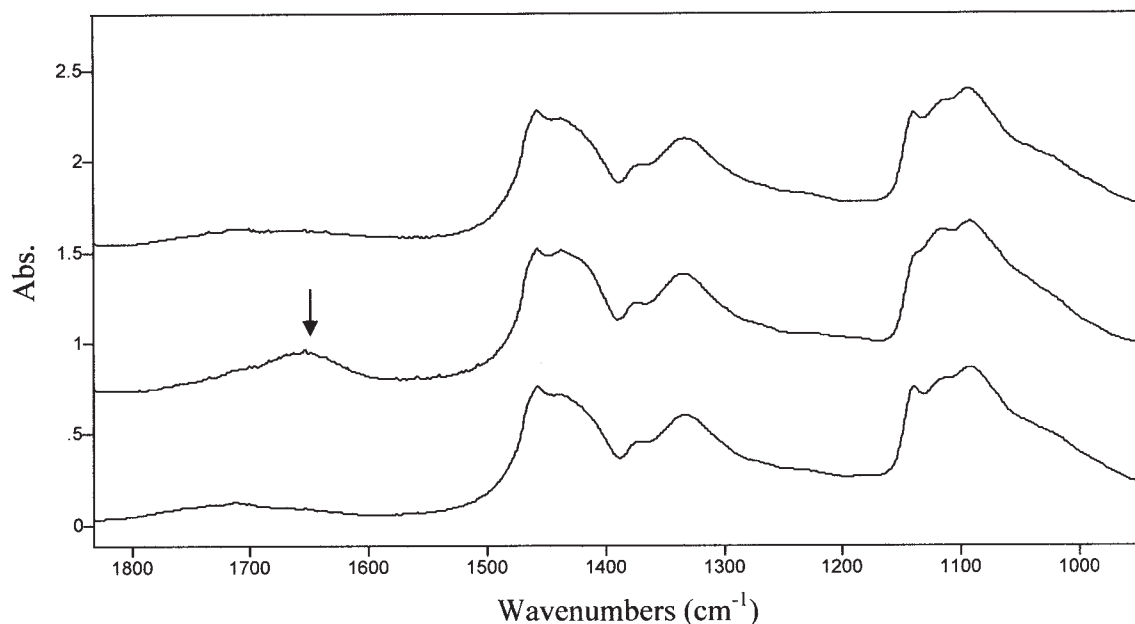


Figure 3 FTIR spectra of EVOH32 specimens (from top to bottom): untreated, retorted, and retorted and then dried, delaminated from PP/EVOH/PP structures.

ers and sorbs onto the EVOH intermediate barrier layer, as is clearly observed from the FTIR spectrum of the retorted sample (see arrow in Fig. 3). However, the water band is not so clearly seen in the dried samples, suggesting that drying is an effective process in reducing sorption-induced polymer plasticization. Furthermore, from observation of Figure 3, it can also be seen that upon retorting the crystallinity band at 1140 cm^{-1} decreases, an effect that indicates that the crystallinity of the sample has undoubtedly decreased. On the other hand, the retorted and then dried sample distinctly shows the highest absorbance for the crystallinity band, even higher than that of the unmodified sample, an observation that confirms that the crystallinity is the highest for this specimen. Thus, pressurized water vapor, which penetrated the multilayer structure during retorting, is thought to melt and disrupt part of the EVOH crystalline morphology. The subsequent annealing process in the vacuum oven at 70°C for 1 week allowed the polymer chains to reorganize and anneal, giving rise to a significantly improved crystalline structure.

