

# Gasoline Permeation Resistance of the As-Blow-Molded and Annealed Polyethylene, Polyethylene/Polyamide, and Polyethylene/Modified Polyamide Bottles

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**ABSTRACT:** An investigation of the gasoline permeation resistance of the as-blow-molded and annealed polyethylene, polyethylene (PE)/polyamide (PA), and polyethylene/modified polyamide (MPA) bottles is reported. The gasoline permeation resistance improves dramatically after blending PA and MPA barrier resins in PE matrices during blow-molding, and the order of barrier improvement corresponds to the order of barrier improvement of the barrier resins added in PE. Somewhat unexpectedly, the gasoline permeation rates of the annealed PE and/or PE/PA bottles annealed at 90°C or higher temperatures increase significantly with the annealing temperature and time. On the contrary, the gasoline permeation resistance of the annealed PE/MPA bottles increase significantly as the annealing temperature and/or time increase. For instance, the gasoline permeation rate of the PE/MPA bottle annealed at 120°C for 32 h is about 190 times slower than that of the as-blow-molded PE bottle. Further investigations found that, after blending the MPA and PA barrier resins in PE matrices, the relatively nonpolar hydrocarbon components present in the gasoline fuels were significantly blocked, without permeation during the permeation tests, in which the as-blow-molded PE/MPA bottle inhibited the permeation of hydrocarbon components more successfully than did the as-blow-molded PE/PA bottle. In contrast, the amounts of polar components that permeated through the as-blow-molded PE/PA and PE/MPA bottles were very small and about the same as the amount that permeated through the as-blow-molded PE bottle. Possible mechanisms accounting for these interesting behaviors are proposed in this study. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2827–2837, 2001

**Key words:** gasoline permeation resistance; modified polyamide; annealing; hydrocarbon components

## INTRODUCTION

Agricultural chemicals, paint thinner, cleaning naphtha, gasoline, and many other hydrocarbon

solvents are commonly available products that easily permeate polyethylene (PE) containers, thus resulting 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), in a PE matrix, which is a well-proven barrier technology to enhance the resistance of PE containers to hydrocarbon permeation.<sup>1–3</sup> These heterogeneous laminar blends exhibit significantly higher perme-

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ation barrier properties than those of the conventional homogeneous blends associated with uniform dispersed PA within the PE matrix.<sup>4-7</sup>

Because PE/PA blends are thermodynamically immiscible and mechanically incompatible, compatibilizer precursor (CP) resins have often been used to improve the interfacial properties between PE and PA, as well as to enhance the barrier properties of PE/PA/CP blends. In addition, these barrier properties of PE/PA/CP blends greatly depend on the manner of blending and on the resulting morphology.<sup>1-4,8-11</sup> Our latest studies<sup>12-15</sup> indicated that the type and content of CP and PA present in a modified polyamide (MPA) have significant effects on the barrier, morphology, and rheological properties of MPA resins and the corresponding PE/MPA blends. In addition, the melt shear viscosities of polyethylenes and modified polyamide were found to exert a significant influence on the deformation 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 melt shear viscosity ratios of MPA to PE. Such clearly defined laminar structures often accompany the highest permeation resistance to xylene. These particular values of melt shear viscosity ratios (VRs) were referred to as the optimum VRs in our previous study, and the value of optimum VR varied as the compositions of MPA changed.<sup>16-18</sup>

On the other hand, the processing conditions (screw temperatures and speeds) used in the blow-molding process have a significant influence on the morphology and barrier properties of PE/MPA and PE/CP/PA bottles.<sup>19</sup> The xylene permeation rates of a PE/MPA bottle series, prepared at a fixed extrusion temperature, reached a minimum as each bottle series was prepared at an optimum screw speed. This permeation improvement is attributed to more layers of continuous, not broken, MPA laminae present in PE/MPA bottles prepared at the optimum screw speed. Similarly, at a fixed screw speed, the best permeation resistance of each PE/MPA bottle series was always obtained when prepared at an optimum extrusion temperature.

Our latest investigation<sup>20,21</sup> found that the gasoline permeation rate is much higher than either the xylene or the paint thinner permeation rate of PE blown tubes or bottles. About 93% of the filled gasoline permeated out of PE blown tubes in 14 days at 40°C. Similar to results found

for xylene, this poor gasoline permeation resistance can be improved by using proper MPA compositions and carefully controlling the MPA morphology in the PE/MPA blown tubes. However, the barrier resistance of PE/MPA bottles against gasoline permeation is still significantly worse than that against xylene or paint thinner permeation.

The main objective of this study was to investigate the influence of thermal treatment conditions on the gasoline barrier properties of PE, PE/PA, and PE/MPA bottles and, further, to optimize the thermal treatment condition to enhance their barrier properties. In addition to the gasoline compositions before and after permeation tests, the improved gasoline permeation resistance of annealed PE/MPA bottles was investigated in terms of the chemical structure, crystallinity value, amorphous phase structure, and morphology present in their corresponding bottles.

## EXPERIMENTAL

### Materials and Sample Preparation

Different contents of compatibilizer precursor (CP) were used to prepare various modified polyamide (MPA) resins by blending them with the polyamide (PA). The CP used in this study was a zinc-neutralized ethylene/acrylic acid copolymer (kindly supplied by Formosa Chemicals and Fiber Corp., Changhua, Taiwan). The type of PA used was nylon 6 (Sunylon 6N; Formosa Chemicals and Fiber Corp.). The polyethylene (HDPE Taisox 9003) and antioxidant (Irganox B225) used in this study were obtained from Formosa Plastic Corp. (Kaohsiung, Taiwan) and Ciba-Geigy (Summit, NJ), 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 co-rotating 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 resins obtained from the twin-screw extruder were quenched in cold water at about 15°C and cut into the form of pellets. Formation of CP-grafted PA copolymers through the reaction of carboxyl groups of CP with the terminal amine

