

# Permeation Barrier Properties of Polyethylene/Modified Blends of Polyamide and Polyvinylalcohol Containers Against Methanol/Gasoline Fuels

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**ABSTRACT:** One commercial grade of polyamide and/or polyvinylalcohol resins were modified by a compatibilizer precursor to make various compositions of modified polyamide (MPA) and/or modified blends of polyamide/polyvinylalcohol (MPAPVA) through reactive extrusion. Good methanol/gasoline fuel permeation resistance together with clearly defined MPAPVA and MPA laminar structures were found on containers blow-molded from the blends of polyethylene PE/MPAPVA and PE/MPA, respectively. The compositions of MPAPVA and MPA resins were found to exhibit a significant influence on the methanol/gasoline fuel permeation resistance and morphology of PE/MPAPVA and PE/MPA containers, respectively. Possible mechanisms are proposed to explain these interesting phenomena. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2158–2169, 1999

**Key words:** MPA; MPAPVA; PE/MPAPVA; PE/MPA

## INTRODUCTION

Scientists have been looking for a new source of energy to replace gasoline as a fuel for the automobile industry, because it is well known that petroleum will be depleted in less than 50 years. In addition to low cost and availability in large amounts, this new source of energy is required to be friendly to the environment, such as less automobile emission pollution than that of gasoline. In general, the methanol/gasoline fuel (methanol fuel) is one of the good potential replacements for gasoline because it is recognized as a low-cost, good-efficiency, and low air pollution fuel in the

automobile industry. However, current metal fuel tanks cannot be used to contain methanol, because they are susceptible to corrosion. In contrast, plastic fuel containers will be a better choice if their permeation resistance to methanol fuel can be improved to match the needs of the automobile industry in the future.

Containers made of high-density polyethylene (HDPE) are probably the most prevailing and suitable materials for packaging various liquids; however, polyethylene (PE) is notorious for having poor permeation resistance to hydrocarbon solvents, such as gasoline. In an attempt to improve this poor permeation resistance of PE, alternative technologies have been applied.<sup>1–12</sup> These technologies include surface treatment of PE by fluorination or sulfonation,<sup>1,2</sup> multilayer coextrusion of PE, compatibilizer precursor (CP)

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and polyamide (PA),<sup>1,2</sup> laminar-blend blow molding of PE, CP, and PA blends,<sup>3-5</sup> or laminar-blend blow molding of PE and modified polyamide (MPA).<sup>6-12</sup> Among these improved technologies, the "laminar-blend-blow-molding process" forms a layered structure containing numerous discontinuous, overlapping platelets of barrier resins such as PA or MPA in a PE matrix, which is one of the well proven barrier technologies to enhance the resistance of PE containers to hydrocarbon permeation.<sup>3-12</sup> These heterogeneous laminar blends exhibit significantly better hydrocarbon permeation resistance than the conventional homogeneous blends associated with uniform dispersed PA within the PE matrix.<sup>6-16</sup> Unfortunately, the barrier properties of the lamella structure formed by modified polyamide or polyamide/compatibilizer blends is not good enough to prevent the permeation of methanol/gasoline fuels. In contrast, polyvinylalcohol (PVA) is one of the best antisolvent materials and it has been reported<sup>17</sup> that the presence of PVA in PE/PA/CP blends could improve their corresponding permeation barrier resistance to methanol/gasoline fuels. However, detailed mechanisms accounting for this improved permeation resistance, and the influence of the compositions of PE/PA/PVA/CP blends on their corresponding permeation resistance, have never been reported. As far as we know, no further investigation was reported in this area except Mehra's.<sup>17</sup>

A systematic study of the influence of compositions of PE/MPA and PE/modified blends of polyamide/polyvinylalcohol (PE/MPAPVA) containers on their corresponding permeation resistance to methanol/gasoline fuels is reported. The contents of CP, PVA, and PA present in PE/MPAPVA containers were found to have a significant effect on their permeation resistance to methanol/gasoline fuels. Possible mechanisms accounting for these interesting phenomena are suggested in this study.

## EXPERIMENTAL

### Materials and Sample Preparation

One commercial grade of PA and/or PVA resins was modified by a CP to make MPA and/or MPAPVA through reactive extrusion. The compatibilizer precursor used in this study is a zinc-neutralized ethylene/acrylic acid copolymer. The type of PA used was nylon 6, which was obtained

**Table I The Compositions of MPA and MPAPVA Resins**

(wt %)	PA	PVA	CP
MPA <sub>3</sub> PVA <sub>10</sub>	67.500	22.500	10
MPA <sub>7</sub> PVA <sub>10</sub>	78.750	11.250	10
MPA <sub>15</sub> PVA <sub>10</sub>	84.375	5.625	10
MPA <sub>10</sub>	90		10
MPA <sub>3</sub> PVA <sub>20</sub>	60	20	20
MPA <sub>7</sub> PVA <sub>20</sub>	70	10	20
MPA <sub>15</sub> PVA <sub>20</sub>	75	5	20
MPA <sub>20</sub>	80		20
MPA <sub>3</sub> PVA <sub>30</sub>	52.5	17.5	30
MPA <sub>7</sub> PVA <sub>30</sub>	61.25	8.75	30
MPA <sub>15</sub> PVA <sub>30</sub>	65.625	4.375	30
MPA <sub>30</sub>	70		30
UMPA <sub>3</sub> PVA <sub>10</sub>	67.5	22.5	10
UMPA <sub>3</sub> PVA <sub>20</sub>	60	20	20
UMPA <sub>3</sub> PVA <sub>30</sub>	52.5	17.5	30

from Formosa Chemicals and Fiber Corporation with a trade name of Sunylon 6N. The PE (Taisox 9003), PVA (BF 05), and antioxidant (Irganox B225) used in this study were obtained from Formosa Plastic, Chang Chun Petrochemical, and Ciba-Geigy Corporation, respectively.

Before melt blending, PA, PVA, and CP were dried at 80°C for 16 h and 60°C for 8 h, respectively. About 1500 ppm of antioxidant was dry-blended with the dried components of PA/CP or PA/PVA/CP and then fed into a twin screw extruder to prepare MPA or MPAPVA resins, respectively. The extruder was operated at 215°C in the feeding zone and 240°C toward the extrusion die, and at a screw speed of 100 rpm. The compositions of MPA and MPAPVA resins prepared in this study are summarized in Table I.

Each type of MPA and MPAPVA resin prepared above was then dried at 80°C for 16 h, and dry-blended with PE at a weight ratio of 90 : 10 (PE:resin) before blow-molding. The mixed PE/MPA and PE/MPAPVA blends were blow-molded by a blow-molding machine operated at an extrusion temperature of 225°C and a screw speed of 25 rpm. The blow-molded bottles weighed about 50 g and had a capacity of about 500 mL with a wall thickness of about 1 mm. For purposes of comparison, bottles were also prepared from dried-blended PE/PA/PVA/CP blends and base PE using the same screw speed but blow-molded at extrusion temperatures of 225 and 190°C, respectively. These dried-blended PE/PA/PVA/CP

blends will be referred to as the PE/UMPAPVA samples in the following discussion (see Table I).