These observations appear to be supported by SEM microphotographs taken on the thickness of EVOH32 specimens. Figure 4 suggests that the polymer two-phase morphology can be revealed by this technique on $75\text{-}\mu\text{m}$ specimens without the need for etching. The spherical particles observed in some of the photomicrographs were previously attributed to crystalline domains by Matsuyama et al.¹⁷ In Figure 4, the morphology of the untreated specimen is shown to be finer near to the surface [Fig. 4(c)], likely the result of faster cooling after coextrusion, and coarser (attrib-

uted to thicker crystals) at the core of the film. In Figure 4(b), this two-phase morphology is seen to be more finely averaged and, thus, more homogeneous after retorting followed by drying at 70°C . Annealing at 120 and 160°C leads to a more homogeneous and, apparently, coarser granular morphology, suggesting higher crystallinity by crystal thickening. Figure 5 unambiguously reveals that the $10\text{-}\mu\text{m}$ film is characterized by a much finer phase morphology than that of the $75\text{-}\mu\text{m}$ specimens seen in Figure 4. The micrographs in Figure 5 indicate that the two-phase morphology is more clearly resolved in retorted and then dried samples and in annealed specimens, and is less defined (with a less-regular crystalline morphology) in the untreated specimen. Figure 5(b) clearly shows the presence of extensive voiding in the retorted sample, presumably created by the ingress of water vapor during retorting, which appears to distort the polymer morphology and disrupts the crystallinity.

The above observations can thus help explain the lower O_2TR values measured for the retorted and then dried samples in Table II, compared to those of the untreated specimens, on the bases of both an increase in crystallinity and the more homogeneous and robust phase morphology attained: this phenomenon is explained by the fact that crystals are, in general, impermeable to the transport of most low molecular weight permeants and, consequently, an increase in crystallinity usually results in an increase in barrier properties. Nevertheless, other particular morphological effects and features, including crystal shape, size, and orientation distribution,¹⁶ can also have a significant impact on barrier properties and may thus play a role