**Table I Thermal Treatment Conditions for PE, PE/PA, and PE/MPA Bottles**

Samples	Annealing Temperature (°C)	Annealing Time (h)	Samples	Annealing Temperature (°C)	Annealing Time (h)
PE, PE/PA, PE/MPA	—	—	PE <sub>90-8</sub> , PE/PA <sub>90-8</sub> , PE/MPA <sub>90-8</sub>	90	8
PE <sub>60-1</sub> , PE/PA <sub>60-1</sub> , PE/MPA <sub>60-1</sub>	60	1	PE <sub>90-16</sub> , PE/PA <sub>90-16</sub> , PE/MPA <sub>90-16</sub>		16
PE <sub>60-2</sub> , PE/PA <sub>60-2</sub> , PE/MPA <sub>60-2</sub>		2	PE <sub>90-24</sub> , PE/PA <sub>90-24</sub> , PE/MPA <sub>90-24</sub>		24
PE <sub>60-4</sub> , PE/PA <sub>60-4</sub> , PE/MPA <sub>60-4</sub>		4	PE <sub>90-32</sub> , PE/PA <sub>90-32</sub> , PE/MPA <sub>90-32</sub>		32
PE <sub>60-8</sub> , PE/PA <sub>60-8</sub> , PE/MPA <sub>60-8</sub>		8	PE <sub>100-1</sub> , PE/PA <sub>100-1</sub> , PE/MPA <sub>100-1</sub>	100	1
PE <sub>60-16</sub> , PE/PA <sub>60-16</sub> , PE/MPA <sub>60-16</sub>		16	PE <sub>100-2</sub> , PE/PA <sub>100-2</sub> , PE/MPA <sub>100-2</sub>		2
PE <sub>60-24</sub> , PE/PA <sub>60-24</sub> , PE/MPA <sub>60-24</sub>		24	PE <sub>100-4</sub> , PE/PA <sub>100-4</sub> , PE/MPA <sub>100-4</sub>		4
PE <sub>60-32</sub> , PE/PA <sub>60-32</sub> , PE/MPA <sub>60-32</sub>		32	PE <sub>100-8</sub> , PE/PA <sub>100-8</sub> , PE/MPA <sub>100-8</sub>		8
PE <sub>70-1</sub> , PE/PA <sub>70-1</sub> , PE/MPA <sub>70-1</sub>	70	1	PE <sub>100-16</sub> , PE/PA <sub>100-16</sub> , PE/MPA <sub>100-16</sub>		16
PE <sub>70-2</sub> , PE/PA <sub>70-2</sub> , PE/MPA <sub>70-2</sub>		2	PE <sub>100-24</sub> , PE/PA <sub>100-24</sub> , PE/MPA <sub>100-24</sub>		24
PE <sub>70-4</sub> , PE/PA <sub>70-4</sub> , PE/MPA <sub>70-4</sub>		4	PE <sub>100-32</sub> , PE/PA <sub>100-32</sub> , PE/MPA <sub>100-32</sub>		32
PE <sub>70-8</sub> , PE/PA <sub>70-8</sub> , PE/MPA <sub>70-8</sub>		8	PE <sub>110-1</sub> , PE/PA <sub>110-1</sub> , PE/MPA <sub>110-1</sub>	110	1
PE <sub>70-16</sub> , PE/PA <sub>70-16</sub> , PE/MPA <sub>70-16</sub>		16	PE <sub>110-2</sub> , PE/PA <sub>110-2</sub> , PE/MPA <sub>110-2</sub>		2
PE <sub>70-24</sub> , PE/PA <sub>70-24</sub> , PE/MPA <sub>70-24</sub>		24	PE <sub>110-4</sub> , PE/PA <sub>110-4</sub> , PE/MPA <sub>110-4</sub>		4
PE <sub>70-32</sub> , PE/PA <sub>70-32</sub> , PE/MPA <sub>70-32</sub>		32	PE <sub>110-8</sub> , PE/PA <sub>110-8</sub> , PE/MPA <sub>110-8</sub>		8
PE <sub>80-1</sub> , PE/PA <sub>80-1</sub> , PE/MPA <sub>80-1</sub>	80	1	PE <sub>110-16</sub> , PE/PA <sub>110-16</sub> , PE/MPA <sub>110-16</sub>		16
PE <sub>80-2</sub> , PE/PA <sub>80-2</sub> , PE/MPA <sub>80-2</sub>		2	PE <sub>110-24</sub> , PE/PA <sub>110-24</sub> , PE/MPA <sub>110-24</sub>		24
PE <sub>80-4</sub> , PE/PA <sub>80-4</sub> , PE/MPA <sub>80-4</sub>		4	PE <sub>110-32</sub> , PE/PA <sub>110-32</sub> , PE/MPA <sub>110-32</sub>		32
PE <sub>80-8</sub> , PE/PA <sub>80-8</sub> , PE/MPA <sub>80-8</sub>		8	PE <sub>120-1</sub> , PE/PA <sub>120-1</sub> , PE/MPA <sub>120-1</sub>	120	1
PE <sub>80-16</sub> , PE/PA <sub>80-16</sub> , PE/MPA <sub>80-16</sub>		16	PE <sub>120-2</sub> , PE/PA <sub>120-2</sub> , PE/MPA <sub>120-2</sub>		2
PE <sub>80-24</sub> , PE/PA <sub>80-24</sub> , PE/MPA <sub>80-24</sub>		24	PE <sub>120-4</sub> , PE/PA <sub>120-4</sub> , PE/MPA <sub>120-4</sub>		4
PE <sub>80-32</sub> , PE/PA <sub>80-32</sub> , PE/MPA <sub>80-32</sub>		32	PE <sub>120-8</sub> , PE/PA <sub>120-8</sub> , PE/MPA <sub>120-8</sub>		8
PE <sub>90-1</sub> , PE/PA <sub>90-1</sub> , PE/MPA <sub>90-1</sub>	90	1	PE <sub>120-16</sub> , PE/PA <sub>120-16</sub> , PE/MPA <sub>120-16</sub>		16
PE <sub>90-2</sub> , PE/PA <sub>90-2</sub> , PE/MPA <sub>90-2</sub>		2	PE <sub>120-24</sub> , PE/PA <sub>120-24</sub> , PE/MPA <sub>120-24</sub>		24
PE <sub>90-4</sub> , PE/PA <sub>90-4</sub> , PE/MPA <sub>90-4</sub>		4	PE <sub>120-32</sub> , PE/PA <sub>120-32</sub> , PE/MPA <sub>120-32</sub>		32