#### Permeation Barrier Resistance of Bottles and Hot-Pressed Sheets

The permeation barrier resistance of the blow-molded bottles against methanol/gasoline fuels was evaluated by measuring the weight losses of the methanol/gasoline fuels filled in the bottles. Bottles of PE, PE/MPA, PE/MPAPVA, and PE/UMPAPVA were initially filled with 300 g of various methanol/gasoline fuels. These methanol/gasoline fuels were prepared by mixing methanol and gasoline at weight ratios of 0 : 100, 20 : 80, 40 : 60, 60 : 40, 80 : 20, and 100 : 0, respectively. The weight losses of the methanol/gasoline fuels were determined after holding the filled bottles at 40°C for 14 days. On the other hand, the permeation resistance of MPA, MPAPVA, and UMPAPVA against methanol/gasoline fuels was determined based on their hot-pressed sheets, because MPA, MPAPVA, and UMPAPVA resins are difficult to blow mold because of their poor melt strengths. However, it is difficult to make hot-pressed sheets of PVA, because it degrades quickly during the melting process. The dried pellets of MPA, MPAPVA, and UMPAPVA were hot-pressed at 230°C into about 1-mm thick and then cut into circles of a diameter of 14 cm. For purposes of comparison, similar hot-pressed sheets were also prepared from base PE resin using the same compression-molding machine, whereas operated at a compression temperature of 170°C. The circular PE, MPA, MPAPVA, and UMPAPVA sheets were sealed as lids on the top of test flasks filled with 300 g of methanol/gasoline fuels. The permeation barrier properties of these circular sheets were then determined by measuring the weight losses of methanol/gasoline fuels after holding the flasks at 40°C for 14 days.

#### Morphology and Thermal Properties

To observe the deformation structures of MPA, MPAPVA, and UMPAPVA in PE/MPA, PE/MPAPVA, and PE/UMPAPVA bottles, respectively, these blow-molded bottles were fractured in liquid nitrogen and etched with formic acid. The etched samples were then gold-coated and examined using a Jeol JSM-5200 Scanning Electron Microscopy.

The melting temperatures and crystallinity values of PE, PA, CP, MPA, and MPAPVA resins

were determined by a differential scanning calorimeter. The differential scanning calorimeter experiments were measured at a heat rate of 10°C/min. The perfect heat fusions reported for PE,<sup>18</sup> PA,<sup>19</sup> and PVA<sup>20</sup> are 293, 191, and 156 J/g, respectively, which were used for the calculation of the crystallinity values of each corresponding sample.

#### Rheological Properties

The melt indexes (MIs) of PE, PA, CP, MPA, and MPAPVA samples were determined at 230°C and 2.16 kg according to ASTM D1238. The instrument used in determining these MIs was a Kayness Led Eye Set AT 250 Capillary Rheometer. However, it is difficult to determine the MIs of PVA samples, because they degrade quickly during the melting process. On the other hand, the melt shear viscosities ( $\eta_s$ ) of PE, PA, PVA, MPA, and MPAPVA resins were measured at 230°C and shear rates ranging from 15 to 120 1/s using a Rosand Precision Advanced Capillary Extrusion Rheometer equipped with a capillary of 1-mm diameter. These  $\eta_s$ , measured at various shear rates up to approximately 100 1/s, are used to correlate with the deformation behavior of MPA, MPAPVA, and UMPAPVA in PE during the blow-molding of PE/MPA, PE/MPAPVA, and PE/UMPAPVA blends, respectively, because the shear rates of polymer melts during extrusion and blow-molding are generally recognized to be less than 100 1/s.

## RESULTS AND DISCUSSION

#### Rheological Properties

The MIs and melt shear viscosities ( $\eta_s$ ) of PE, CP, PA, PVA, MPA, and MPAPVA resins are summarized in Table II and Figure 1, respectively. As expected, the melt shear viscosities of these samples tend to increase with decreasing MIs. It is noteworthy that the melt shear viscosity of PE is the highest among the resins shown in Figure 1, wherein the melt shear viscosity of PA is higher than that of PVA resin. In contrast, the  $\eta_s$  of MPA and MPAPVA resins are significantly higher than those of their corresponding base PA and PVA resins and increase consistently with the CP contents contained in MPA and MPAPVA resins, respectively. However, it is worth noting that  $\eta_s$  of MPAPVA resins are much lower than those of

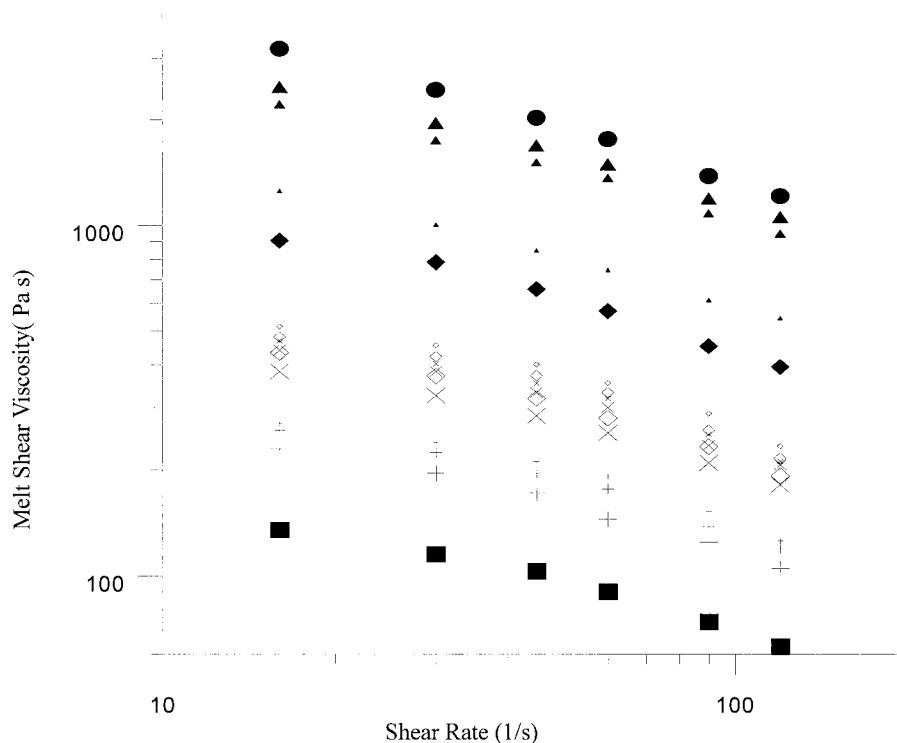
**Table II** Melt-Flow Indexes of PE, CP, PA, MPA, and MPAPVA Resins Measured at 230°C/2.16 kg

Sample	MPA <sub>3</sub> PVA <sub>10</sub>	MPA <sub>7</sub> PVA <sub>10</sub>	MPA <sub>15</sub> PVA <sub>10</sub>	MPA <sub>3</sub> PVA <sub>20</sub>	MPA <sub>7</sub> PVA <sub>20</sub>	MPA <sub>15</sub> PVA <sub>20</sub>
MI (g/10 min)	2.18	2.35	2.55	1.91	2.30	2.51
Sample	MPA <sub>3</sub> PVA <sub>30</sub>	MPA <sub>7</sub> PVA <sub>30</sub>	MPA <sub>15</sub> PVA <sub>30</sub>	MPA <sub>10</sub>	MPA <sub>20</sub>	MPA <sub>30</sub>
MI (g/10 min)	1.83	2.25	2.46	2.4	1.7	1.5
Sample	PE	CP	PA			
MI (g/10 min)	0.36	9.2	2.6			

corresponding MPA resins with the same amount of CP present within them.

