

Barrier Resistance of Polyethylene, Polyethylene/Modified Polyamide, and Polyethylene/Blends of Modified Polyamide and Ethylene Vinyl Alcohol Bottles Against Permeation of Polar and Nonpolar Mixed Solvents

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Received 27 February 2004; accepted 28 December 2004

DOI 10.1002/app.21837

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The main objective of this study is to investigate the barrier properties and mechanisms of polyethylene (PE), PE/modified polyamide (MPA), and PE/blends of MPA and ethylene vinyl alcohol copolymer (MPAEVOH) bottles against permeation of polar/nonpolar (acetone/white spirit) mixed solvents. The mixed solvent permeation resistance improves dramatically after blending MPA and MPAEVOH barrier resins in PE matrices during blow molding. By using the proper MPAEVOH compositions, the white spirit permeation rate of PE/MPAEVOH bottles at 40°C can be about 145 times slower than that of the PE bottle specimen; however, it is still 2.5 times faster than that of the PE/MPA bottles. In contrast, the rate of polar acetone solvent permeation through the PE bottle is much slower than that of white spirit and only slightly faster than that through the PE/MPA and PE/MPAEVOH bottle specimens. In contrast, the permeation rates of acetone/white spirit mixed solvents into PE/MPA bottles are at least 20–60 times faster than the summation permeation rates calculated using the

simple mixing rule when the acetone contents in the mixed solvents are between 10 and 70 wt %. It is somewhat interesting that, after blending the proper amounts of EVOH in MPA, the mixed solvent permeation rates of PE/MPAEVOH bottles are dramatically reduced and are very close to the summation permeation rates calculated using the simple mixing rule when the acetone contents are in the particular “window” range. These interesting barrier properties of PE/MPA and PE/MPAEVOH bottle specimens were investigated in terms of the free volumes, barrier properties, molecular interactions in the amorphous phases of the barrier resins, and their resulting morphological structures that present in their corresponding bottles. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1333–1344, 2005

Key words: barrier resistance; polyethylene; polyamide; ethylene vinyl alcohol; polar and nonpolar mixed solvents; compatibilizer precursor

INTRODUCTION

It is well known that organic liquids such as xylene, white spirits, cleaning naphtha, gasoline, and many other pure and/or mixed hydrocarbon solvents can easily permeate through polyethylene (PE) and polypropylene containers; such permeation results in pollution, safety, and health problems. A “laminar-blend–blow-molding process” forms a layered structure containing numerous discontinuous, overlapping platelets of barrier resins such as polyamide (PA), poly(vinyl alcohol) (PVA), and/or ethylene vinyl alcohol copolymers (EVOH) in a PE matrix, which is one of the well-proven barrier technologies to enhance the resistance of PE containers to hydrocarbon permeation.^{1–3} Because PE/PA, PE/PVA, and PA/EVOH

blends are thermodynamically immiscible and mechanically incompatible, compatibilizer precursor (CP) resins have often been used to improve the interfacial properties between PE and PA, PVA, and/or EVOH, as well as to enhance the barrier properties of PE/PA/CP blends. These heterogeneous laminar blends exhibit significantly higher permeation barrier properties than the conventional homogeneous blends associated with uniform dispersed PA within the PE matrix.^{4–7}

It is generally recognized that the barrier properties of PE/PA/CP laminar-blend bottles greatly depend on the manner of blending and on the resulting morphology.^{1–4,8–11} Our latest studies^{12–15} indicated that the type and content of CP and PA present in a modified PA (MPA) have significant effects on the barrier, morphological, and rheological properties of MPA resins and the corresponding PE/MPA blends. In addition, the melt shear viscosities of PE and MPA were found to exhibit a significant influence on the defor-

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mation and morphology of MPA during the blow-molding process of PE/MPA blends. Clearly defined laminar structures of MPA are always observed at some particular values of the melt shear viscosity ratios of MPA to PE. Such clearly defined laminar structures often accompany the highest permeation resistance to xylene.¹⁶⁻¹⁸ By using proper compositions and processing conditions,^{18,19} the xylene and white spirit permeation resistance of PE/MPA bottles at 28 and 40°C were improved by about 250 and 350 times that of pure PE bottles, respectively.¹⁸⁻²⁰ Further investigation²¹ found that these laminar-blend structured bottles exhibited excellent permeation resistance even against mixtures of nonpolar hydrocarbon solvents (e.g., gasoline). By using proper MPA compositions and annealing treatment,²² the gasoline permeation resistance of the PE/MPA bottle at 40°C was improved by about 190 times that of pure PE bottles. Somewhat surprisingly, dramatically poor permeation resistance was found²³ on these PE/MPA laminar-blend structured bottles filled with mixtures of polar and nonpolar white spirit solvents. For instance, the permeation rates of the ethyl glycol ethyl ether (EGEE) and white spirit mixed solvents of PE/MPA bottles are at least 18 times faster than the summation permeation rates calculated using the simple mixing rule when the EGEE contents present in the mixed solvents are between 10 and 70 wt %. In contrast, it is worth noting that the gasoline permeation resistance of PE/MPA laminar-blend structured bottles can be further improved by blending the proper amounts of EVOH in MPA. In fact, the gasoline permeation rates of PE/MPA and EVOH copolymer blend (PE/MPAEVOH) bottles can be about 3 times slower than those of the PE/MPA bottles prepared using the optimum composition and processing conditions.

The main objective of this study is to investigate the barrier properties and mechanisms of the barrier properties of PE/MPAEVOH bottles against polar acetone/nonpolar white spirit mixed solvent permeation and to optimize the compositions of MPAEVOH to further enhance their mixed solvent barrier properties. In fact, by using proper MPAEVOH compositions, the acetone/white spirit mixed solvent permeation resistance of PE/MPAEVOH bottles is dramatically better than that of PE/MPA bottles when the acetone contents present in the mixed solvents are in the particular "window" range. Possible mechanisms accounting for these interesting barrier properties of PE/MPAEVOH bottles are proposed.

EXPERIMENTAL

Materials and sample preparation

The type of PA used in this study is nylon 6 (Sunylon 6N), which was obtained from Formosa Chemicals

TABLE I
Compositions of MPAEVOH Resins

Samples	MPA (%)	EVOH (%)
MPA ₁ EVOH ₂	33.33	66.67
MPA ₂ EVOH ₁	66.67	33.33
MPA ₄ EVOH ₁	80.00	20.00
MPA ₅ EVOH ₁	83.33	16.67
MPA ₇ EVOH ₁	87.50	12.50
MPA ₉ EVOH ₁	90.00	10.00

and Fiber Corporation (Chughua, Taiwan). The CP used in this study is a zinc-neutralized ethylene/acrylic acid copolymer, which was kindly supplied by Formosa Chemicals and Fiber Corporation. The MPA resin was prepared by reactive extrusion of the melt blending of CP and PA. The PE (high-density PE, Taisox 9003), EVOH with 32 mol % ethylene contents (Eval F104), and antioxidant (Irganox B225) used in this study were obtained from Formosa Plastic Corporation (Taipei, Taiwan), Kuraray Co. Ltd. (Osaka, Japan) and Ciba-Geigy Corporation (Basel, Switzerland), respectively.