groups of PA was previously reported during the preparation of MPA.<sup>12,13</sup> Each type of MPA pellets, prepared from the twin-screw extruder, was 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/PA blends were then blow-molded in a Jonh Huah TPH-550 extrusion-blow-molding machine at an extrusion temperature of 230°C and a screw speed of 400 rpm. A conventional polyethylene screw was used to extrude the PE/MPA blend before blow-molding. The blow-molded bottles weighed about 100 g, with a capacity of about 750 mL and a wall thickness of about 2 mm. For purposes of comparison, bottles were also prepared from base PE resin by using the same screw and blow-molding machine, operated at an extrusion temperature of 190°C and a screw speed of 400 rpm.

The prepared as-blow-molded PE, PE/PA, and PE/MPA bottles were annealed at varying temperatures for various amounts of time. The annealing temperatures used in this study were 60, 70, 80, 90, 100, 110, and 120°C, respectively. At each annealing temperature, the bottles were annealed for 1, 2, 4, 8, 16, 24, and 36 h, respectively.

Table I summarizes the thermal treatment conditions and sample designations of the PE, PE/PA, and PE/MPA bottles prepared in this study.

### Permeation Testing

The permeation barrier properties of the as-blow-molded and annealed bottles were evaluated by measuring the weight loss of gasoline contained in the bottles. PE, PE/PA, and PE/MPA bottles were initially filled with 380 g of gasoline. The weight loss of gasoline was determined after placing the filled bottles at 40°C for 14 days. On the other hand, 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 gasoline. The permeation barrier properties of the circular

sheet were then determined by measuring the weight loss of gasoline after placing the flasks at 40°C for 14 days. The gasoline permeation rate of each bottle or hot-pressed sheet was estimated based on the average permeation rate of at least three bottles or hot-pressed sheet samples, respectively.

### Compositions of Gasoline Fuels Before and After Permeation Tests

The compositions of unleaded gasoline fuels before and after permeation tests of the bottles were determined using a China 8900 gas chromatograph (GC) equipped with a hydrogen flame-ionization detector. A Restek Alumina Plot capillary column [0.53 mm (diameter)  $\times$  30 m (length)] was used for separation of the methanol/gasoline fuels. The gasoline fuels before and after permeation tests were injected into the GC at 230°C to determine their compositions. Helium (He), flowing at 20 cc/min, was used as the carrier gas at 220°C. To improve the separation efficiency, the capillary column temperature was raised from 30 to 210°C at a heating rate of 4°C/min. The detector temperature was set at 230°C. The main components contained in unleaded gasoline fuels are nonpolar linear, cyclic, and aromatic hydrocarbons (about 5 to 10 carbons) and some polar liquids, such as acetone, ethanol, and other additives. For purposes of comparison and convenience, the residual weight percentage (wt %) of the hydrocarbon components with 5 to 10 main-chain carbon atoms (i.e., *n*-pentane, xylene, toluene, and decalin) and polar components (i.e., acetone and ethanol) of the gasoline fuel were selected and determined by GC to illustrate the compositions of the residual gasoline fuels after permeation tests. The residual wt % of each solvent was determined by the area ratio of each solvent peak after the permeation test to that before the permeation test.

### Thermal Properties

The thermal properties of PE, PA, CP, and MPA in PE, PE/PA, and PE/MPA bottles were determined using differential scanning calorimetry (DSC) (Du Pont 2010 calorimeter, Wilmington, DE). 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 about 15 mg were placed in standard aluminum sample pans

for each DSC experiment. The crystallinity values of PE and CP were estimated using baselines drawn from 30 to 160°C and a perfect heat of fusion of PE of 293 J/g.<sup>22</sup> The crystallinity values of PA or MPA present in PE/CP/PA and PE/MPA bottles were evaluated using baselines drawn from 170 to 250°C and a perfect heat of fusion of 190 J/g.<sup>23</sup> Baselines used in the experiments were adjusted to have a maximum fluctuation of less than 0.04 mW over the temperature range of interest. With these baselines, the maximum variation of the heat of fusion was normally around  $\pm 3$  J/g, which resulted in 1% error in estimating the crystallinity value.

### Morphology of the As-Blow-Molded and Annealed Bottles

To observe the deformation structures of MPA and PA resins in the as-blow-molded and annealed PE/PA and PE/MPA bottles, respectively, these bottles were first sectioned by a scalpel, then etched with formic acid. The etched samples were then gold-coated and examined by scanning electron microscopy (SEM) (JSM-5200 scanning electron microscope; JEOL, Peabody, MA). For purposes of comparison, the etched samples of the as-blow-molded and annealed PE bottles were also examined by SEM.

## RESULTS AND DISCUSSION

### Gasoline Permeation Properties of PE, PA, CP, and MPA Hot-Pressed Sheets and PE, PE/PA, and PE/MPA As-Blow-Molded Bottles

The gasoline permeation rates of PE, PA, CP, and MPA hot-pressed sheets are summarized in Table II. Among the three base resins (i.e., PE, CP, and PA), the PA sheet exhibits the best resistance, whereas the CP sheet exhibits the worst resistance, against gasoline permeation. In contrast, the MPA sheet exhibits much better gasoline permeation resistance than does the PA sheet. The gasoline permeation rate of the MPA sheet is about 49 and 7 times slower than those of PE and PA sheets, respectively (see Table II). Similar to the results found for hot-pressed sheets, the gasoline permeation resistance of the as-blow-molded PE bottle is the poorest among the PE, PE/PA, and PE/MPA bottles prepared in this study. As shown in Table II, the gasoline permeation resistance improves dramatically after