As indicated in our previous investigations,<sup>6-9</sup> formation of CP-grafted-PA copolymers, through the reaction of carboxyl groups of CP with the terminal amine groups of PA, was found during the preparation of MPA resins. For instance, short CP chains may be dispersed into PA matrix and grafted into several long PA molecules and are present as huge "crosslinked" CP/PA copolymers in the PA matrix. Presumably,  $\eta$ s of CP-grafted-PA copolymers can be higher than those of CP and PA resins. By the same analogy, the possible reaction of carboxyl groups of CP

with the hydroxy groups of PVA and terminal amine groups of PA can also generate the huge "crosslinked" CP/PVA/PA copolymers and make their  $\eta$ s significantly higher than those of their parent PA and PVA resins. However, the melt shear viscosity of PA is significantly higher than that of PVA resin used in this study; therefore, the  $\eta$ s of MPAPVA resins are much lower than those of corresponding MPA resins with the same amount of CP present within them. Apparently, the CP/PA and CP/PVA/PA copolymers are still thermoplastic, and the "crosslinking" level is not high. However, the word "crosslinked" is only used to emphasize the



**Figure 1** Melt shear viscosities of (+) MPA<sub>3</sub>PVA<sub>10</sub>, (+) MPA<sub>7</sub>PVA<sub>10</sub>, (+) MPA<sub>15</sub>PVA<sub>10</sub>, (×) MPA<sub>3</sub>PVA<sub>20</sub>, (×) MPA<sub>7</sub>PVA<sub>20</sub>, (×) MPA<sub>15</sub>PVA<sub>20</sub>, (◇) MPA<sub>3</sub>PVA<sub>30</sub>, (◇) MPA<sub>7</sub>PVA<sub>30</sub>, (◇) MPA<sub>15</sub>PVA<sub>30</sub>, (●) PE, (◆) PA, (■) PVA, (▲) MPA<sub>10</sub>, (▲) MPA<sub>20</sub>, and (▲) MPA<sub>30</sub> measured at 230°C and various shear rates.

**Table III Crystallinity Values ( $W_c$ ) and Melting Temperatures ( $T_m$ s) of PE, CP, PA, PVA, MPA, and MPAPVA Resins**

Sample	MPA <sub>3</sub> PVA <sub>10</sub>	MPA <sub>7</sub> PVA <sub>10</sub>	MPA <sub>15</sub> PVA <sub>10</sub>	MPA <sub>3</sub> PVA <sub>20</sub>	MPA <sub>7</sub> PVA <sub>20</sub>	MPA <sub>15</sub> PVA <sub>20</sub>
Measured $W_c$ (%)	29.9	28.7	27.4	27.8	27.6	26.7
Theoretical $W_c$ (%)	41.1	39.8	39.2	38.4	37.3	36.8
$T_m$ s (°C)	225.7	223.5	222.3	223.1	221.9	220.4
Sample	MPA <sub>3</sub> PVA <sub>30</sub>	MPA <sub>7</sub> PVA <sub>30</sub>	MPA <sub>15</sub> PVA <sub>30</sub>	MPA <sub>10</sub>	MPA <sub>20</sub>	MPA <sub>30</sub>
Measured $W_c$ (%)	26.9	26.4	25.3	29	27	26
Theoretical $W_c$ (%)	35.7	34.8	34.3	38.6	36.2	33.8
$T_m$ s (°C)	221.5	220.1	219.6	223.0	220.7	219.5
Sample	PA	PVA	PE	CP		
Measured $W_c$ (%)	41	52	71	17		
$T_m$ s (°C)	224.2	226.1	136.2	95.1		

more complex and huge structure of the CP-grafted CP/PA and CP/PVA/PA copolymer molecules than those of their parent CP, PA, and PVA molecules.

### Thermal Properties

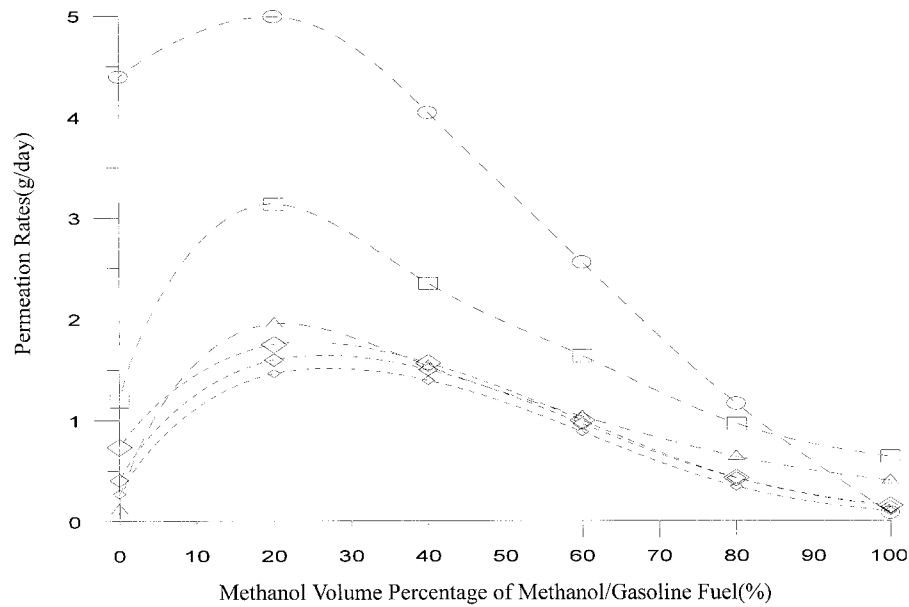
The crystallinity values ( $W_c$ ) and melting temperatures ( $T_m$ s) of PE, CP, PA, PVA, MPA, and MPAPVA resins are listed in Table III. The melting temperature and crystallinity value of PVA resin are slightly higher than those of PA. On the other hand, it is noteworthy that  $W_c$  and  $T_m$ s of MPA and MPAPVA resins are significantly lower than their parent PA and PVA. In fact,  $W_c$  and  $T_m$ s of MPA or MPAPVA were further found to decrease as the CP contents present in MPA or MPAPVA increase. Presumably, the decrease in  $W_c$  of MPA or MPAPVA can be mainly attributed to the reduced  $W_c$  caused by reducing the amounts of PA or PVA in the MPA or MPAPVA as the content of less crystallizable CP increases. The theoretical crystallinity values of MPA and MPAPVA resins calculated by mixing rule are summarized in Table III. These theoretical values reduce significantly with decreasing contents of PA and/or PVA contained in MPA and MPAPVA, respectively; however, they are still lower than their measured  $W_c$ . As mentioned above, "crosslinked" CP/PA and CP/PA/PVA copolymers can be formed during preparation of MPA and MPAPVA resins. These copolymers are generally recognized as less crystallizable polymers than their parent PA and PVA resins. It is, therefore, reasonable to suggest that these copolymers can also reduce the  $W_c$  and  $T_m$ s of MPA and MPAPVA resins as their CP contents increase. As a consequence,  $W_c$  and  $T_m$ s of MPA