Before melt blending, PA and CP were dried at 80°C for 16 h and at 60°C for 8 h, respectively. About 1500 ppm of antioxidant was dry blended with the dried components of PA/CP at an 85:15 weight ratio and then fed into an Ekegai PCM 45 corotating twin-screw extruder to make MPA resins. The extruder was operated at 220°C in the feeding zone and at 240°C toward the extrusion die at a screw speed of 100 rpm. The CP MPA obtained from the twin-screw extruder was quenched in cold water at about 15°C and cut into pellets. Formation of CP-g-PA copolymers through the reaction of the carboxyl groups of CP with the terminal amine groups of PA has been reported during the preparation of MPA.^{12,13} The MPAEVOH blends were prepared by melt blending of the MPA and EVOH. The dried components of MPA and EVOH at varying weight ratios were then fed into a Fure Shuen 40SP-H single-screw extruder to prepare the MPAEVOH resins. The extruder was operated at 220°C in the feeding zone and at 235°C toward the extrusion die at a screw speed of 600 rpm. The MPAEVOH resins obtained from the single-screw extruder were quenched in cold water at about 15°C and cut into pellets. The compositions of the MPAEVOH specimens prepared in this study are summarized in Table I. The MPA, EVOH, and each type of MPAEVOH pellet prepared from the twin-screw extruder were dried at 80°C for 16 h and then dry blended with PE at a 10:90 weight ratio.

The mixed PE/MPA and PE/MPAEVOH blends were then blow molded in a Jonh Huah TPH-550 extrusion blow-molding machine using an extrusion temperature of 230°C and a screw speed of 400 rpm. The extrusion blow-molding machine was purchased from Jonh Huah Corporation, Taichung, Taiwan. A

conventional PE screw was used to extrude the PE/MPA and PE/MPAEVOH blends before blow molding. The blow-molded bottles weigh about 50 g and have a capacity of about 500 mL and a wall thickness of about 1 mm. For comparison, bottles were also prepared from base PE resin by using the same screw and blow-molding machine operating at an extrusion temperature of 190°C and a screw speed of 400 rpm.

The paint mixed solvents used for the permeation tests were prepared by mixing white spirit and acetone, because they are well known as the typical main solvents for surface coatings.

Thermal properties

The thermal properties of PE, PA, CP, EVOH, MPA, and MPAEVOH resins were determined using a DuPont 2010 differential scanning calorimeter (DSC). All scans were carried out at a heating rate of 10°C/min under flowing nitrogen at a flow rate of 25 mL/min. The instrument was calibrated using pure indium. Samples weighing 10 and 0.5 mg were placed in the standard aluminum sample pans for determinations of the degree of crystallinity and melting temperature, respectively.

Free-volume properties

The free-volume characteristics of the polymer were determined using a positron annihilation lifetime instrument equipped with a fast-fast coincidence spectrometer and a ^{22}Na source that was sandwiched between a number of films on both sides to ensure complete annihilation of positrons in the sample. A short-lived component (τ_1 , ca. 0.12 ns), an intermediate-lived component (τ_2 , ca. 0.35–0.4 ns), and a long-lived component (τ_3 , ca. 1.8–2.5 ns), which are the three resolved lifetime components obtained, are attributed to the *para*-positronium, free positron, and *ortho*-positronium (*o*-Ps) states, respectively. The longest lifetime component (τ_3) with intensity I_3 is attributed to the pick-off annihilation of the *o*-Ps in the free-volume sites that are present mainly in the amorphous regions of the polymer matrix.²⁴

The annihilation of *o*-Ps in the spherical free-volume cavities can be described by a simple quantum mechanical model, which assumes the *o*-Ps atom to be localized in a spherical potential well with an electron layer of thickness ΔR . This model provides the relationship between the radius (R_f) of the free-volume hole and the *o*-Ps lifetime (τ_3) as follows²⁵:

$$\frac{1}{\tau_3} = 2 \left[1 - \frac{R_f}{R_0} + \frac{1}{2\pi} \sin\left(\frac{2\pi R_f}{R_0}\right) \right] \quad (1)$$

where $R_0 = R_f + \Delta R$ and the ΔR parameter was determined by fitting the experimental values of τ_3

obtained for materials of known hole size such as zeolites. A ΔR value of 1.66 Å was used in this study.²⁶

The fractional free volume, defined as the ratio of the free volume to the total volume of the polymer, was calculated using following equation^{27,28}:

$$F_v = C \cdot V_f \cdot I_3 \quad (2)$$

where C is a constant, I_3 is the intensity of the *o*-Ps lifetime, and V_f is the mean volume of the free-volume holes calculated using the mean R_f obtained as follows:

$$V_f = 4/3 \pi R_f^3 \quad (3)$$

The errors of the I_3 and τ_3 values were around $\pm 0.05\%$ and ± 0.01 ns for the specimens, respectively.

Morphology of PE/MPA and PE/MPAEVOH bottles

In order to observe the deformation structures of MPA and MPAEVOH resins in the respective PE/MPA and PE/MPAEVOH bottles, these bottles were first sectioned with a scalpel and then etched with formic acid. The etched samples were then gold coated and examined using a Jeol JSM-5200 scanning electron microscope, which was purchased from Jeol Technics Ltd. (Tokyo).

Permeation tests

The permeation barrier properties of the bottles were evaluated by measuring the weight losses of the solvents contained in the bottles. PE, PE/PA, and PE/MPA bottles were initially filled with 250 g of pure paint solvents or the mixed paint solvents. The weight losses of the pure and/or mixed paint solvents were determined after maintaining the filled bottles at 40°C for 14 days. The equipment used for the permeation experiment was an oven equipped with a PID controller, which gives a temperature fluctuation of $\pm 1^\circ\text{C}$. In contrast, the permeation barrier properties of PA and MPA resins were determined based on their hot-pressed sheets, because it is well known that pure PA and MPA resins are difficult to process by blow molding because of their poor melt strengths. The dried pellets of PA and MPA were hot pressed into about 2 mm thick sheets and cut into 14-cm diameter circles. The circular PA and MPA sheets were sealed as lids on the top of test flasks filled with 250 g of the solvents. The permeation barrier properties of the circular sheets were then determined by measuring the weight losses of the solvents after keeping the flasks at 40°C for 14 days. The solvent permeation rate of each of the bottle or hot-pressed sheets was estimated based on