**Table II Gasoline Permeation Rates of PE, PA, CP, and MPA Hot-Pressed Sheets and PE, PE/PA, and PE/MPA As-Blow-Molded Bottles at 40°C**

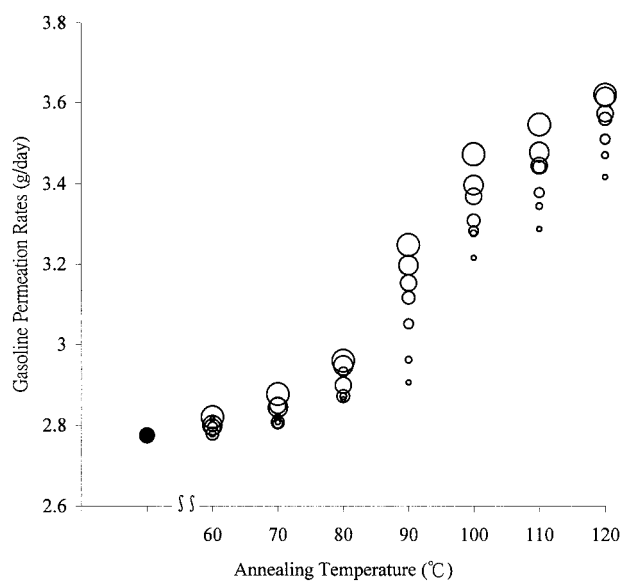
	Specimens						
	Hot-Pressed Sheets				As-Blow-Molded Bottles		
	PE	PA	CP	MPA	PE	PE/PA	PE/MPA
Gasoline permeation rate (g/day)	$8.9 \times 10^{-1}$	$1.3 \times 10^{-1}$	1.3	$1.8 \times 10^{-2}$	2.8	$1.9 \times 10^{-1}$	$2.2 \times 10^{-2}$

blending PA or MPA in PE during blow-molding, and the order of barrier improvement corresponds to the order of barrier improvement of the barrier resins added in PE. After blending 10 wt % of MPA or PA in PE, the gasoline permeation rate of the as-blow-molded PE/MPA or PE/PA bottles is, respectively, about 130 or 15 times slower than that of the as-blow-molded PE bottle.

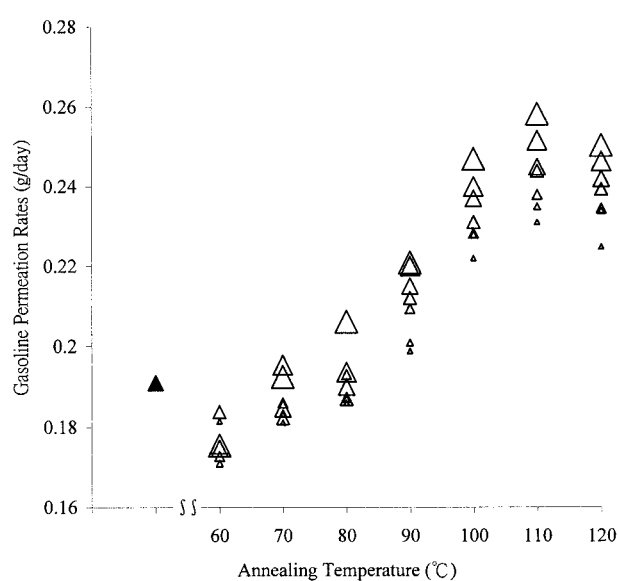
#### Gasoline Permeation Properties of the Annealed PE, PE/PA, and PE/MPA Bottles

Somewhat unexpectedly, the gasoline permeation rates increased significantly after the as-blow-molded PE bottles were annealed at temperatures ranging from 60 to 120°C for varying amounts of time (see Fig. 1). In fact, their gasoline permeation rates increased consistently with in-

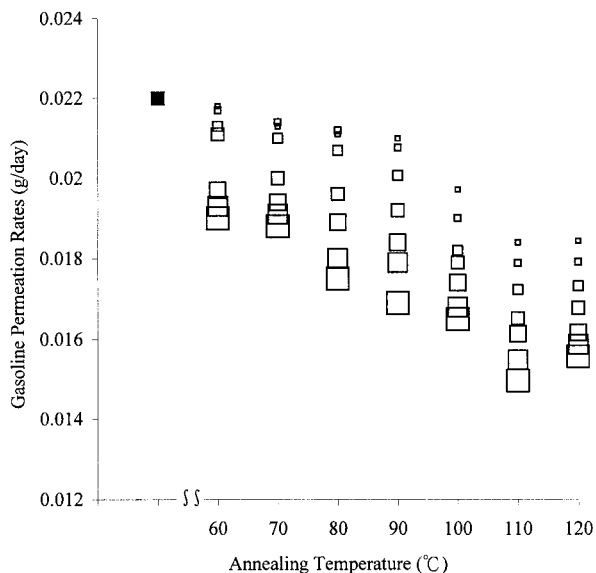
creases in annealing temperature and time. For instance, the gasoline permeation rate of the PE bottle annealed at 120°C for 32 h was about 30% faster than that of the as-blow-molded PE bottle. Similar to the results found for the annealed PE bottles, the gasoline permeation rates also increased significantly with the annealing temperature and time, when PE/PA bottles were annealed at 90°C or higher temperatures (see Fig. 2). However, the gasoline permeation rates of the PE/PA bottle decreased slightly when it was annealed at 60°C for varying amounts of time. In contrast, as shown in Figure 3, the gasoline permeation rates of the annealed PE/MPA bottles decreased consistently with increases in annealing temperature and time. After annealing the PE/MPA bottle at 120°C for 32 h, the gasoline permeation rate of the annealed PE/MPA bottle



**Figure 1** Gasoline permeation rates of the as-blow-molded PE bottle (●) and PE bottles annealed at various temperatures for 1 (○), 2 (○), 4 (○), 8 (○), 16 (○), 24 (○), and 32 (○) h.



**Figure 2** Gasoline permeation rates of the as-blow-molded PE/PA bottle (▲) and PE/PA bottles annealed at various temperatures for 1 (△), 2 (△), 4 (△), 8 (△), 16 (△), 24 (△), and 32 (△) h.