and MPAPVA resins decrease as their CP contents increase, because the possibility of formation of these copolymers is higher as their CP contents increase.

### Barrier Properties of PE, PE/MPA, PE/MPAPVA, and PE/UMPAPVA Bottles

The methanol/gasoline fuel permeation rates of PE, PE/MPA, PE/MPAPVA, and PE/UMPAPVA bottles are shown in Figures 2–4. The base PE bottle exhibited much better permeation resistance to pure methanol than PE/MPA, PE/MPAPVA, and PE/UMPAPVA bottles. However, the methanol/gasoline fuel permeation rates of PE bottle increase significantly after adding certain amounts of gasoline in methanol. In fact, the permeation resistance of PE bottle against methanol/gasoline fuels tends to become even worse than that of PE/MPA, PE/MPAPVA, and PE/UMPAPVA bottles as the gasoline volume percentage (Vol %) contained in methanol/gasoline fuels increases. It is noteworthy that the methanol/gasoline fuel permeation rates of all bottles prepared in this study increase significantly when the methanol Vol % contained in methanol/gasoline fuels is 20 to approximately 80%. As reported in the literature,<sup>21</sup> the vapor pressure values of the methanol/gasoline fuels are much higher than those of pure methanol and gasoline from a few to about 80 methanol Vol %. This significantly high driving force of vapor pressure can be the main reason that the permeation resistance of all the bottles is much worse than that of bottles containing only pure methanol or gasoline.

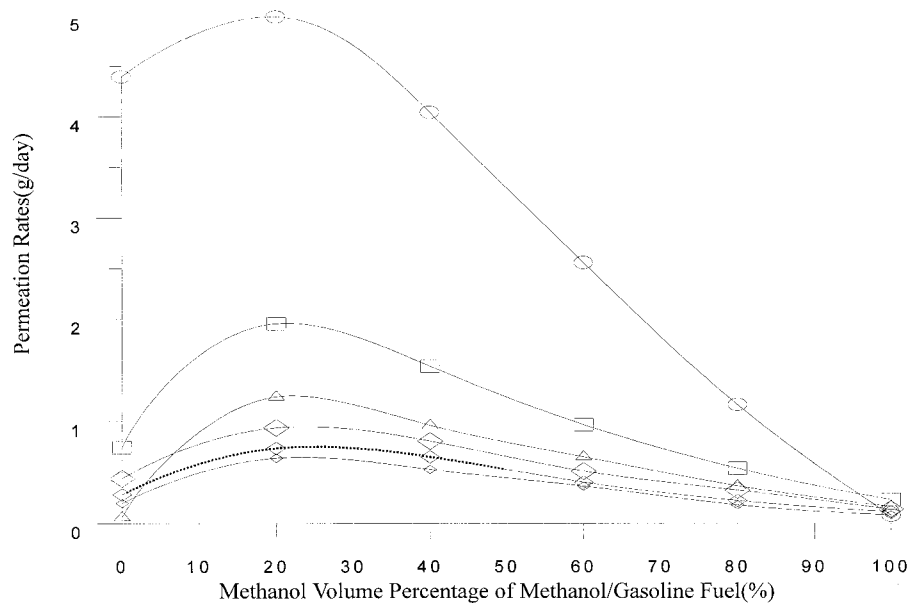
On the other hand, it is noteworthy that the permeation resistance of PE/MPAPVA bottles against methanol/gasoline fuels with 20 to 80



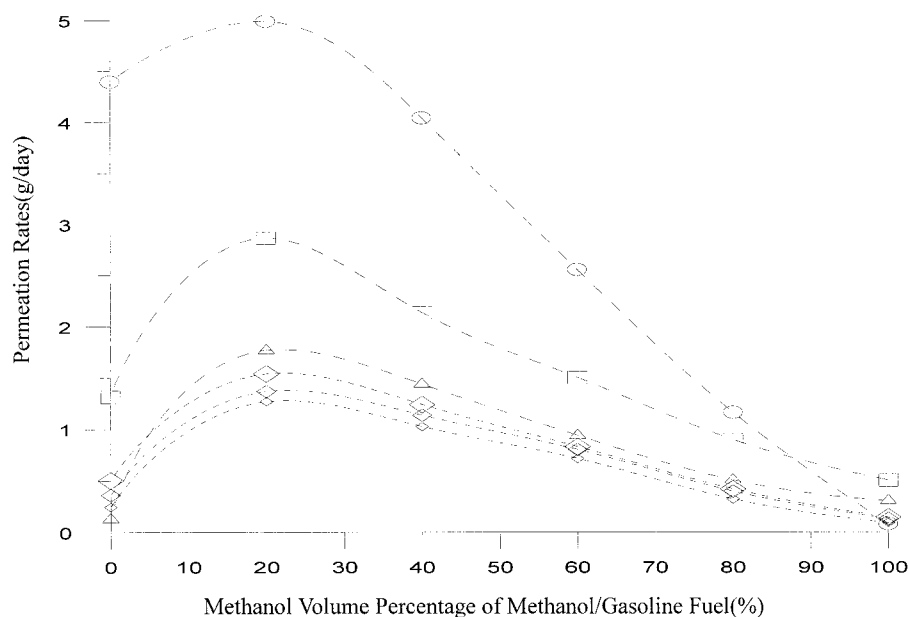
**Figure 2** Methanol/gasoline fuel permeation rates of (○) PE, (◇) PE/MPA<sub>3</sub>PVA<sub>10</sub>, (◇) PE/MPA<sub>7</sub>PVA<sub>10</sub>, (◇) PE/MPA<sub>15</sub>PVA<sub>10</sub>, (△) PE/MPA<sub>10</sub>, and (□) PE/UMPA<sub>3</sub>PVA<sub>10</sub> bottles.

methanol Vol % is significantly better than that of PE/MPA and PE/UMPA PVA bottles with the same CP content (see Figs. 2–4). In addition, the permeation resistance of PE/MPA PVA bottles against methanol/gasoline fuels continues to improve as the PVA contents contained in MPAPVA

increase. For example, the permeation rate of a PE/MPA<sub>3</sub>PVA<sub>20</sub> bottle against methanol/gasoline fuel with 20 Vol % of methanol is about 10, 30, 50, and 70% lower than those of PE/MPA<sub>7</sub>PVA<sub>20</sub>, PE/MPA<sub>15</sub>PVA<sub>20</sub>, PE/MPA<sub>20</sub>, and PE/UMPA<sub>3</sub>PVA<sub>20</sub> bottles, respectively.



