Effects of Processing Conditions on the Barrier Properties of Polyethylene (PE)/Modified Polyamide (MPA) and Modified Polyethylene (MPE)/Polyamide (PA) Blends

JEN-TAUT YEH, CHIEN-CHUNG CHAO, CHIN-HER CHEN

Graduate School of Textile and Polymer Engineering, Department of Textile Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan, Republic of China

ABSTRACT: Different modified polyamide (MPA) and modified polyethylene (MPE) resins were prepared by reactive extrusion of different contents of a compatibilizer precursor (CP) with either polyamide (PA) or polyethylene (PE). The MPE and MPA resins were then blow-molded with designed amounts of PA or PE resins to prepare four different sets of MPE/PA and PE/MPA bottles with the same CP, PA, and PE compositions. Somewhat surprisingly, the xylene permeation resistance of the MPE bottles is worse than that of the base PE bottle and decreases consistently as MPE contains more CP. In contrast, the MPE/PA and PE/MPA bottles exhibit much better xylene permeation resistance than that of the base PE bottle, wherein the PE/MPA bottles show significantly better permeation resistance than that of the corresponding MPE/PA bottles prepared at the same blow-molding conditions. On the other hand, it is worth noting that the xylene permeation rate of each of the MPE/PA and PE/MPA bottles prepared at a fixed extrusion temperature reaches a minimum when prepared with an optimum screw speed near 400 rpm. Similarly, at a fixed screw speed, the highest permeation resistance of each PE/MPA bottle is always obtained when prepared at an optimum extrusion temperature of about 230ºC. However, the xylene permeation resistance of each MPE/PA bottle improves consistently when prepared at the higher extrusion temperatures used in this study. These interesting phenomena were investigated in terms of the morphology, thermal analysis of the PE/MPA and MPE/PA blends, the compatibility between PE (or MPE) and MPA (or PA), and the viscosity ratios of MPA (or PA) to PE (or MPE) during the blow-molding process. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1997–2008, 2000

Key words: modified polyamide; reaction extrusion; permeation resistance; viscosity ratio

INTRODUCTION

Hydrocarbon solvents, such as agricultural chemicals, paint thinner, and gasoline, are commonly available products that easily permeate polyethylene (PE) containers; such permeation results in pollution, safety, and health problems. To attempt to improve the poor permeation resistance of PE, alternative technologies have been applied including surface treatment of PE by fluorination or sulfonation,[1,2] multilayer coextrusion of PE, a compatibilizer precursor (CP), and polyamide (PA),[1,2] or a laminar-blend blow molding of PE, CP, and PA blends.[3–5] Surface treatment is not

widely used because of concerns for environmental safety and health and also because it requires substantial capital investment. In contrast, coextrusion blow molding is widely used in fabricating barrier containers for packaging hydrocarbon solvents, but is generally not available for products with complex shapes. A "laminar-blend-blow-molding process" forms a layered structure containing numerous discontinuous, overlapping platelets of barrier resins such as PA, in a PE matrix, which is one of the well-proven barrier technologies to enhance the resistance of PE containers to hydrocarbon permeation.[3–5] These heterogeneous laminar blends exhibit significantly higher permeation barrier properties than those of the conventional homogeneous blends associated with uniformly dispersed PA within the PE matrix.[6–9] The laminar platelets are formed by melt processing PE, PA, and CP in a specially designed blow-molding machine. This process lends itself to a wide variety of container designs and to processing convenience.

As PE/PA blends are thermodynamically immiscible and mechanically incompatible, CPs 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 depend greatly on the manner of blending and on the resulting morphology.[3,4,6,7,10–13] Our latest studies[14–17] 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 MPAs and the corresponding PE/MPA blends. Possible mechanisms accounting for the above interesting results were also discussed.[17] Most recently, the melt shear viscosities of PEs and modified PA were found to exhibit 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 the 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 the optimum VR varied as the compositions of the MPA changed.[18–20] In fact, very good xylene permeation barrier properties accompanied with clearly defined MPA laminar structures can be obtained by the blow molding of carefully chosen compositions of PE/MPA blends.

In addition to the compositions of these PE/MPA blends, the processing conditions are also believed to have a significant influence on the morphology and rheological and barrier properties of blow-molded bottles from PE/MPA blends. The main objective of this study was to investigate the effect of processing conditions (screw temperatures and speeds) on the morphology and rheological and barrier properties of PE/MPA and MPE/PA blends and to further optimize the processing conditions to enhance the barrier properties of PE/MPA blends.