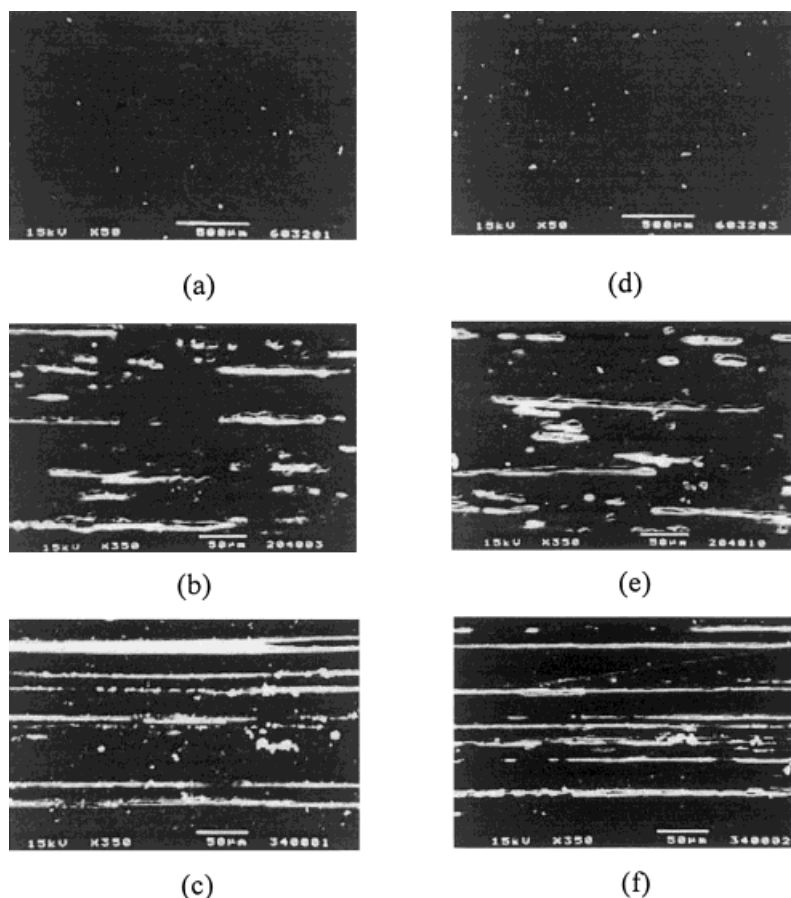


**Figure 3** Gasoline permeation rates of the as-blow-molded PE/MPA bottle (■) and PE/MPA bottles annealed at various temperatures for 1 (□), 2 (□), 4 (□), 8 (□), 16 (□), 24 (□) and 32 (□) h.

decreased by about 30% compared to that of the as-blow-molded PE/MPA bottle, which is equivalent to about 190 and 240 times slower than those of the as-blow-molded and corresponding annealed PE bottles, respectively.

#### Morphology of the As-Blow-Molded and Annealed PE, PE/PA, and PE/MPA Bottles

Typical micrographs of the fracture surfaces of PE, PE/PA, and PE/MPA bottles are summarized in Figure 4. Many clearly defined MPA laminae were found distributed in PE matrices through the wall thickness direction of the as-blow-molded PE/MPA bottle [see Fig. 4(c)]. Somewhat broken and less-demarcated PA laminae were found on the fracture surface of the as-blow-molded PE/PA bottle [see Fig. 4(b)]. Presumably, the level of barrier improvements of PE/MPA and PE/PA bottles depends significantly on the barrier properties of the base barrier resins. Moreover, the de-



**Figure 4** Fracture surfaces of the as-blow-molded (a) PE, (b) PE/PA, (c) PE/MPA; and (d) PE. (e) PE/PA and (f) PE/MPA bottles annealed at 110°C for 32 h.

marcated and elongated MPA laminae can further prolong the permeation period of the permeant molecules and improve the gasoline permeation resistance of the PE/MPA bottle over that of the PE/PA bottle with its relatively obscure and broken PA laminar structures.

On the other hand, it is interesting to note that no significant change in fracture surface morphology was found on the annealed PE, PE/PA, and PE/MPA bottles compared to that of their as-blow-molded bottles [see Fig. 4(d)–(f)]. Based on these premises, the significant change in the gasoline permeation resistance of the annealed PE, PE/PA, and PE/MPA bottles described earlier is not likely the result of the morphology change after the annealing treatments.