**Figure 3** Methanol/gasoline fuel permeation rates of (○) PE, (◇) PE/MPA<sub>3</sub>PVA<sub>20</sub>, (◇) PE/MPA<sub>7</sub>PVA<sub>20</sub>, (◇) PE/MPA<sub>15</sub>PVA<sub>20</sub>, (△) PE/MPA<sub>20</sub>, and (□) PE/UMPA<sub>3</sub>PVA<sub>20</sub> bottles.



**Figure 4** Methanol/gasoline fuel permeation rates of (○) PE, (◇) PE/MPA<sub>3</sub>PVA<sub>30</sub>, (◇) PE/MPA<sub>7</sub>PVA<sub>30</sub>, (◇) PE/MPA<sub>15</sub>PVA<sub>30</sub>, (△) PE/MPA<sub>30</sub>, and (□) PE/UMPA<sub>3</sub>PVA<sub>30</sub> bottles.

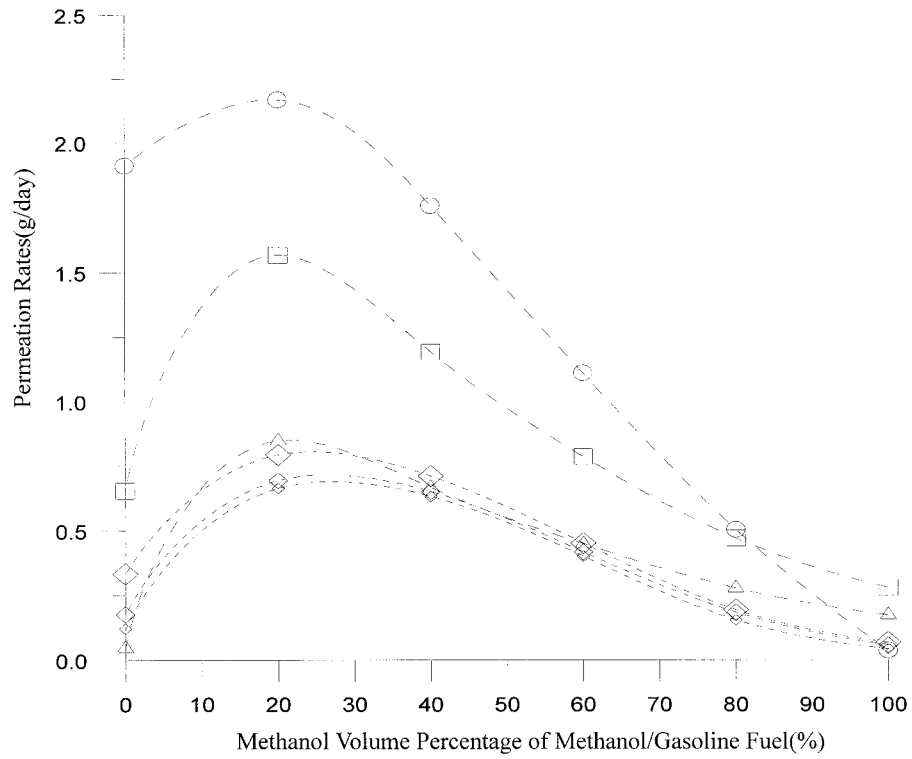
Finally, it was found that the CP content present in MPA and MPAPVA is also an important factor that affects the barrier properties of PE/MPA and PE/MPAPVA bottles. As shown in Figures 2–4, the permeation resistance of PE/MPA and PE/MPAPVA bottles against methanol/gasoline fuels is best when the CP content contained in MPA and MPAPVA reaches about 20 wt %, respectively. For instance, the permeation rate of PE/MPA<sub>3</sub>PVA<sub>20</sub> against methanol/gasoline fuel with 20 Vol % of methanol is about 40% of those of PE/MPA<sub>3</sub>PVA<sub>10</sub> and PE/MPA<sub>3</sub>PVA<sub>30</sub> and only about 10% of that of a base PE bottle.

#### Barrier Properties of Hot-Pressed PE, MPA, and MPAPVA Sheets

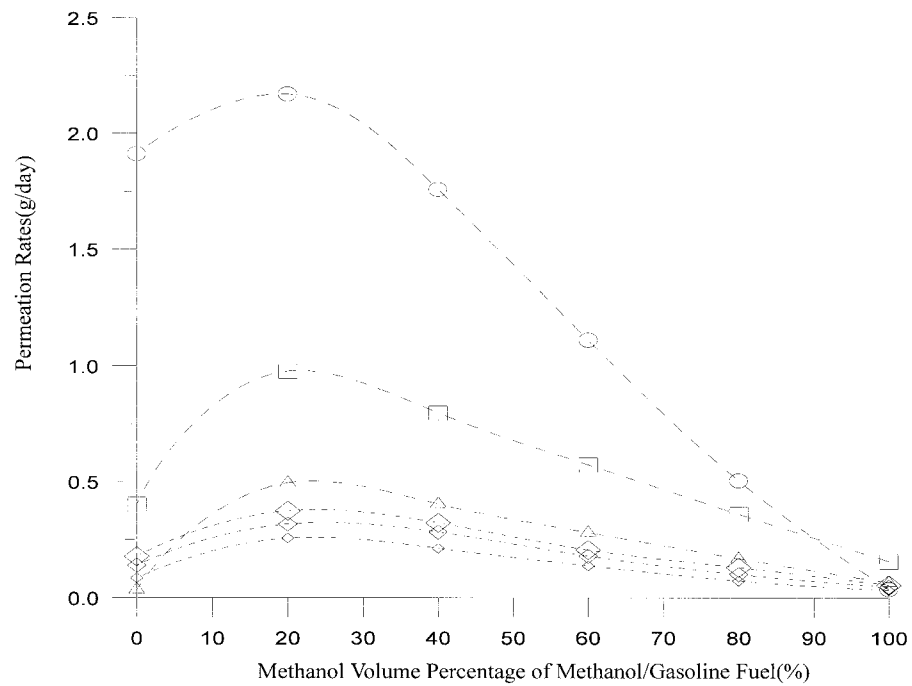
The methanol/gasoline fuel permeation resistances of hot-pressed sheets of PE, MPA, and MPAPVA sheets are summarized in Figures 5–7. Similar to those found in the previous section, the barrier resistance of hot-pressed MPA, MPAPVA, and even UMPAPVA sheets against methanol/gasoline fuels is better than that of the hot-pressed PE sheet. The MPAPVA sheets exhibit significantly better permeation resistance than that of corresponding MPA and UMPAPVA sheets with the same CP content contained in them. This improved permeation resistance of MPAPVA sheets continues to improve as their