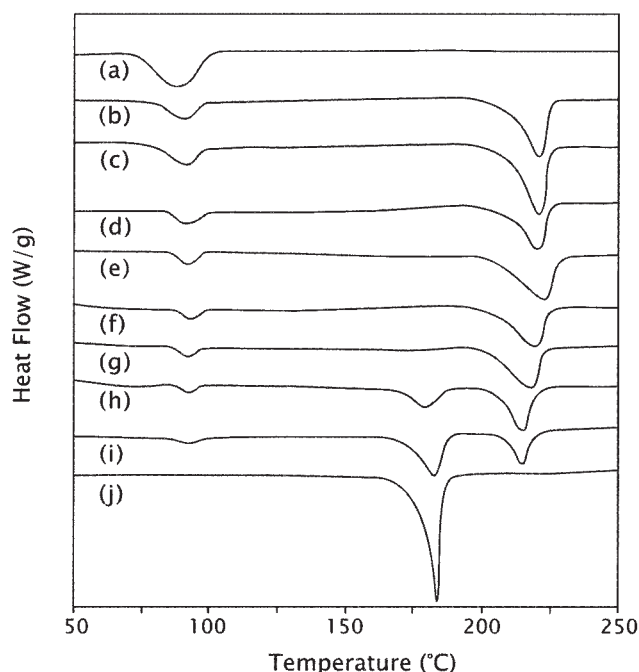


Figure 1 DSC thermograms of CP (curve a), MPA (curve b), MPA₉EVOH₁ (curve c), MPA₇EVOH₁ (curve d), MPA₅EVOH₁ (curve e), MPA₄EVOH₁ (curve f), MPA₂EVOH₁ (curve g), MPA₁EVOH₁ (curve h), MPA₁EVOH₂ (curve i), and EVOH specimens (curve j).

the average permeation rate of at least three bottles or hot-pressed sheet samples, respectively.

RESULTS AND DISCUSSION

Thermal properties of MPA, EVOH, and MPAEVOH specimens

Figure 1 summarizes the typical DSC thermograms of CP, MPA, EVOH and MPAEVOH specimens. Two main melting endotherms with peak temperatures of around 183.4 and 222.3°C were found on the DSC thermograms of EVOH and MPA specimens, respec-

tively. Similar to that found in the thermogram of the CP specimen, a small melting endotherm with a peak temperature of about 92.4°C was found on the thermogram of the MPA resin. Presumably, this melting endotherm is attributable to the melting of the residual traces of CP present in the MPA specimen. After blending EVOH in MPA, the main melting endotherms corresponding to those of EVOH and MPA specimens were both found on most DSC thermograms of MPAEVOH specimens. However, the peak temperatures associated with the main melting endotherm of MPA and EVOH were significantly reduced with increasing MPA contents present in the MPAEVOH resins. Moreover, the main melting endotherm associated with the EVOH resins quickly disappeared as the MPA contents in MPAEVOH increased. In fact, almost no EVOH melting endotherm could be found on the MPAEVOH thermograms as the weight ratios of MPA to EVOH reached about 4 (i.e., the MPA₄EVOH₁ sample).

Table II summarizes the percentage of crystallinity (W_c) of MPA, EVOH, and MPAEVOH specimens. The W_c value of the MPA specimen is significantly lower than that of the EVOH specimen (26.8 vs. 38.4%). Most of the MPAEVOH specimen W_c values are even slightly lower than that of the MPA specimen and increase with increasing EVOH contents present in MPAEVOH specimens. However, it is interesting to note that the W_c values of MPAEVOH specimens are significantly smaller than the summation W_c values of MPA and EVOH present in MPAEVOH specimens as calculated using the simple mixing rule (see Table II). In fact, the W_c values of the EVOH-rich phases are significantly smaller than those of pure EVOH present in the MPAEVOH specimens calculated using the simple mixing rule and are almost equal to zero when the weight ratios of MPA to EVOH are >2. In contrast, the W_c values of MPA-rich phases present in MPAEVOH specimens are always larger than those of pure MPA

TABLE II
Melting Temperature (T_m) and Percentage Crystallinity (W_c) of MPA, EVOH, and MPAEVOH Specimens

Specimens	EVOH-rich phase			MPA-rich phase			Overall crystallinity (%)
	T_m (°C)	Crystallinity (%)	Crystallinity calcd using simple mixing rule (%)	T_m (°C)	Crystallinity (%)	Crystallinity calcd using simple mixing rule (%)	
MPA	—	—	—	222.3	26.8	26.8	26.8
MPA ₉ EVOH ₁	—	0	3.8	221.7	25.8	24.1	25.8
MPA ₇ EVOH ₁	—	0	4.8	220.7	24.7	23.5	24.7
MPA ₅ EVOH ₁	—	0	6.4	220.1	23.7	19.8	23.7
MPA ₄ EVOH ₁	—	0	7.7	219.8	22.3	21.4	22.3
MPA ₂ EVOH ₁	176.5	1.4	12.8	219.2	21.8	17.8	23.1
MPA ₁ EVOH ₁	181.5	8.0	19.2	216.2	15.2	13.4	23.2
MPA ₁ EVOH ₂	182.3	17.1	25.6	215.8	10.9	8.9	28.0
EVOH	183.4	38.4	38.4	—	—	—	38.4

TABLE III
Free Volume Properties of PE, CP, PA, MPA, and EVOH Resins

Sample	R_f (Å)	V_f (Å ³)
PE	3.04	117.7
CP	3.02	115.3
PA	2.32	52.5
MPA	2.45	61.9
EVOH	2.07	37.1

R_f , the average radius of free-volume cavities; V_f , the average volume of free-volume cavities.

crystals present in MPAEVOH specimens calculated using the simple mixing rule.

These interesting thermal properties suggest that EVOH and MPA are miscible with each other to some extent in MPA- and EVOH-rich phases, wherein EVOH molecules interact and are miscible with MPA molecules on the molecular level. Presumably, the two main endotherms found in most MPAEVOH specimens are mainly attributed to the melting of MPA and EVOH crystals present in the MPA-rich and EVOH-rich phases that present in MPAEVOH specimens, respectively. However, the MPA and EVOH in MPAEVOH resins can interfere with each other during the course of crystallization and thus significantly reduce both melting peak temperatures of EVOH and MPA when increasing the MPA and EVOH contents, respectively. Moreover, making EVOH molecules "soluble" in the MPA-rich phase without phase separation

is easier than making MPA molecules soluble in the EVOH-rich phase without phase separation. In contrast, MPA crystallizes first upon cooling because it has a high melt temperature expelling out the amorphous EVOH molecules from the growing crystallization front. The EVOH phase when MPA is a predominant phase can be effectively trapped between the crystals of MPA. This might result in inhibition of the crystallization kinetics of the EVOH phase occurring at lower temperatures, leading to less crystallinity than that predicted by the simple mixing rule.