### Thermal Properties of PE, PE/PA, and PE/MPA Bottles

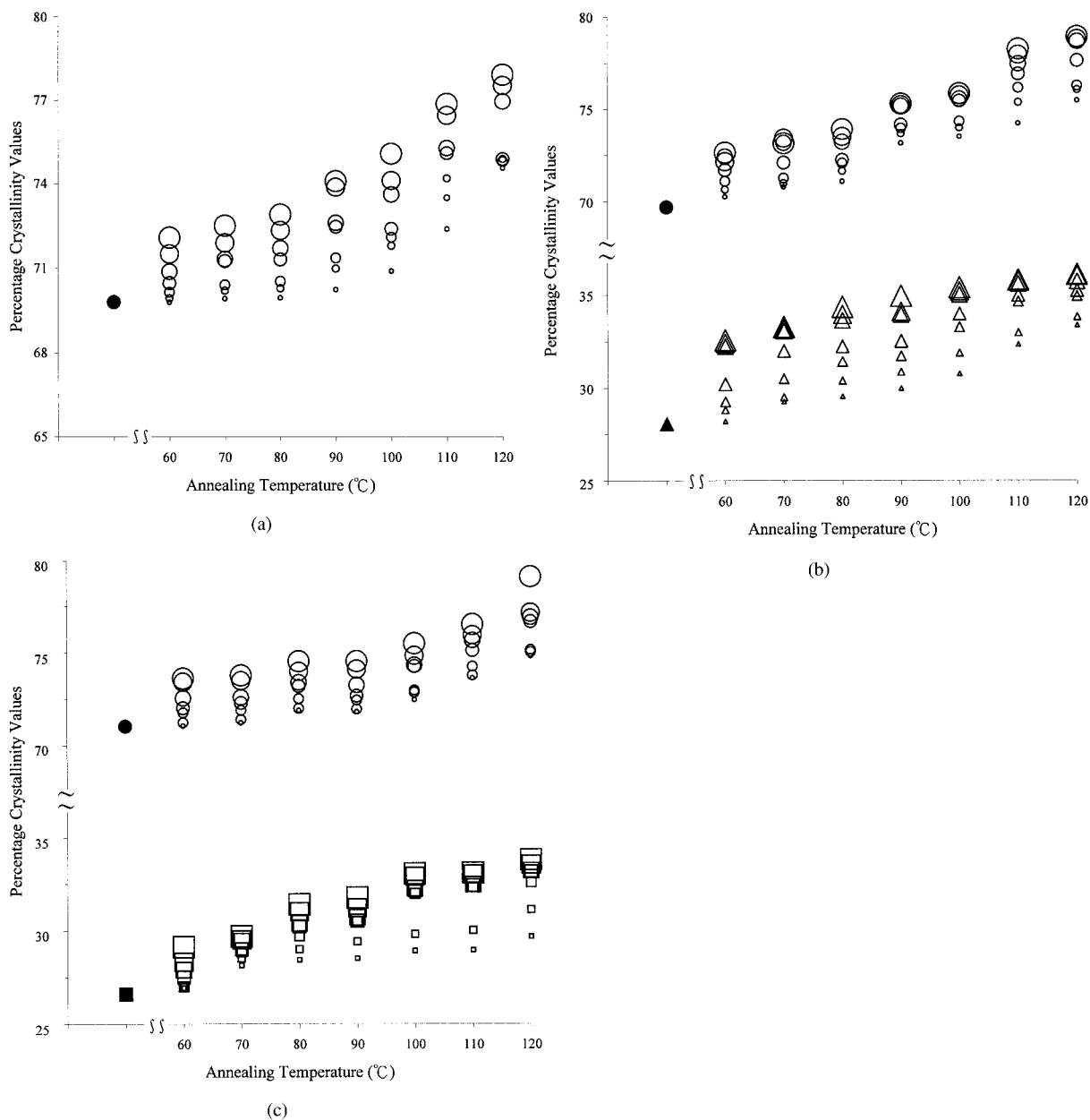
The crystallinity ( $W_c$ ) values of PE in the as-blow-molded and annealed PE, PE/PA, and PE/MPA bottles are summarized in Figure 5(a)–(c). At any annealing temperature used in this study, the  $W_c$  values of PE in these annealed bottles are higher than that in the as-blow-molded PE bottle, and increase significantly as the annealing time increases. In fact, it is also interesting to note that, at a fixed annealing time,  $W_c$  values of PE in the annealed PE, PE/PA, and PE/MPA bottles increase significantly as the annealing temperatures increase. As shown in Figure 5(a)–(c),  $W_c$  values of PE in the annealed bottles increase by about 8% after annealing them at 120°C for 32 h. Similarly,  $W_c$  values of PA and MPA in annealed PE/PA and PE/MPA bottles also increase significantly with the annealing treatments. For instance,  $W_c$  values of PA and MPA in the annealed bottles increase by about 6 and 5%, respectively, after annealing them at 120°C for 32 h.

### Compositions of Gasoline Fuels Before and After Permeation Tests

The typical compositions of the gasoline fuels before and after permeation tests of the as-blow-molded and annealed bottles are summarized in Figures 6, 7, and 8. Significant amounts of hydrocarbon components with 5 to 10 main-chain carbon atoms (e.g., *n*-pentane, toluene, xylene, and decalin) in gasoline fuels permeated through the as-blow-molded PE bottle, whereas the polar components (e.g., acetone and ethanol) remained, almost completely intact, without permeation after

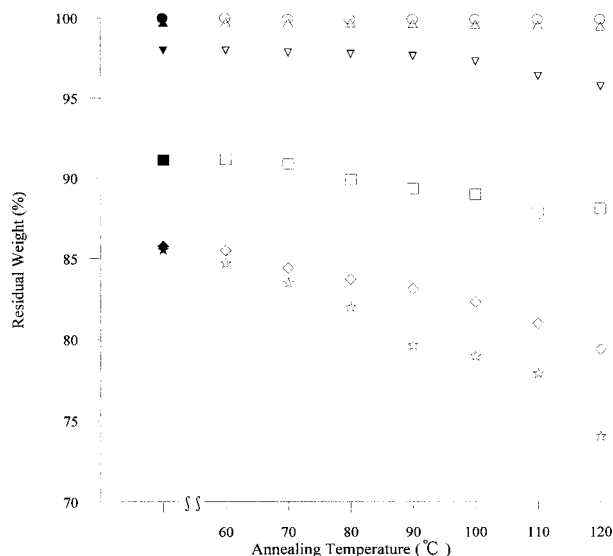
14 days at 40°C (see Fig. 6). By contrast, after blending the barrier resins in PE matrix, the relatively nonpolar hydrocarbon components present in the gasoline fuel were significantly blocked without permeation during the permeation tests, in which the as-blow-molded PE/MPA bottle blocked the permeation of hydrocarbon components more successfully than did the as-blow-molded PE/PA bottle (see Figs. 7 and 8). However, the amounts of polar components (e.g., acetone and ethanol) that permeated through the as-blow-molded PE/PA and PE/MPA bottles were very small and about the same as the amount that permeated through the as-blow-molded PE bottle. Somewhat unexpectedly, the permeated amounts of both nonpolar hydrocarbon and polar components of the annealed PE bottles were even greater than those of the as-blow-molded PE bottle, and increased consistently with increases in annealing temperature and time (see Fig. 6). As shown in Figure 7, similar trends were found for the PE/PA bottles annealed at 90°C or higher temperatures for varying amounts of time. On the contrary, after any annealing treatment performed on PE/MPA bottles, the permeated amounts of both the relatively nonpolar hydrocarbon and polar components decreased consistently with increases in annealing temperature and time (see Fig. 8).