PVA contents increase. For instance, MPA<sub>3</sub>PVA<sub>10</sub> exhibits the best, but MPA<sub>15</sub>PVA<sub>20</sub> exhibits the poorest permeation resistance against methanol/gasoline fuels among the MPA<sub>x</sub>PVA<sub>20</sub> sheet series (see Fig. 6). In contrast, UMPAPVA sheets exhibit only slightly better methanol/gasoline permeation resistance than the PE sheet, wherein CP, PA, and PVA present in UMPAPVA resins were not preblended in a twin screw extruder, but only dry-blended before hot-pressing. On the other hand, similar to those found in the previous section, the permeation resistance of MPAPVA and MPA sheets against methanol/gasoline fuels also reach their best levels as their CP contents approach 20 wt %. These results clearly suggest that CP-modified PA and PVA enhance the barrier properties of MPAPVA even better than those of MPA resins with the same CP contents. Moreover, the levels of barrier improvements of PE/MPA and PE/MPAPVA bottles depend significantly on the CP and PVA contents present in MPA and MPAPVA, and the barrier properties of the MPA and MPAPVA resins prepared.

Presumably, the permeant molecules are believed to diffuse through the polymers mainly by penetrating through their amorphous regions, because diffusion through crystalline regions of polymers is difficult. Moreover, it is generally recognized that the molecular composition and con-

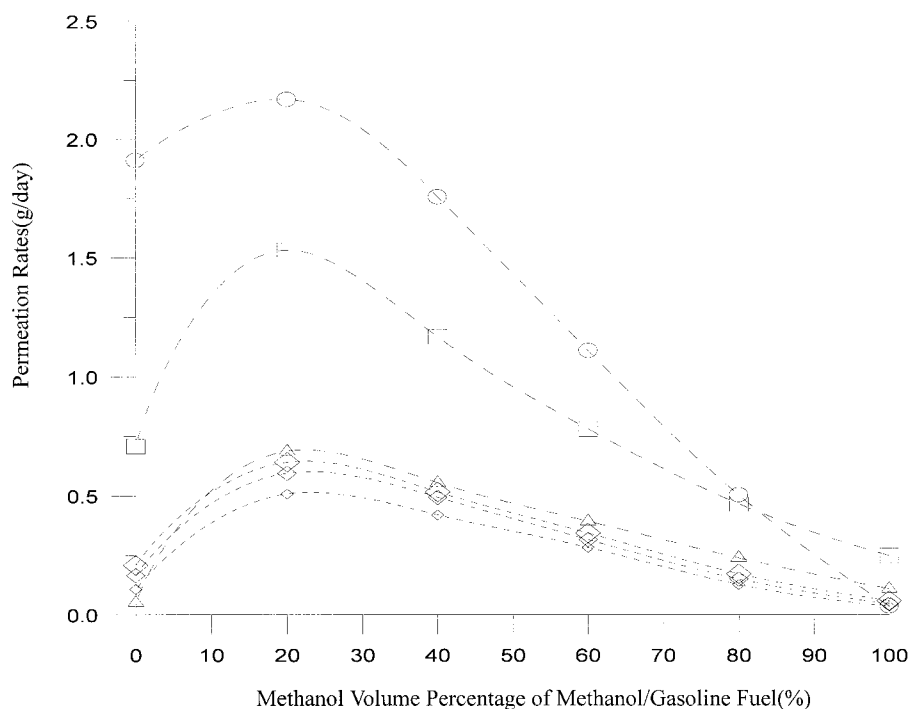


**Figure 5** Methanol/gasoline fuel permeation rates of (○) MPA<sub>3</sub>PVA<sub>10</sub>, (◇) MPA<sub>7</sub>PVA<sub>10</sub>, (◇) MPA<sub>15</sub>PVA<sub>10</sub>, (○) PE, (△) MPA<sub>10</sub>, and (□) UMPA<sub>3</sub>PVA<sub>10</sub> sheets.



**Figure 6** Methanol/gasoline fuel permeation rates of (○) MPA<sub>3</sub>PVA<sub>20</sub>, (◇) MPA<sub>7</sub>PVA<sub>20</sub>, (◇) MPA<sub>15</sub>PVA<sub>20</sub>, (○) PE, (△) MPA<sub>20</sub>, and (□) UMPA<sub>3</sub>PVA<sub>20</sub> sheets.



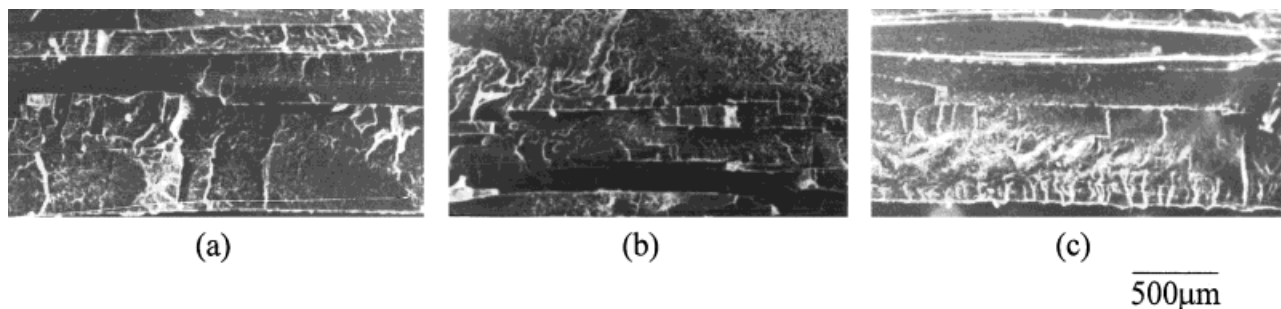


**Figure 7** Methanol/gasoline fuel permeation rates of (○) MPA<sub>3</sub>PVA<sub>30</sub>, (◇) MPA<sub>7</sub>PVA<sub>30</sub>, (△) MPA<sub>15</sub>PVA<sub>30</sub>, (○) PE, (△) MPA<sub>30</sub>, and (□) UMPA<sub>3</sub>PVA<sub>30</sub> sheets.

figuration in the amorphous phase of the polymer can greatly affect its barrier properties. The presence of polar amide, terminal amine, hydroxy groups, and intermolecular hydrogen bonding in MPA, MPAPVA, and UMPAPVA can allow few nonpolar gasoline molecules to enter into and permeate through their amorphous regions as compared with nonpolar PE molecules. In addition, the "crosslinked" structures of CP/PA and CP/PA/PVA copolymers formed during preparation of MPA and MPAPVA can significantly reduce their free volume and further prohibit the nonpolar gasoline molecules from entering and permeating through the amorphous regions of MPA and MPAPVA resins, respectively. As a consequence, the permeation resistance of the MPA and MPAPVA against nonpolar gasoline molecules is significantly better than that of PE although PE is associated with a higher  $W_c$ . In contrast, UMPAPVA sheets only exhibit slightly better permeation resistance than PE sheet, because no crosslinked CP/PA/PVA copolymer is believed to be present in the UMPAPVA resins, whereas CP, PA, and PVA were dry-blended rather than preblended in a twin screw extruder before hot-pressing. On the other hand, the numbers of hydroxy groups and intermolecular hydrogen bond-

ing per unit length of PVA main chain molecules are higher than the numbers of amide, amine groups, and intermolecular hydrogen bonding present in per unit length of the PA main chain molecules. Presumably, these higher numbers of polar groups and intermolecular hydrogen bonding present in PVA can further prohibit the nonpolar gasoline molecules from entering and permeating through its amorphous regions. As a consequence, the permeation resistance of MPAPVA against methanol/gasoline fuels is worse than that of MPA with the same CP content, and improves consistently with the amounts of PVA present in MPAPVA resins.