Free-volume properties of MPA, EVOH, and MPAEVOH specimens

Table III summarizes the free-volume properties of PE, CP, PA, MPA, and EVOH resins. Among these base resins, PE exhibits the largest whereas EVOH shows the smallest average volume (V_f) and radius (R_f) of the free-volume cavities, respectively. In comparison with PA, MPA exhibits a slightly larger R_f value, which is still significantly smaller than those of the PE and CP specimens. Figure 2 provides a summary of the free-volume properties of MPAEVOH resins. The R_f and V_f values of the MPAEVOH sample series tend to increase as the blended MPA contents increase. However, it is interesting to note that the annihilation intensity (I_3) values of MPAEVOH specimens tend to be reduced with increasing MPA contents, in which the I_3 values reflect the relative average numbers of free-volume cavities present in the unit

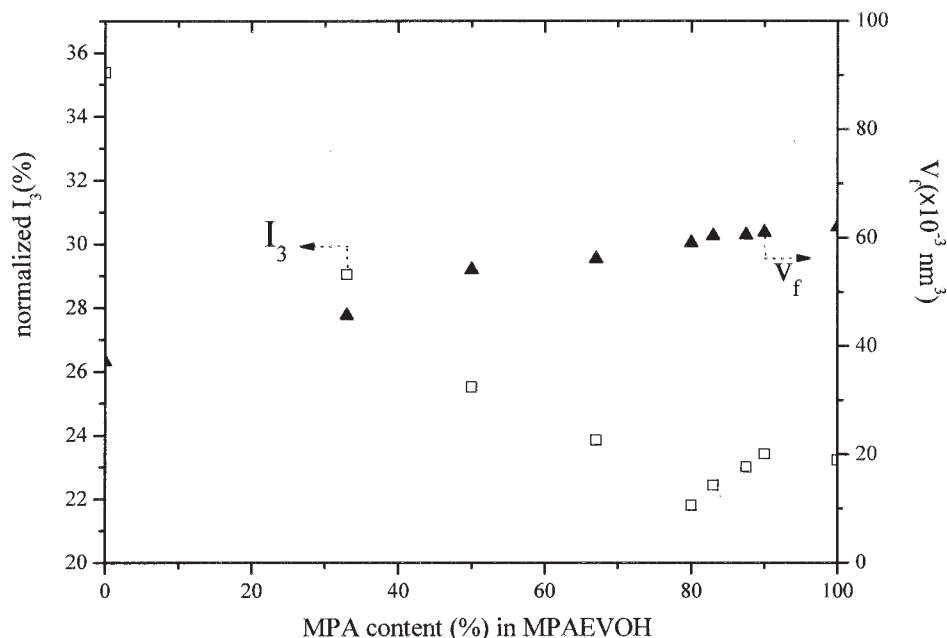


Figure 2 (□) The annihilation intensity (normalized I_3) and (▲) average free volume cavity size (V_f) of MPAEVOH specimens. The normalized I_3 is the value of I_3 normalized as the ratio of the original I_3 values to the weight percentages of their amorphous phases.

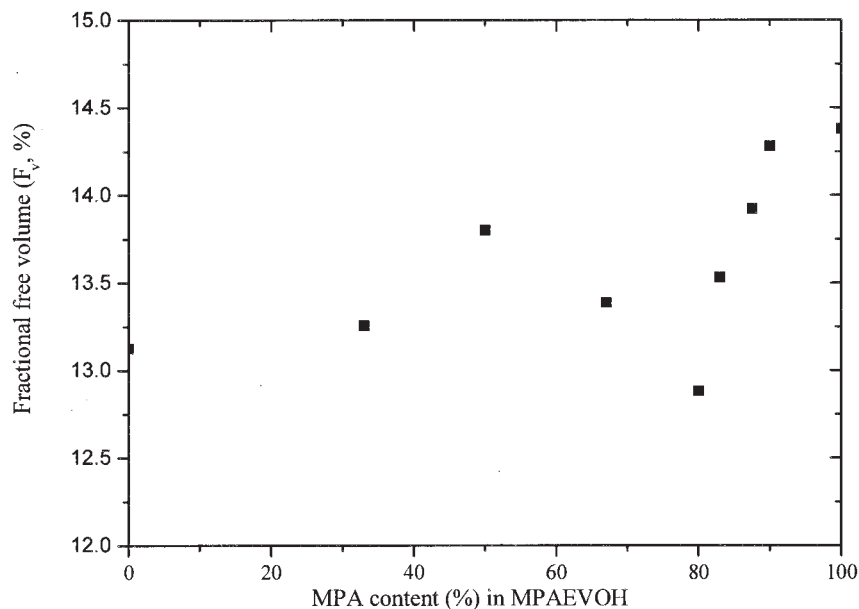


Figure 3 (■) Fractional free volumes of the MPAAEVOH sample series.

volume of the amorphous phases of MPAAEVOH resins. Moreover, a noticeable “negative deviation” was found as the weight ratios of MPA to EVOH reached about 4. Similarly, as shown in Figure 3, a clear negative deviation was found on the plot of the fractional free volumes of MPAAEVOH specimens versus their MPA contents, because the MPA contents are close to about 80 wt %, although the fractional free volumes of MPAAEVOH specimens consistently increase as the MPA contents increase from 0 to about 50 wt %.

The sources for these interesting free-volume properties are not completely clear. However, it is generally recognized that the size and distribution of the free-volume cavities of polymers are related to the molecular structure and molecular interaction present in their amorphous phases. Strong molecular interactions, such as inter- and/or intramolecular hydrogen bondings, can attract and hold the polymer molecules in a more condensed way and thus cause a relatively small average free volume. As reported in our latest investigation,²⁵ the presence of MPA can interfere and/or break the hydrogen bonds originally present in EVOH resins, because new hydrogen bonds were found through the interaction of the carbonyl and/or amide groups of MPA with the hydroxyl groups of EVOH resins. Further Fourier transform IR (FTIR) investigations indicate that the strengths of the intermolecular hydrogen bonds of MPAAEVOH specimens are significantly reduced as the MPA contents increase, wherein the self-associated hydroxyl–hydroxyl bonds within EVOH resins almost disappear as the MPA contents increase to more than about 80 wt %. Similarly, the X-ray diffraction peak and FTIR spectrum corresponding to EVOH crystals and self-associ-

ated hydroxyl–hydroxyl bonds within EVOH resins, respectively, disappear as the MPA contents in the MPAAEVOH specimens are >80 wt %.²⁵ Based on these premises, it is reasonable to understand that, after blending MPA in the EVOH resin, the dense molecular structure originally present in the amorphous regions of EVOH specimens was disrupted and changed into sparser structures as the MPA contents increased. As a consequence, the V_f values of the MPAAEVOH specimens are larger than that of the base EVOH resin and increase significantly as their MPA contents increase. Moreover, as evidenced by DSC thermograms of MPAAEVOH specimens, EVOH and MPA are miscible with each other to some extent and present as MPA- and EVOH-rich separate phases in most of the MPAAEVOH specimens prepared in this study. However, making EVOH molecules soluble in the MPA-rich phase without phase separation is easier than making MPA molecules soluble in the EVOH-rich phase without phase separation. In fact, at some optimum MPAAEVOH compositions, EVOH can be blended in MPA-rich phases without or with only slight phase separation, wherein EVOH molecules are miscible and strongly interact with MPA molecules. Under such circumstances, the free-volume cavities originally present in the EVOH phases disappear almost completely and thus cause a noticeable negative deviation on the plots of I_3 versus MPA contents as the MPA contents present in MPAAEVOH specimens reach about 80 wt %. Presumably, this significant reduction in the I_3 of MPAAEVOH specimens with MPA contents near 80 wt % can reduce the fractional free volumes of MPAAEVOH specimens, although their V_f values tend to increase as the blended MPA contents increase.