It is not completely clear what accounts for these interesting permeation properties. It is generally recognized that permeant molecules can hardly diffuse through crystalline regions of polymers, and the molecules are believed to diffuse through the polymers by mostly penetrating through their amorphous regions. It is reasonable, therefore, to suggest that the molecular composition and structure in the amorphous phase of the polymer can greatly affect its barrier properties. The presence of polar amide, terminal amine groups, and intermolecular hydrogen bonding in PA and MPA molecules can scarcely allow the relatively nonpolar hydrocarbon molecules, compared to the nonpolar PE molecules, to enter into and permeate through the amorphous regions of PA and MPA laminae, although the  $W_c$  value of PE is much greater than  $W_c$  values of PA and MPA resins. In addition, as reported in our previous investigations,<sup>12–14</sup> short CP chains can be grafted into several long PA sequences during reactive extrusion and may be well dispersed as crosslinked structures in the amorphous regions of the PA matrix during crystallization of PA. These crosslinked structures of CP/PA copoly-



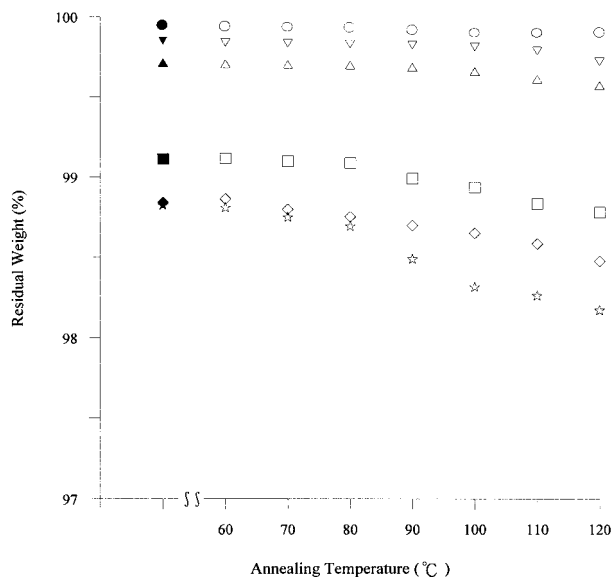
**Figure 5** (a) Percentage crystallinity values of the as-blow-molded PE bottle (●) and PE bottles annealed at various temperatures for 1 (○), 2 (○), 4 (○), 8 (○), 16 (○), 24 (○), and 32 (○) h. (b) Percentage crystallinity values of PE (●) in the as-blow-molded PE/PA bottle and PE/PA bottles annealed at various temperatures for 1 (○), 2 (○), 4 (○), 8 (○), 16 (○), 24 (○), and 32 (○) h; percentage crystallinity values of PA (▲) in the as-blow-molded PE/PA bottle and PE/PA bottles annealed at various temperatures for 1 (△), 2 (△), 4 (△), 8 (△), 16 (△), 24 (△), and 32 (△) h. (c) Percentage crystallinity values of PE (●) in the as-blow-molded PE/MPA bottle and PE/MPA bottles annealed at various temperatures for 1 (○), 2 (○), 4 (○), 8 (○), 16 (○), 24 (○), and 32 (○) h; percentage crystallinity values of MPA (▲) in the as-blow-molded PE/MPA bottle and PE/MPA bottles annealed at various temperatures for 1 (□), 2 (□), 4 (□), 8 (□), 16 (□), 24 (□), and 32 (□) h.



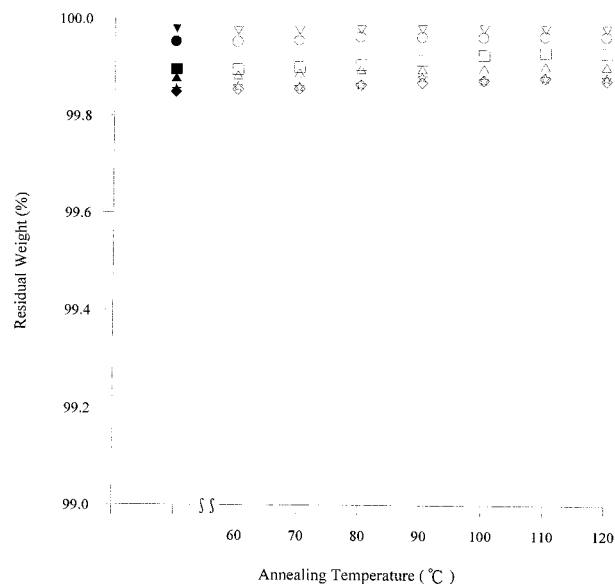


**Figure 6** Residual weights of pentane ( $\star$ ,  $\ast$ ), toluene ( $\blacklozenge$ ,  $\diamond$ ), xylene ( $\blacksquare$ ,  $\square$ ), decalin ( $\blacktriangledown$ ,  $\triangledown$ ), acetone ( $\blacktriangle$ ,  $\triangle$ ), and ethanol ( $\bullet$ ,  $\circ$ ) in the as-blow-molded and annealed PE bottles annealed at various temperatures for 32 h, respectively. The solid symbols represent the residual weights of the as-blow-molded PE bottles.

mers can reduce the permeant space in the amorphous regions of PA and prohibit the permeant molecules from entering into and permeating



**Figure 7** Residual weights of pentane ( $\star$ ,  $\ast$ ), toluene ( $\blacklozenge$ ,  $\diamond$ ), xylene ( $\blacksquare$ ,  $\square$ ), decalin ( $\blacktriangledown$ ,  $\triangledown$ ), acetone ( $\blacktriangle$ ,  $\triangle$ ), and ethanol ( $\bullet$ ,  $\circ$ ) in the as-blow-molded and annealed PE/PA bottles annealed at various temperatures for 32 h, respectively. The solid symbols represent the residual weights of the as-blow-molded PE/PA bottles.