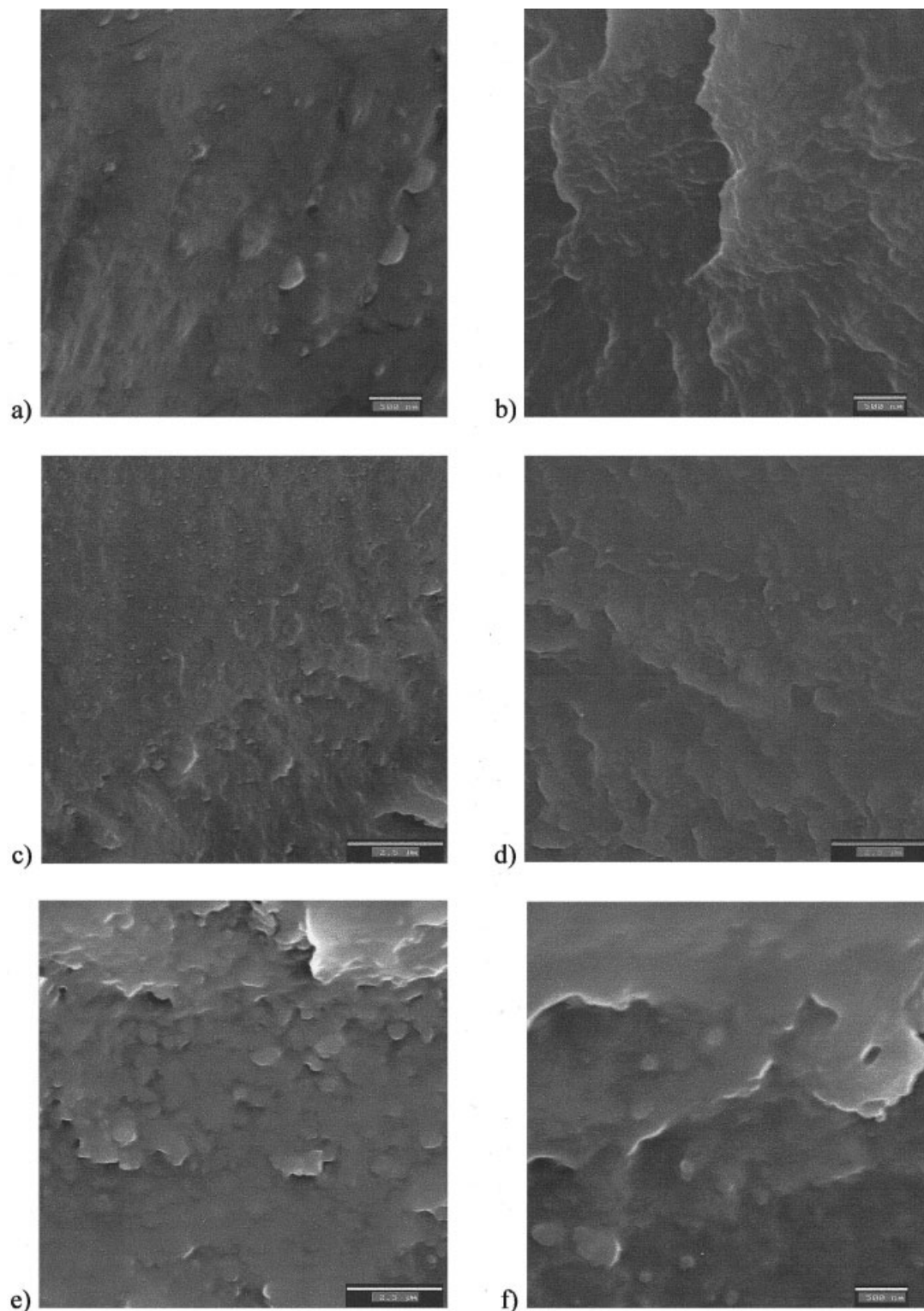


Figure 4 SEM micrographs of EVOH32 (75 μm) specimens: (a) untreated, (b) retorted and then dried, (c) untreated showing a skin/core morphology difference, (d) annealed at 120°C for 20 min, (e) and (f) annealed at 160°C for 20 min.

in explaining some of the small permeability variations observed between annealed and retorted and then dry specimens. Thus, crystallinity and permeability do not necessarily follow a linear relationship.²¹

For a given crystallinity, phase morphology—mainly through tortuosity and chain immobilization factors—can lead to unexpected outcomes for the barrier results.