TABLE IV
White Spirit and Acetone Permeation Properties of PE, EVOH, MPA, and MPAEVOH Hot-Pressed Sheets

Specimens	White spirit		Acetone	
	Permeation rate (g/day)	Barrier improvement	Permeation rate (g/day)	Barrier improvement
PE	3.0×10^{-1}	1	1.7×10^{-1}	1
MPA	4.1×10^{-3}	73.5	1.5×10^{-1}	1.1
MPA ₉ EVOH ₁	4.0×10^{-3}	75.1	9.0×10^{-2}	1.9
MPA ₇ EVOH ₁	3.2×10^{-3}	93.1	7.9×10^{-2}	2.2
MPA ₅ EVOH ₁	3.1×10^{-3}	97.3	5.4×10^{-2}	3.1
MPA ₄ EVOH ₁	2.5×10^{-3}	121.2	2.4×10^{-2}	7.1
MPA ₂ EVOH ₁	1.8×10^{-3}	171.8	1.6×10^{-2}	10.9
MPA ₁ EVOH ₁	1.1×10^{-3}	270.8	9.6×10^{-3}	17.7
MPA ₁ EVOH ₂	1.1×10^{-3}	275.4	5.1×10^{-3}	33.4
EVOH	9.9×10^{-4}	305.9	3.1×10^{-3}	54.7

Therefore, the fractional free volumes of MPAEVOH specimens are relatively small as their MPA contents are near 80 wt %.

Permeation properties of PE, MPA, EVOH, and MPAEVOH hot-pressed sheets

The white spirit and acetone permeation properties of PE, EVOH, MPA, and MPAEVOH hot-pressed sheets are summarized in Table IV. Among these hot-pressed sheets, EVOH and MPA sheet specimens exhibit significantly better resistance against white spirit or acetone permeation than the PE sheet specimen, and the EVOH sheet specimen shows the best permeation resistance. As shown in Table III, the white spirit permeation rates of MPA and EVOH sheets are 73.5 and 306 times slower, respectively, than the PE sheet. In contrast to white spirit permeation properties, the acetone permeation rates of MPA and EVOH sheet specimens are dramatically faster than their white spirit permeation rates. For instance, the acetone permeation rates of MPA and EVOH sheets are about 37 and 3 times faster, respectively, than their white spirit permeation rates and are only slightly slower than those of PE sheet specimens. In contrast, it is interesting to note that, after blending EVOH in MPA, the white spirit and acetone permeation resistance of MPAEVOH sheets improves as their EVOH contents increase. For example, the barrier improvements of MPAEVOH sheet specimens against white spirit and acetone permeation increase from 75.1 and 1.9 to 270.8 and 17.7, respectively, as their EVOH contents increase from 10 to 50 wt %.

The origination of these interesting barrier properties of these hot-pressed specimens is not completely lucid. It is generally recognized that permeant molecules can hardly diffuse through crystalline regions of polymers, and they are believed to diffuse through the polymers by mostly penetrating through their amorphous regions. Therefore, it is reasonable to suggest

that the molecular composition and characteristic of the free-volume cavities in the amorphous phase of the polymer can greatly affect its barrier properties. As shown in the previous section, the V_f and R_f values of the free-volume cavities of the PE specimen are significantly larger than those of MPA and EVOH specimens. These sparse molecular structures present in PE amorphous regions provide more space and shorten the permeant path through which permeant molecules permeate. Moreover, the presence of polar amide, terminal amine groups and intermolecular hydrogen bondings in the amorphous regions of MPA and EVOH can barely allow the relatively nonpolar white spirit molecules to enter into and permeate through their amorphous regions. In comparison with MPA, the EVOH specimen exhibits significantly smaller V_f and R_f values and higher polarity, and the V_f and R_f values of MPAEVOH specimens are consistently reduced with increasing amounts of EVOH blended in MPA. Therefore, the resistance of the PE sheet specimen against white spirit permeation is significantly worse than that of MPA and MPAEVOH specimens, and the white spirit permeation resistance of MPAEVOH specimens improves as their EVOH contents increase.

In comparison with the nonpolar white spirit molecules, polar MPA or EVOH molecules can absorb and help more polar acetone molecules to enter and permeate through the amorphous regions of MPA and EVOH resins. Conversely, relatively nonpolar PE molecules can barely allow the polar acetone molecules to enter and permeate through the amorphous regions of PE resins. Therefore, the acetone permeation rates of MPA, EVOH, and MPAEVOH sheet specimens are dramatically faster than their white spirit permeation rates and are only slightly slower than that of PE sheet specimens, although the V_f and R_f values of MPA and EVOH specimens are significantly smaller than those of the PE specimen.

TABLE V
Permeation Properties of PE, PE/MPA, and PE/MPAEVOH Bottles Filled with White Spirit and Acetone

Specimens	White spirit		Acetone	
	Permeation rate (g/day)	Barrier improvement	Permeation rate (g/day)	Barrier improvement
PE	9.1×10^{-1}	1	1.2×10^{-1}	1
PE/MPA	2.5×10^{-3}	364.4	1.3×10^{-2}	9.7
PE/MPA ₉ EVOH ₁	9.5×10^{-3}	95.9	5.7×10^{-2}	2.1
PE/MPA ₇ EVOH ₁	9.0×10^{-3}	101.2	5.2×10^{-2}	2.5
PE/MPA ₅ EVOH ₁	8.8×10^{-3}	103.4	4.7×10^{-2}	2.6
PE/MPA ₄ EVOH ₁	6.2×10^{-3}	146.2	3.3×10^{-2}	3.7
PE/MPA ₂ EVOH ₁	2.7×10^{-2}	33.6	4.7×10^{-2}	2.6
PE/MPA ₁ EVOH ₁	8.3×10^{-2}	11.0	5.2×10^{-2}	2.3
PE/MPA ₁ EVOH ₂	2.3×10^{-1}	3.9	5.5×10^{-2}	2.2