**Figure 8** Residual weights of pentane ( $\star$ ,  $\ast$ ), toluene ( $\blacklozenge$ ,  $\diamond$ ), xylene ( $\blacksquare$ ,  $\square$ ), decalin ( $\blacktriangledown$ ,  $\triangledown$ ), acetone ( $\blacktriangle$ ,  $\triangle$ ), and ethanol ( $\bullet$ ,  $\circ$ ) in the as-blow-molded and annealed PE/MPA bottles annealed at various temperatures for 32 h, respectively. The solid symbols represent the residual weights of the as-blow-molded PE/MPA bottles.

through the amorphous regions of MPA laminae. Conversely, the nonpolar PE molecules can prevent the polar components (e.g., acetone and ethanol) from permeating through their amorphous regions more effectively than can PA and MPA molecules. However, the major components present in gasoline fuels are relatively nonpolar hydrocarbon components. As a consequence, the PE/MPA and PE as-blow-molded bottles exhibited, respectively, the best and the worst gasoline permeation resistance among the PE, PE/PA, and PE/MPA as-blow-molded bottles prepared in this study.

It is not completely clear what underlying mechanism would account for the interesting barrier properties of the annealed bottles. As described in the previous section,  $W_c$  values of PE, PA, and MPA specimens all increase with increases in annealing temperature and time. This increase in  $W_c$  may significantly lengthen the permeant path of permeant molecules and, hence, improve the gasoline permeation resistance of the annealed PE, PE/PA, and PE/MPA bottles. Presumably, this increased  $W_c$  is partly the result of the crystallization of the amorphous molecules during the annealing process, which can result in more sparse amorphous structures than those of

the as-blow-molded resins. Moreover, the amorphous structures of the annealed PE resins can be even more sparse than those of the annealed MPA resins because the permeation temperature (i.e., 40°C) is well above the glass-transition temperature of the PE resins, but below that of the MPA resins. These sparse molecular structures present in PE amorphous regions can provide more space for permeant molecules to permeate through, shorten the permeant path of gasoline molecules, and thus counterbalance the beneficial effect of  $W_c$  on the gasoline barrier resistance of the annealed PE bottles. Therefore, the gasoline permeation rates of most of the annealed PE bottles at 40°C increase significantly as the annealing temperature and time increase.

In contrast, the elongated and clearly defined MPA laminae present in the PE/MPA bottles block the permeant path and make gasoline permeation harder to achieve than in PE and/or PE/PA bottles with less-demarcated PA laminae. MPA is not only a better barrier resin than PA and PE resins, but the crosslinked CP/PA copolymer structure also makes the permeant space ( $V_f$ ) in the amorphous regions of MPA even smaller than that of PA. In addition, after the annealing treatments performed in this study,  $V_f$ 's of MPA laminae are not likely to increase to the level that can counterbalance the beneficial effect of the improved  $W_c$  of MPA on the gasoline barrier resistance of the annealed PE/MPA bottles, because the test temperature is well below the glass-transition temperatures of the annealed MPA resins. As a consequence, the improved  $W_c$  values of the annealed and elongated MPA laminae consistently allow PE/MPA bottles to exhibit better gasoline permeation resistance as their annealing temperatures and time increase. On the other hand, the broken and less-elongated PA laminae found in the PE/PA bottles cannot block the permeant path of gasoline molecules as effectively as can the elongated MPA laminae in the PE/MPA bottles, although PA is a better barrier resin than PE against gasoline permeation. The possible increase in  $V_f$  of the PE matrix after annealing predominates, making the permeant path more suitable for gasoline molecules to penetrate through and, hence, increasing the gasoline permeation rates of the PE/PA bottles annealed at 90°C and higher temperatures for varying amounts of time.

## CONCLUSIONS

Very poor gasoline permeation resistance was found in the as-blow-molded PE bottle. After blending 10 wt % of MPA or PA in PE, the gasoline permeation rates of the as-blow-molded PE/MPA or PE/PA bottles at 40°C are, respectively, about 130 or 15 times slower than that of the as-blow-molded PE bottle. Somewhat unexpectedly, the gasoline permeation rates of the annealed PE bottles and PE/PA bottles, annealed at 90°C or higher temperatures, increased significantly with the annealing temperature and time. On the contrary, the gasoline permeation resistance of the annealed PE/MPA bottles improved consistently with the annealing treatments. In fact, the gasoline permeation rate of the PE/MPA bottle annealed at 120°C for 32 h is about 190 and 240 times slower than those of the corresponding as-blow-molded and annealed PE bottles, respectively.

Morphological analysis found that many elongated and clearly defined MPA laminae are present in the as-blow-molded PE/MPA bottle. In contrast, broken and much less demarcated PA laminae were found on the fracture surfaces of the as-blow-molded PE/PA bottles. After the annealing treatments, no significant change in the fracture surface morphology was found on these annealed PE, PE/PA, and PE/MPA bottles. The crystallinity values of the annealed PE, PA, and MPA specimens all increased with increases in annealing temperature and time. Significant amounts of relatively nonpolar hydrocarbon components present in the gasoline fuels were found to permeate through the as-blow-molded PE bottles, whereas polar components remained, almost completely intact, without permeation after 14 days at 40°C. In contrast, after blending the barrier resins in PE matrices, the relatively nonpolar hydrocarbon components were significantly blocked without permeation during the permeation tests, in which the as-blow-molded PE/MPA bottle inhibited the permeation of hydrocarbon components more successfully than did the as-blow-molded PE/PA bottle. However, the amounts of polar components that permeated through the as-blow-molded PE/PA and PE/MPA bottles were very small and about the same as the amount that permeated through the as-blow-molded PE bottle. Somewhat unexpectedly, the permeated amounts of both nonpolar and polar components of the annealed PE bottles and/or PE/PA bottles annealed at temperatures higher than 90°C were

even greater than those of the as-blow-molded PE bottle, and increased consistently with increases in annealing temperature and time. On the contrary, the permeated amounts of both nonpolar and polar components of the annealed PE/MPA bottles decreased consistently with the annealing treatments. Possible mechanisms accounting for these interesting gasoline barrier properties are discussed in this study.

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