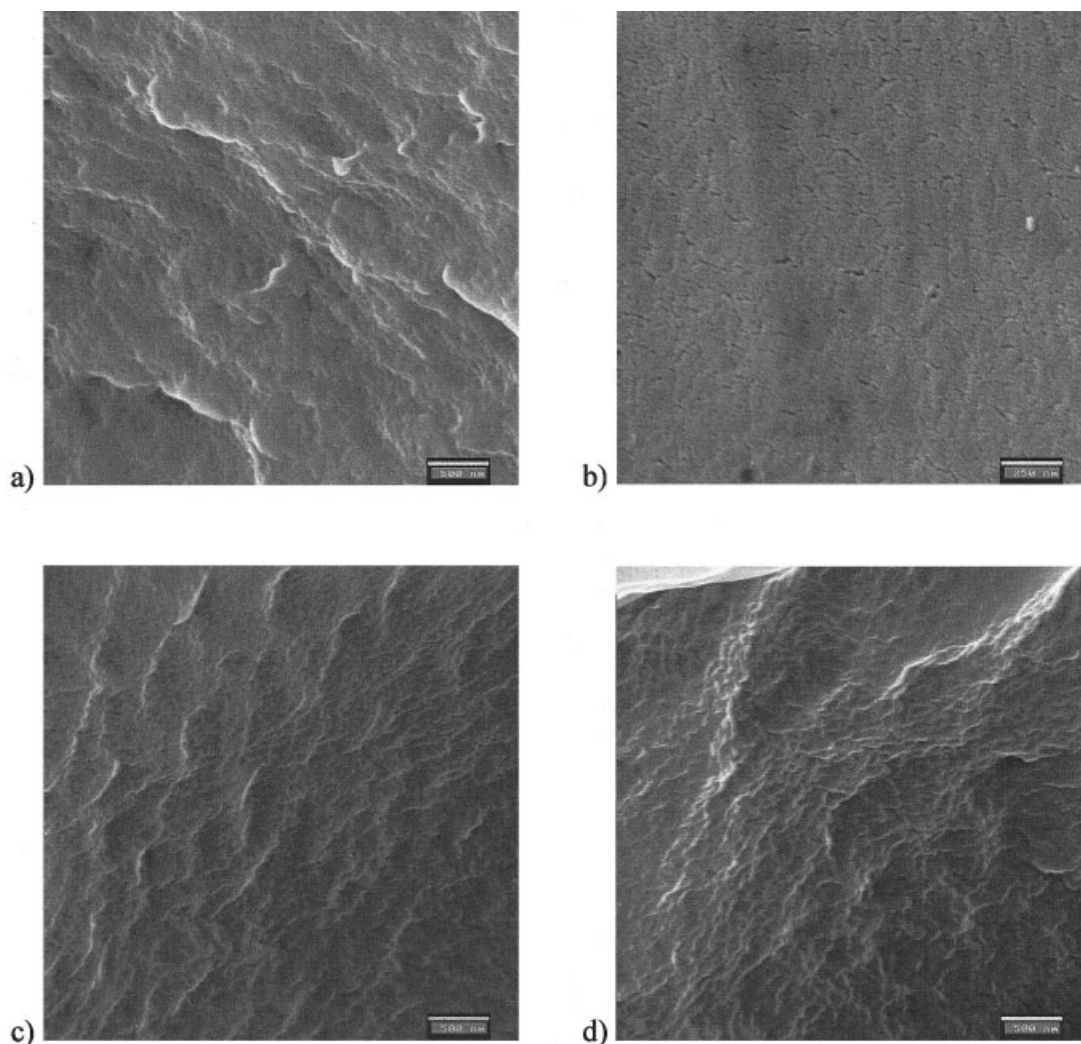


Figure 5 SEM micrographs of EVOH32 (10 μm) specimens: (a) untreated, (b) retorted, (c) retorted and then dried, and (d) annealed at 160°C for 20 min.

FTIR and morphological results can also help to explain why a total recovery in barrier properties after retorting cannot be achieved (see Fig. 1) for the most hydrophilic samples. This is explained by the morphological deterioration sustained by the material during the humid thermal treatment. However, and as opposed to this behavior, the barrier properties of the higher ethylene content copolymers (i.e., EVOH38, EVOH44, and EVOH48) seemed to improve after recovery from retorting. This change in trend is possibly related to the smaller morphological deterioration sustained by these latter materials during retorting (see later in text). However, it is difficult to understand—on the sole account of this effect—an improvement in barrier properties, unless a more favorable morphology with respect to permeability is achieved after retorting. Nevertheless, it should be kept in mind that higher ethylene content copolymers have a much lower oxygen barrier and thus other circumstantial effects can have a stronger impact on the barrier per-

formance of the materials. For example, one explanation for the cited observation could be based on results from a previous work, which reported a maximum in barrier properties for these copolymers at about 30%RH.¹⁸ Thus, it was reported that moisture, present at this low sorption level, is thought to block the free volume of the polymer by hydrogen bonding, in a regime that extends between the dry state and the extensive polymer plasticization occurring at medium and high RH. Consequently, the observed improvement in barrier properties for these samples, arising after recovery from retorting, could be attributed to the sample falling in the optimum barrier regime. Although this optimum barrier regime also exists for the low ethylene content copolymers, these samples may either not fall on it or/and the more extensive crystallinity deterioration seen for these materials may override the cited positive effect. Another potential factor to be considered is the potential modification of the structural poly(propylene) layers during retorting.