Permeation properties of PE, PE/MPA, and PE/MPAEVOH bottles

Table V summarizes the permeation properties of PE, PE/MPA, and PE/MPAEVOH bottles filled with white spirit and acetone. In contrast to those found for sheet specimens, PE/MPA bottles exhibited the best barrier properties against white spirit permeation among the PE, PE/MPA, and PE/MPAEVOH bottles prepared in this study. As shown in Table V, the white spirit permeation rate of the PE/MPA bottle is 364 times slower than that of the PE bottle. Somewhat surprisingly, after blending EVOH in MPA, the PE/MPAEVOH bottle specimens exhibit worse white spirit permeation resistance than the PE/MPA bottle specimen. For example, even at an optimum 4:1 weight ratio of MPA to EVOH, the white spirit permeation rate of the PE/MPA₄EVOH₁ bottle is still 2.5 times faster than that of the PE/MPA bottle, wherein the PE/MPA₄EVOH₁ bottle exhibits better white spirit permeation resistance than other PE/MPAEVOH bottle specimens prepared from other MPAEVOH compositions. In contrast to the nonpolar white spirit, the amounts of acetone permeated through the PE bottles are very small and only slightly larger than those of the PE/MPA and PE/MPAEVOH bottles. Table V shows that the acetone permeation rates of PE bottles are only about 2–10 times faster than those of PE/MPAEVOH and PE/MPA bottles.

Figure 4 provides a summary of the permeation properties of PE bottles filled with mixed solvents of white spirit and acetone. Similar to those found in our previous investigation,²⁰ the mixed solvent permeation rates of PE bottles are approximately equal to the summation permeation rate of the solvents present in the mixed paint solvents calculated using the simple mixing rule. Moreover, the permeation rates of PE/MPA bottles filled with the mixed solvents of white spirit and acetone are dramatically faster than the summation permeation rates of the solvents present in the mixed solvents calculated using the simple mixing rule (see Fig. 5). The permeation rates of the white

spirit and acetone mixed solvents in PE/MPA bottles are at least 20–60 times faster than the summation permeation rates calculated using the simple mixing rule when the acetone contents present in the mixed solvents are between 10 and 70 wt %. However, as the polar solvent contents deviate from the particular window range, the mixed solvent permeation rates of white spirit and acetone in PE/MPA bottles are quickly reduced and approach the summation permeation rates calculated using the simple mixing rule. In contrast, after blending EVOH in the MPA matrix, the resistance of PE/MPAEVOH bottles against mixed solvent permeation is dramatically improved even when the polar solvent contents are in the particular window range. In fact, the resistance of PE/MPAEVOH bottles against mixed solvent permeation

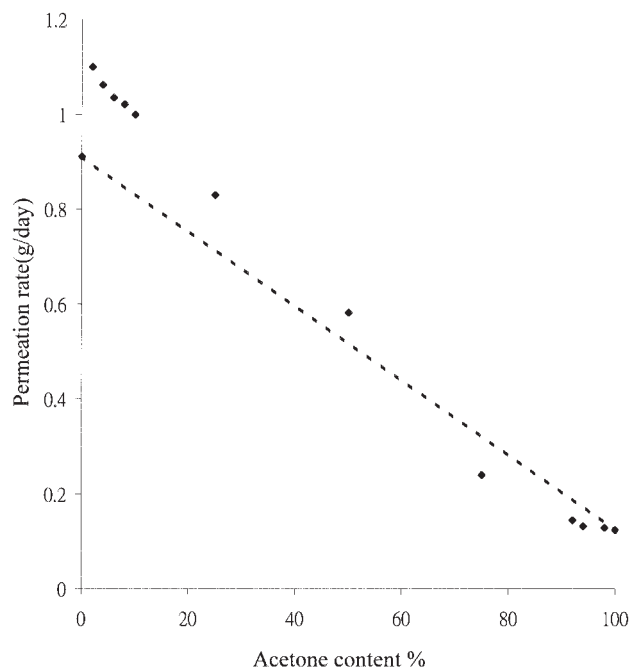


Figure 4 The permeation properties of the PE bottles filled with white spirit and acetone mixed solvents at 40°C.

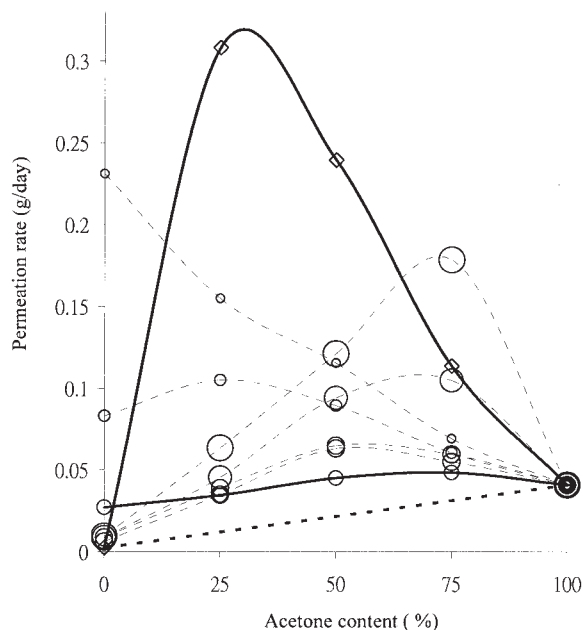


Figure 5 Permeation rates of white spirit and acetone mixed solvents of (\diamond) PE/MPA, (\circ) PE/MPA₃EVOH₁, (\circ) PE/MPA₇EVOH₁, (\circ) PE/MPA₅EVOH₁, (\circ) PE/MPA₄EVOH₁, (\circ) PE/MPA₂EVOH₁, (\circ) PE/MPA₁EVOH₁, and (\circ) PE/MPA₁EVOH₂ bottles at 40°C. The dashed line represents the value calculated using the simple mixing rule.

reaches the best value when the MPAAEVOH resins were prepared with an optimum composition (i.e., MPA₂EVOH₁). As shown in Figure 5, at the particular window range, the permeation rates of white spirit and acetone mixed solvents of the PE/MPA₂EVOH₁ bottle are dramatically lower than those of the PE/MPA bottle and are very close to the summation permeation rates of the solvents present in the mixed solvents calculated using the simple mixing rule.

Morphology of PE/MPA and PE/MPAAEVOH bottles

Typical micrographs of the fracture surfaces of PE, PE/MPA, and PE/MPAAEVOH bottles are summarized in Figure 6. Many clearly defined MPA laminae were distributed in the PE matrices parallel to the wall direction of the PE/MPA bottle. In contrast, after blending EVOH barrier resins in MPA, less defined MPAAEVOH laminae were found on the fracture surfaces of the PE/MPAAEVOH bottles [see Fig. 6(b–h)]. In fact, broken, much less demarcated laminae together with dispersed droplets were found on the fracture surfaces of the PE/MPAAEVOH bottles when the EVOH contents were more than 25 wt %.