In addition to the functional groups and crosslinked molecules of CP/PA and CP/PA/PVA molecules present in their amorphous phases, the  $W_c$  of the MPA and MPAPVA resins can also affect their barrier properties. As mentioned previously, the crystallinity values of MPA and MPAPVA resins reduce significantly with an increase of the CP contents present in them. This reduction in  $W_c$  may significantly shorten the permeant path of gasoline molecules and compromise the beneficial effect of crosslinked CP/PA and CP/PA/PVA molecules on the barrier properties of MPA and MPAPVA resins. As a conse-



**Figure 8** Fracture surfaces of (a) PE/MPA<sub>3</sub>PVA<sub>10</sub>, (b) PE/MPA<sub>7</sub>PVA<sub>10</sub>, and (c) PE/MPA<sub>15</sub>PVA<sub>10</sub> bottles.

quence, the permeation resistances of MPA and MPAPVA are best when their CP contents reach an optimum value of about 20 wt %.

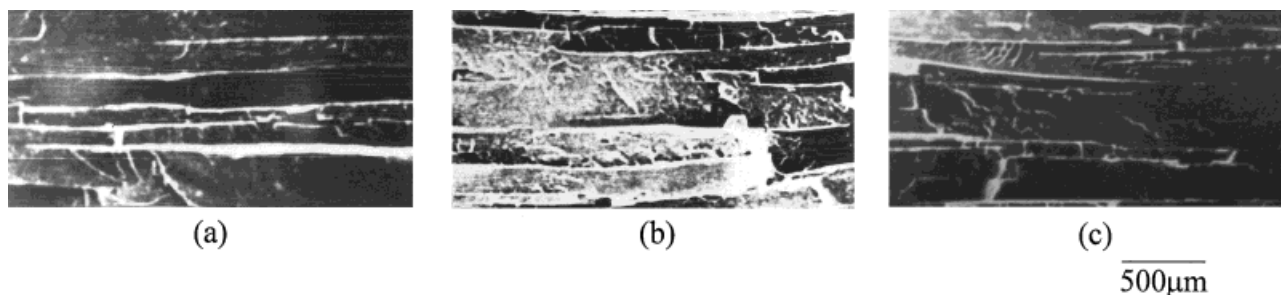
#### Morphology of PE/MPAPVA and PE/UMPAPVA Bottles

The fracture surfaces of PE/MPAPVA bottles are shown in Figures 8–10. Many MPAPVA laminae were found distributed in PE matrices through the wall thickness direction of the PE/MPAPVA bottles. As reported in our previous investigations,<sup>6–12</sup> similar MPA laminar structures were found on the fracture surfaces of PE/MPA bottles. In fact, more clearly defined MPAPVA laminar structures were found as the CP contents contained in MPAPVA increased (see Figs. 8–10). In contrast, only obscure laminae were found on the fracture surfaces of PE/UMPAPVA bottles, although these obscure laminar structures became slightly clearer as the CP contents of UMPAPVA resins increased (see Fig. 11).

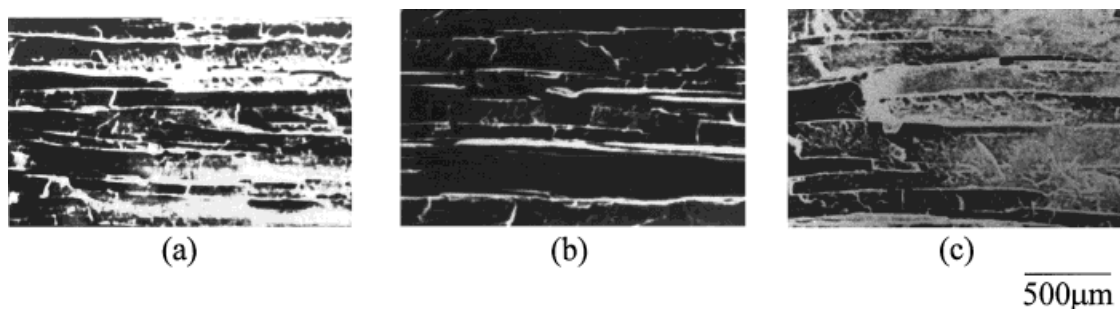
Presumably, the clearly defined MPAPVA or MPA laminae can further improve the permeation resistance of PE/MPAPVA or PE/MPA bottles against methanol/gasoline fuels, respectively, because the permeation time of the gasoline mol-

ecules can be prolonged by the clearly defined MPAPVA or MPA laminae present in PE matrix.

The underlying mechanisms accounting for these interesting phenomena are not clear at this point. Presumably a good level of interfacial adhesion between MPAPVA (or MPA) and the PE matrix is necessary for the formation of laminar structures, because MPAPVA or MPA cannot be stretched easily by PE with a higher melt shear viscosity when the interfacial adhesion between MPAPVA (or MPA) and the PE matrix is poor during the blow-molding process. As mentioned previously, the melt shear viscosities of MPAPVA and MPA are lower than that of PE, and increase significantly with the CP contents present in them, because the possibility of formation of the crosslinked CP/PA/PVA and CP/PA copolymers increases as their CP contents increase. These CP/PA/PVA and CP/PA copolymers of higher  $\eta_s$  are believed to be more compatible with PE and adhere better to PE than PA and PVA resins, because it is well recognized that PA and PVA are thermodynamically immiscible with PE and poorly adhered to PE during blow-molding. Based on these premises, it is reasonable to suggest that MPAPVA and MPA resins can be biaxially



**Figure 9** Fracture surfaces of (a) PE/MPA<sub>3</sub>PVA<sub>20</sub>, (b) PE/MPA<sub>7</sub>PVA<sub>20</sub>, and (c) PE/MPA<sub>15</sub>PVA<sub>20</sub> bottles.