TABLE III
DSC Results and Oxygen Transmission Rate
for Treated Poly(propylene) Specimens

Specimen	T_m (°C)	ΔH (J/g)	Peak width (°C)	OTR (cm ³ /m ⁻² /day ⁻¹)
PP nontreated	164.3	82.3	14.9	23.375
PP oven	164.1	94.4	16.4	—
PP retorted	163.7	91.1	17.2	23.125

DSC experiments showed higher crystallinity (reflected in a higher melting enthalpy) after retorting for the poly(propylene) (see Table III). Consequently, an increase in crystallinity for the thicker structural layers after retorting may also contribute to produce lower permeability for the retorted sample after recovery. Nevertheless, Table III also shows that the permeability improvement undergone by the poly(propylene) structural layers is only of about 1% and thus it cannot account for the more significant reductions observed in the multilayer structure.

Another curious observation in Table II for these higher ethylene content samples is the higher permeability of annealed specimens versus that of specimens that were untreated or retorted and then dried. For these annealed samples the crystallinity was found to be higher by FTIR compared to that of samples that were untreated and retorted and then dried (results not shown). The structure and thermal characteristics of annealed poly(propylene) were also analyzed and the enthalpy of fusion of this specimen was found to be higher than that for untreated and retorted PP (see Table III). The PP layers were also analyzed using FTIR. The absorbance peak at 841 cm⁻¹ was identified

TABLE IV
FTIR Absorbance of the 1440 cm⁻¹ Peak Divided by the
Absorbance of the 1333 cm⁻¹ Reference Peak

Material	Not		Annealed		
	treated	Annealed	Retorted	and retorted	Retorted and dry
EVOH26	1.26	1.45	1.13	1.25	1.28
EVOH29	1.25	1.43	1.12	1.20	1.28
EVOH32	1.24	1.40	1.14	1.16	1.26
EVOH38	1.21	1.38	1.19	1.19	1.25
EVOH44	1.21	1.34	1.19	1.19	1.24

in the literature¹⁹ as a crystalline peak and the peak at 973 cm⁻¹ was used as an internal standard because it has proved to be insensitive to chain conformation, that is, to the amorphous/crystalline ratio.^{19,20} Figure 6 confirms the previous DSC results and suggests that the higher crystallinity is for the annealed sample, followed closely by the retorted specimen and by the untreated specimen. The crystallinity content thus does not explain the unexpected barrier behavior for annealed EVOH38, EVOH44, and EVOH48. For these samples either a relative humidity or a morphology differential argument must be considered, as explained above.

From the above results and from an applied problem-solving perspective, it is apparent that a drying step after sterilization of the package can restore or even improve the barrier performance of the materials by removing sorbed moisture and by rebuilding a more favorable morphology. Whether this additional step is viable at an industrial scale is beyond the scope of the present study. Nevertheless, being aware of the