These results suggest that PE can easily stretch MPA into elongated laminae, because MPA was modified to provide good adherence to the PE matrix and was associated with optimum melt viscosity and strength

that can be drawn into continuous laminar structures during the blow-molding process of PE/MPA blends. In contrast, the interfacial adhesion between PE and EVOH is not good enough to keep PE stretching EVOH into elongated and demarcated laminae during the blow-molding process of PE/EVOH blends. After blending EVOH into the MPA resin, as evidenced by DSC thermograms and described in the previous section, only at low enough EVOH contents can EVOH be blended in MPA-rich phases and mixed as nearly one miscible phase without phase separation, wherein EVOH molecules are miscible, strongly interact with MPA molecules, and cocrystallize with MPA molecules. However, EVOH and MPA are miscible with each other to some extent and present as MPA- and EVOH-rich separate phases in most of the MPAAEVOH specimens prepared in this study. Under such circumstances, the MPA-rich phase can be drawn by PE into more elongated and demarcated laminae, whereas the EVOH-rich phase can only be stretched into less demarcated and/or broken laminae or even dispersed as fine droplets in PE/MPAAEVOH bottles when the EVOH contents are greater than certain amounts.

The underlying mechanisms accounting for the interesting barrier properties of white spirit and acetone mixed solvents described in the previous section are not completely clear. Presumably, the level of barrier improvements of bottle specimens depend not only on the barrier properties of the base barrier resins but also on their resulting morphology that present in PE/MPA and PE/MPAAEVOH bottle specimens. The demarcated and elongated laminae of barrier resins can significantly block the permeant path, prolong the permeation period of the permeant molecules, and improve the permeation resistance of PE/MPA and PE/MPAAEVOH bottle specimens better than that of the PE bottle, although only 10 wt % barrier resins were blended in the PE/MPA and PE/MPAAEVOH bottle specimens. Moreover, the presence of EVOH in the MPAAEVOH specimens improved their barrier properties better than those of the MPA specimen. However, as shown above, broken, much less demarcated laminae and even dispersed droplets of EVOH-rich phases were found on the fracture surfaces of the PE/MPAAEVOH bottles as the EVOH contents increase. These broken and much less demarcated laminae can cause a deleterious effect on the barrier properties of PE/MPAAEVOH bottles and counterbalance the beneficial effect made by the presence of EVOH in MPA-rich laminae. Consequently, the permeation resistance of PE/MPAAEVOH bottles reaches the best level as the EVOH contents reach an optimum value of around 20 wt %.

In contrast to pure white spirit and/or acetone solvents, the polar and nonpolar solvent molecules present in the mixed solvents have to compete to enter into and permeate through the empty spaces of the

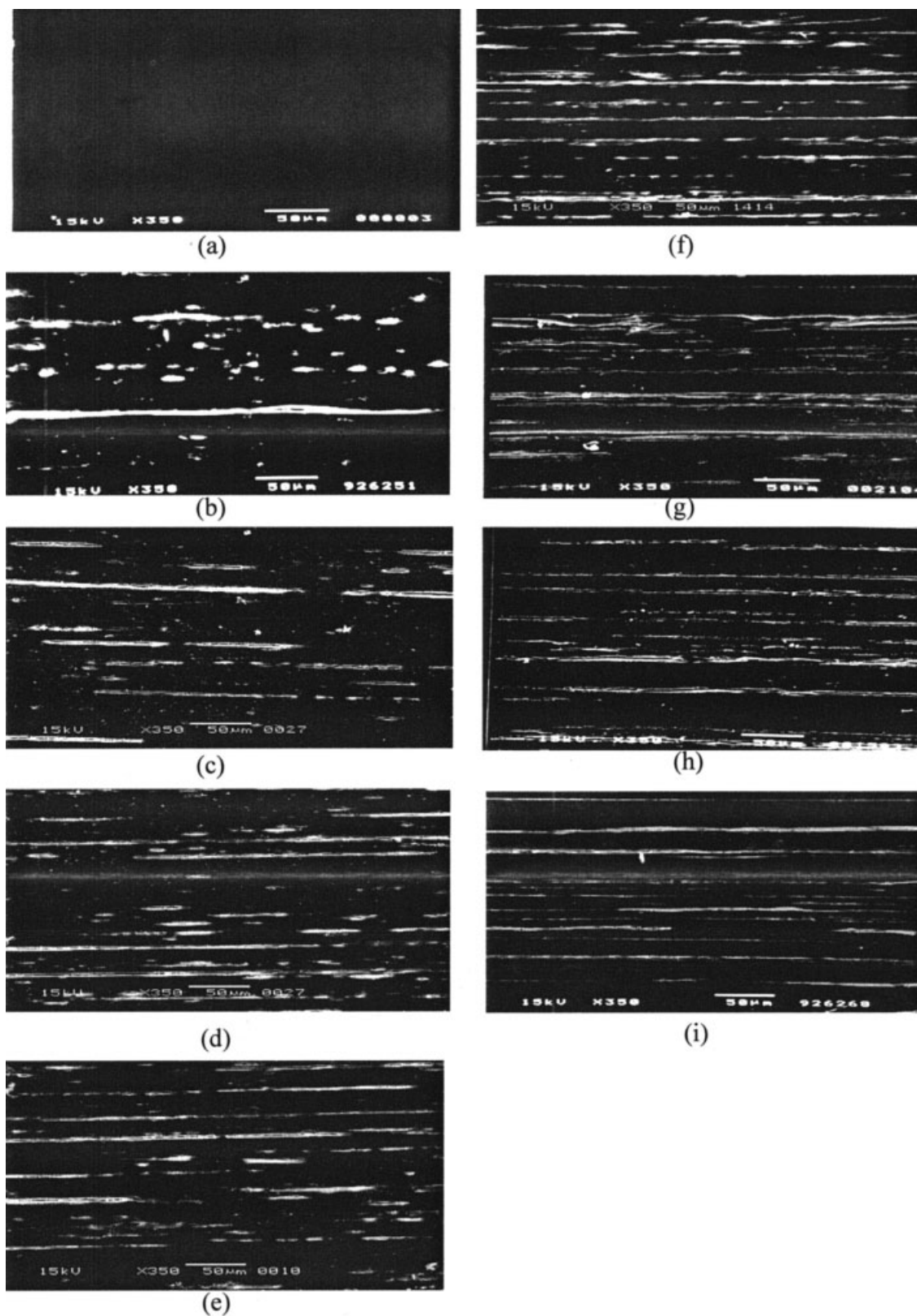


Figure 6 Typical SEM micrographs of the fracture surfaces of (a) PE, (b) PE/MPA₁EVOH₂, (c) PE/MPA₁EVOH₁, (d) PE/MPA₂EVOH₁, (e) PE/MPA₄EVOH₁, (f) PE/MPA₅EVOH₁, (g) PE/MPA₇EVOH₁, (h) PE/MPA₉EVOH₁, and (i) PE/MPA bottle specimens.