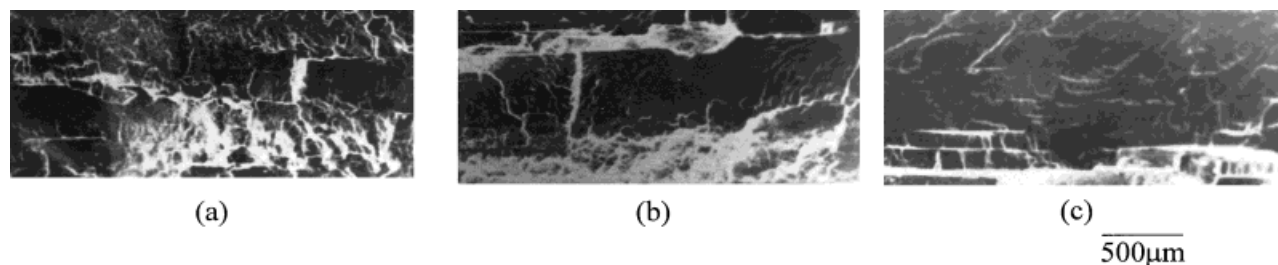
**Figure 10** Fracture surfaces of (a) PE/MPA<sub>3</sub>PVA<sub>30</sub>, (b) PE/MPA<sub>7</sub>PVA<sub>30</sub>, and (c) PE/MPA<sub>15</sub>PVA<sub>30</sub> bottles.

stretched easily by the PE matrix into demarcated laminar structures as long as they are well adhered to PE and are associated with an optimum  $\eta_s$ , wherein the MPAPVA and MPA melts are strong enough to be stretched by PE during the blow-molding process. In contrast, no cross-linked CP/PA/PVA copolymer is believed to be present in UMPAPVA resins of low  $\eta_s$ , wherein CP, PA, and PVA were only dry-blended rather than preblended in a twin screw extruder. Therefore only obscure UMPAPVA laminar structures were found on the fracture surfaces of PE/UMPAPVA bottles.

## CONCLUSIONS

The permeation resistance of PE/MPAPVA bottles against methanol/gasoline fuels is significantly better than that of PE/MPA and PE/UMPAPVA bottles of the same CP content. In fact, the permeation resistance of PE/MPAPVA bottles or hot-pressed MPAPVA sheets against methanol/gasoline fuels was further found to improve with increasing the PVA contents present in MPAPVA resins. On the other hand, it is noteworthy that the best permeation resistance of PE/

MPAPVA and PE/MPA bottles against methanol/gasoline fuels was obtained as the CP contents contained in MPAPVA and MPA reached optimum values of about 20 wt %. Further investigations found many MPAPVA laminae distributing in PE matrices through the wall thickness direction of the PE/MPAPVA bottles. In fact, more clearly defined MPAPVA laminar structures were found as the CP contents contained in MPAPVA increased. These clearly defined MPAPVA laminae can further improve the permeation resistance of PE/MPAPVA bottles against methanol/gasoline fuels, because the permeation time of the gasoline molecules can be prolonged by these clearly defined MPAPVA laminae present in the PE matrix. In contrast, only obscure laminae were found on the fracture surfaces of PE/UMPAPVA bottles, although these obscure laminar structures become slightly clearer as the CP contents of UMPAPVA resins increased. These results clearly suggest that CP-modified PA and PVA enhance the barrier properties of MPAPVA more than those of MPA resins with the same CP contents. Moreover, the level of barrier improvements of PE/MPA and PE/MPAPVA bottles depends significantly on the CP contents present in MPA and MPAPVA, the barrier properties and



**Figure 11** Fracture surfaces of (a) PE/UMPA<sub>3</sub>PVA<sub>10</sub>, (b) PE/UMPA<sub>3</sub>PVA<sub>20</sub>, and (c) PE/UMPA<sub>3</sub>PVA<sub>30</sub> bottles.

laminar structures of the MPA, and MPAPVA resins present in PE/MPA and PE/MPAPVA bottles.

The melt shear viscosities of MPA or MPAPVA resins were found to increase as their CP contents increased. However, their crystallinity values decreased consistently with increasing the CP contents. Presumably, the possible formation of crosslinked CP/PA and CP/PA/PVA copolymers can increase the melt shear viscosities and inhibit crystallization of MPA and/or MPAPVA resins, respectively. These crosslinked copolymers are also believed to improve the barrier properties of MPAPVA and MPA resins against methanol/gasoline fuels by decreasing their free volumes. However, the reduction in  $W_c$  may shorten the permeant path of gasoline molecules and compromise the beneficial effect of crosslinked CP/PA and CP/PA/PVA molecules on the barrier properties of MPA and MPAPVA resins. As a consequence, the permeation resistance of MPA and MPAPVA is best as their CP contents reach optimum values of about 20 wt %.

## REFERENCES

1. Schut, J. H. *Plastics Technol* 1992, 5, 52.
2. Chandramoul, K.; Jabarin, S. A. *Adv Polym Technol* 1995, 14, 35.
3. Subramanian, P. M. U.S. Pat. 4410482, 1983.
4. Subramanian, P. M. U.S. Pat. 4444817, 1984.
5. Leaversuch, R. In *Proceedings of Modern Plastics International*, Lausanne, Switzerland, July 24, 1986; New York: McGraw-Hill, 1986.
6. Yeh, J. T.; Fan-Chiang, C. C.; Cho, M. F. *Polym Bull* 1995, 35, 371.
7. Yeh, J. T.; Fan-Chiang, C. C. *J Polym Res* 1996, 3, 211.
8. Yeh, J. T.; Fan-Chiang, C. C.; Yang, S. S. *J Appl Polym Sci* 1997, 8, 1531.
9. Yeh, J. T.; Fan-Chiang, C. C. *J Appl Polym Sci* 1997, 66, 2517.
10. Yeh, J. T.; Jyan, C. F.; Chou, S. *SPE Antec* 1998, 3, 3567.
11. Yeh, J. T.; Jyan, C. F. *Polym Eng Sci* 1998, 38, 1482.
12. Yeh, J. T.; Jyan, C. F.; Chou, S. *Polym Eng Sci*, to appear.
13. Subramanian, P. M. *Polym Eng Sci* 1985, 25, 483.
14. Subramanian, P. M. *Polym Eng Sci* 1987, 27, 663.
15. Subramanian, P. M. In *Conference Proceedings: Technical Association of Pulp and Paper Industry; Laminations and Coating Conference*, 1984; 341.
16. Subramanian, P. M.; Mehra, V. *SPE Antec* 1986, 32, 301.
17. Mehra, V. K. U.S. Pat. 4,950,513, 1990.
18. Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1973; Vol. 1; p. 388.
19. Brandrup, J.; Immergut, E. H. (Eds.). *Polymer Handbook*, 2nd ed.; John Wiley & Sons: New York, 1975; p. V82.
20. Gaur, U.; Wunderlich, B. B.; Wunderlich, B. *J Phys Chem, Ref. Data* 12, 1983, 29.
21. Furey, R. L.; Perry, K. L. *SAE Technical Paper Series*; ASE: Warrendale, PA, 1991, 912415.