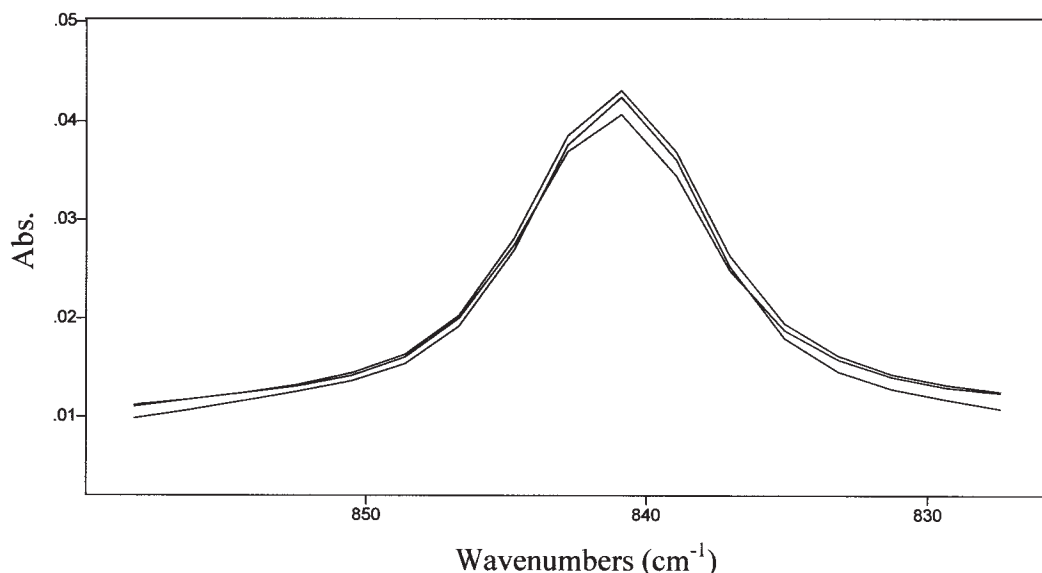


Figure 6 Normalized crystallinity band at 841 cm⁻¹ of poly(propylene) specimens (from higher to lower intensity) heated in the oven at 120°C for 20 min, retorted, and untreated.

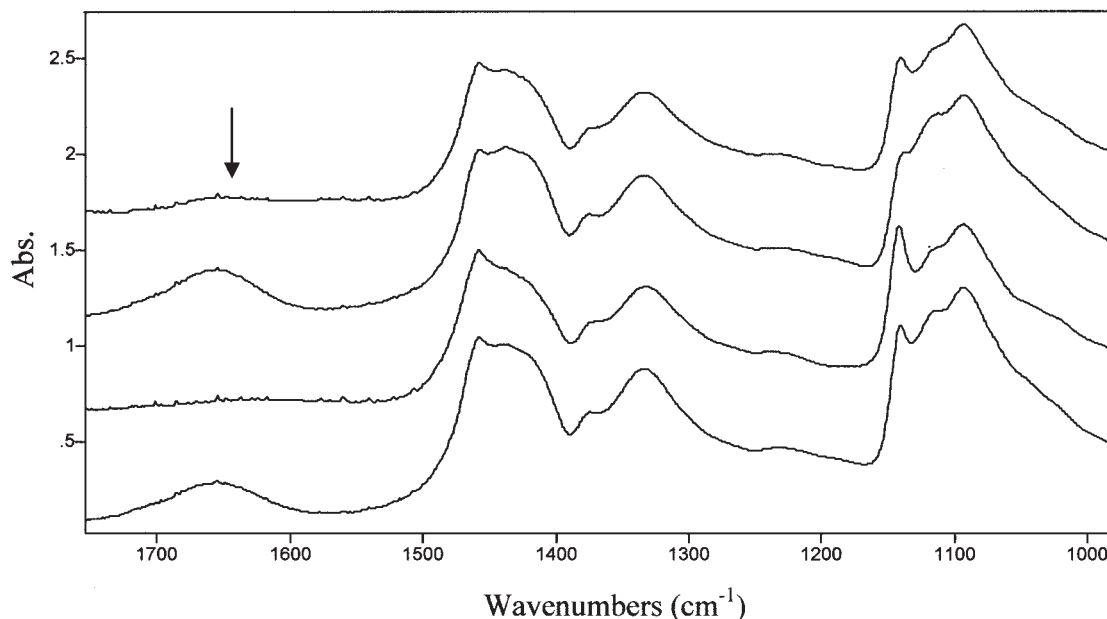


Figure 7 FTIR spectra of EVOH26 specimens (from top to bottom): untreated, retorted, annealed at 160°C for 20 min, and annealed and then retorted.

implications of crystallinity and its morphology on barrier properties and of the ability of water sorption to modify the polymer morphology, it was considered worthwhile to study the influence of the initial thermal history on the performance of materials upon retorting. To do so, specimens of all samples were subjected to an annealing treatment before the retorting process and were then analyzed in their resistance against morphology alterations upon retorting.