amorphous regions of the PE resins, although nonpolar PE molecules in the amorphous regions tend to absorb the nonpolar molecules more than the polar molecules. As shown in previous section, the nonpolar white spirit molecules can enter into and permeate through the amorphous regions of the PE resins at a much faster rate than the polar acetone molecules. Presumably, the polar acetone molecules present in the mixed solvents can enter into the amorphous regions of PE bottles and hence slow down the permeation rates of nonpolar white spirit molecules by blocking their permeant paths. However, as shown in our recent investigation,²⁰ the equilibrium vapor pressures of the acetone/white spirit mixed solvent are at least 100–300 mmHg higher than the vapor pressure calculated using the simple mixing rule, when the acetone contents present in the mixed solvents are between 10 and 75 wt %. It is generally recognized that the permeation rates of the mixed solvents can be greatly enhanced as the vapor pressures present in the bottle specimens increase. The “blocking” effect of the polar solvents of the mixed solvents can compromise the deleterious effect of the vapor pressures of the mixed solvents on the barrier properties of PE bottles. As a consequence, the mixed paint solvent permeation rates of PE bottles are approximately equal to the summation permeation rate of the solvents present in the paint mixed solvents calculated using the simple mixing rule.

However, the polar and nonpolar molecules contained in the mixed solvents are likely to enter into and permeate through the amorphous regions of the PE/MPA and PE/MPAEVOH bottles in a separate manner, because the nonpolar PE and polar MPA and EVOH molecules tend to absorb the nonpolar and polar solvent molecules, respectively. Under such circumstances, the polar acetone molecules present in the mixed solvents are likely to enter into and swell the amorphous regions of the MPA and EVOH resins during the course of permeation and are not likely to block the permeant paths of the nonpolar solvent molecules in the amorphous regions of PE resins. Moreover, the permeation rates of the mixed solvents can be greatly enhanced by the significantly increased vapor pressures of mixed solvents in PE/MPA bottles, wherein the polar and nonpolar solvent molecules are pressurized to permeate through different “swollen channels” in the amorphous regions of MPA and PE resins, respectively. Therefore, the mixed solvent permeation rates of PE/MPA bottles are dramatically faster than the summation permeation rates of the solvents present in the mixed solvents calculated using the simple mixing rule, because their polar and nonpolar solvent contents are in the particular window region.

In contrast, during the permeation process of the mixed solvents, the EVOH molecules present in MPA-

rich laminar phases or in the dispersed EVOH droplets of PE/MPAEVOH bottle specimens tend to attract more polar acetone molecules than MPA molecules, because the polarity of the EVOH molecules is expected to be higher than that of MPA molecules. The permeant acetone molecules will tend to fill and swell the amorphous regions of the EVOH resin, but not the amorphous regions of the MPA resin that present in the MPA-rich laminas. Under such circumstances, the MPA resins that present in the MPA-rich laminas can still exhibit excellent barrier resistance against white spirit permeation, because significant amounts of white spirit permeant molecules can still enter into the amorphous regions of MPA resins. However, after blending too much EVOH in MPA resins, the broken, much less demarcated MPA-rich laminas and the EVOH dispersed droplets can no longer block the permeant path, prolong the permeation period of the permeant molecules, and improve the permeation resistance of PE/MPAEVOH bottle specimens, although the EVOH barrier resins can still absorb significant amounts of polar acetone molecules in their amorphous regions. Consequently, by blending optimum amounts of EVOH in MPA, the mixed solvent permeation rates of PE/MPA₂EVOH₁ bottles are significantly less than those of PE/MPA bottle specimens and are approximately equal to the summation permeation rates calculated using the simple mixing rule as their polar and nonpolar solvent contents are in the particular window region.

CONCLUSIONS

After blending proper 10 wt % compositions of MPA or MPAEVOH in PE, the white spirit permeation rates of the PE/MPA or PE/MPAEVOH bottles at 40°C are dramatically slower than that of the PE bottle. With an optimum MPAEVOH composition, the white spirit permeation rate of the PE/MPA₄EVOH₁ bottle at 40°C can be about 145 times slower than that of the PE bottle specimen; however, that is still 2.5 times faster than that of the PE/MPA bottle specimen. In contrast, the rates of acetone polar solvents permeated through the PE bottles are much slower than that of the white spirit and only slightly faster than those through the PE/MPA and PE/MPAEVOH bottle specimens. Similar to those found in our previous investigation, the permeation rates of acetone/white spirit mixed solvents of PE/MPA bottles are at least 20–60 times faster than the summation permeation rates calculated using the simple mixing rule, when the acetone contents are between 10 and 70 wt %. It is somewhat interesting that, after blending proper amounts of EVOH in MPA, the mixed solvent permeation rates of PE/MPAEVOH bottle specimens are dramatically reduced and are very close to the summation permeation rates calculated using the simple mixing rule

when the acetone contents are in the particular window range. Further investigation reveals that, among all base resins, PE and EVOH exhibit the largest and the smallest average volume and radius of the free-volume cavities, respectively. The R_f , V_f , and fractional free volume values of the MPAAEVOH sample series tend to increase as the blended MPA contents increase. However, it is interesting to note that a noticeable negative deviation was found on the plot of the fractional free volumes and/or V_f of MPAAEVOH specimens versus their MPA contents, as the MPA contents are close to about 80 wt %. Two main melting endotherms found in most MPAAEVOH specimens are attributed to the melting of MPA and EVOH crystals present in the MPA-rich and EVOH-rich phases present in MPAAEVOH specimens, respectively. However, at some optimum MPAAEVOH compositions, EVOH can be blended in MPA-rich phases without or with only slight phase separation, wherein EVOH molecules are miscible, strongly interact with MPA molecules, and cocrystallize with MPA molecules. Morphological analyses demonstrated that many elongated and clearly defined MPA laminae are present in the PE/MPA bottle. In contrast, after blending EVOH barrier resins in MPA, less-defined MPAAEVOH laminae were found on the fracture surfaces of the PE/MPAAEVOH bottles. In fact, broken and much less demarcated laminae together with dispersed EVOH-rich droplets were found on the fracture surfaces of the PE/MPAAEVOH bottles when the EVOH contents are more than 25 wt %. These interesting barrier properties of PE/MPA and PE/MPAAEVOH bottle specimens were explained in terms of free volumes, barrier properties, molecular interactions in the amorphous phases of the barrier resins, and resulting morphological structures that present in their corresponding bottles.

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