To validate the adequacy of this methodology, the different multilayer structures were first annealed for 20 min in an oven at a selected optimum temperature that had previously been determined through FTIR (160°C for the EVOH26, EVOH29, EVOH32, and EVOH38, and 140°C for EVOH44 and EVOH48); then, the specimens were retorted in the autoclave, delaminated, and the EVOH layer FTIR recorded. The optimum temperature was set at a temperature beyond

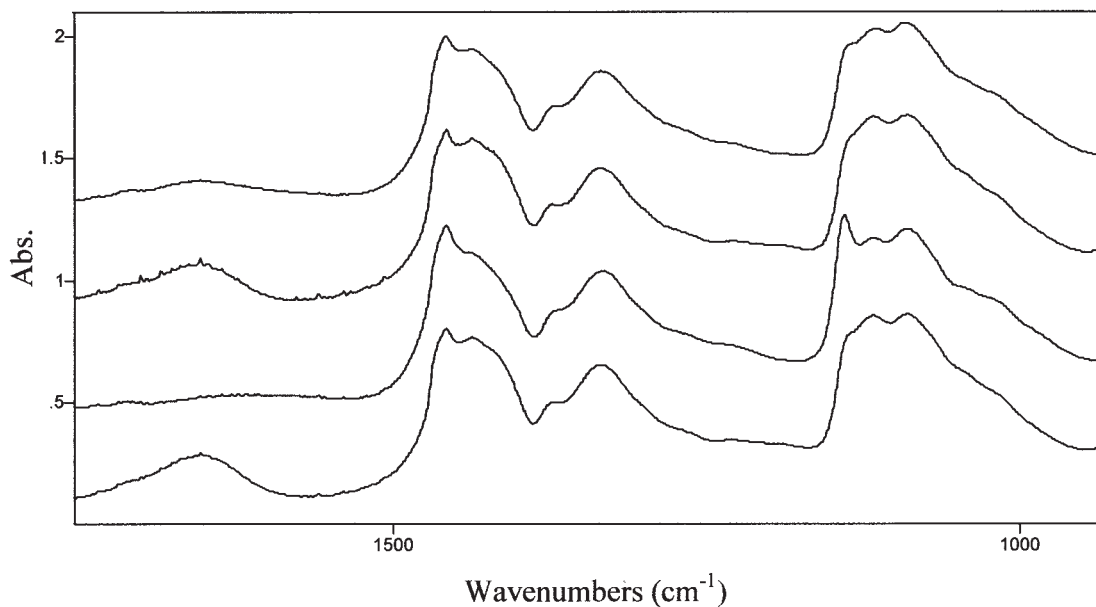


Figure 8 FTIR spectra of EVOH38 specimens (from top to bottom): untreated, retorted, annealed at 160°C for 20 min, and annealed and then retorted.

which crystallinity was seen to decrease through annealing resulting from extensive melting and fast recrystallization. The rationale behind this annealing experiment was to provide the most adequate polymer morphology in terms of crystallinity content and robustness (i.e., higher crystalline density) before retorting. Variations in crystallinity were estimated through the ratio of the absorbance of the crystallinity band at 1140 cm^{-1} to that of the band at 1333 cm^{-1} . The values of this ratio for the various copolymer grades and thermal histories are displayed in Table IV. From the results, it can be seen that preannealed EVOH26, EVOH29, and EVOH32 specimens can attain a higher level of crystallinity after retorting than that of retorted-only specimens. In fact, preannealed sample EVOH26 (see Fig. 7) even shows a degree of crystallinity after retorting similar to that of the untreated specimen (dried under vacuum at 70°C for 1 week). For EVOH38, EVOH44, and EVOH48 (see Fig. 8 for EVOH38), prior annealing of the specimens did not lead to improved morphology compared to that of untreated specimens. Figure 7 also shows that after sterilization of annealed EVOH26, there is less water sorbed in the structure of the polymer than that in the untreated specimen after retorting. This is reflected by the lower intensity of the 1658 cm^{-1} in-plane OH bending band of water.

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