EXPERIMENTAL

Materials and Sample Preparation

Different contents of CP were used to prepare different MPA and modified PE (MPE) resins by blending them with the PA and PE, respectively. The CP used in this study was a 30% zinc-neutralized ethylene/acrylic acid copolymer, which was kindly supplied by Formosa Chemicals and Fiber Corp., Taiwan. The type of PA used was nylon 6, which was obtained from the Formosa Chemicals and Fiber Corp. with the trade name of Sunylon 6N. The PE (HDPE Taisox 9003) and antioxidant (Irganox B225) used in this study were obtained from the Formosa Plastic Corp., Taiwan and the Ciba–Geigy Corp., 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 the antioxidant was dry-blended with the dried components of PA/CP or PE/CP and then fed into an Ekegai PCM 45 corotating twin-screw extruder to make the MPA or MPE resins, respectively. The extruder was operated at 220°C in the feeding zone and at 240°C toward the extrusion die with a screw speed of 100 rpm. The compositions of the MPA and MPE resins prepared with different contents of CP are summarized in Table I. Formation of CP-grafted-PA copolymers through the reaction of carboxyl groups of CP with the terminal amine groups of PA was reported during the preparation of MPA.[14,15] Each type of MPA pellet prepared from the twin-screw extruder was dried at 80°C for 16 h and then dry-blended with PE at a weight ratio of 90:10. In contrast, each type of MPE pellet was dried at 80°C for 16 h and then dry-blended with PA at various weight ratios (see Table II).

Table I   Compositions of MPA and MPE Resins

Composition	Sample							
	MPA_{10}	MPA_{15}	MPA_{20}	MPA_{40}	MPE_1	$MPE_{1.5}$	MPE_2	MPE_4
PA (wt %)	90	85	80	60				
PE (wt %)					98.90	98.36	97.83	95.74
CP (wt %)	10	15	20	40	1.10	1.64	2.17	4.26

For purposes of comparison, the contents of PE, CP, and PA contained in the MPE_1/PA, $MPE_{1.5}$/PA, MPE_2/PA, and MPE_4/PA bottles are equal to those of the PE/MPA_{10}, PE/MPA_{15}, PE/MPA_{20}, and PE/MPA_{40} bottles, respectively. The purpose of preparation of these PE/MPA and MPE/PA bottles is to understand the influence of the processing sequence on the barrier properties of the corresponding PE/MPA and MPE/PA bottles. Each MPA was formed by reacting CP with PA before blow molding with PE, but PE is not expected to react with CP during the preparation of MPE.

The mixed PE/MPA and MPE/PA blends were then blow-molded in a Jonh Huah TPH-330 extrusion-blow-molding machine equipped with a conventional PE screw operating at varying conditions. The extrusion temperatures used in this study were 195, 215, 230, and 250°C. At each extrusion temperature, four different screw speeds, 200, 400, 600, and 800 rpm, were used to extrude most of the PE/MPA and MPE/PA parisons before blow molding. The blow-molded bottles weighed about 50 g and had a volume of about 500 mL and a wall thickness of about 1 mm. For purposes of comparison, bottles were also prepared from base PE resin using the same screw and blow-molding machine while operating at an extrusion temperature of 190°C and a screw speed of 400 rpm.

Permeation Test

The permeation barrier properties of the blow-molded bottles were evaluated by measuring the weight loss of the xylene contained in the bottles. Bottles of PE, PE/MPA, and MPE/PA were initially filled with 250 g of xylene. The weight loss of xylene was determined after keeping the filled bottles at 40°C for 14 days. On the other hand, the permeation barrier properties of the 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 due to their poor melt strengths. The dried pellets of PA and MPA were hot-pressed into about 1-mm-thick sheets and cut into circles of a diameter of 14 cm. The circular PA and MPA sheets and circular sheets sectioned from the base PE and MPE bottles were sealed as lids on the top of test flasks filled with 250 g of xylene. The permeation barrier properties of the circular sheets were then determined by measuring the weight loss of xylene after placing the flasks at 40°C for 14 days. A minimum of three bottles and/or hot-pressed sheet samples of each specimen were tested. The xylene permeation rate of each of the bottles or hot-pressed sheets was estimated based on the average permeation rate of at least three bottle or hot-pressed sheet samples, respectively. The variations of the measured permeation rates of the PE, PE/MPA, and MPE/PA bottles were normally around $\pm 4.8 \times 10^{-3}$ g/day, $\pm 2.55 \times 10^{-3}$ g/day, and $\pm 3.93 \times 10^{-3}$ g/day, respectively. These variations result in ± 0.1, ± 0.8, and ± 0.8 errors in estimating the permeation rates of the PE, PE/MPA, and MPE/PA bottles, respectively. The barrier improvement is de-

Table II   Compositions of MPE/PA Bottles

Composition	Sample			
	MPE_1/PA	$MPE_{1.5}$/PA	MPE_2/PA	MPE_4/PA
PA (wt %)	9	8.5	8	6
MPE_1 (wt %)	91			
$MPE_{1.5}$ (wt %)		91.5		
MPE_2 (wt %)			92	
MPE_4 (wt %)				94

fined as the weight loss of the pure PE sample over that of the other samples.

Degrees of Crystallinity and Morphology

The degrees of crystallinity of the base PE, PA, CP, MPA, and MPE resins were determined by differential scanning calorimetry (DSC). The DSC experiments were measured at a heating rate of 10°C/min. All scans were carried out under flowing nitrogen at a flow rate of 25 mL min^{-1}. The instrument was calibrated using pure indium. The cited heats of fusion for perfectly crystalline PE[21] and PA[22] are 293 and 190 J/g, respectively, which values were used for the calculation of the crystallinity value of each corresponding sample. The DSC thermograms of the MPE resins exhibited only one melting endotherm close to the main melting peak of the PE crystals. No distinct melting endotherm corresponding to the melting of the CP crystals was found. These results suggest that CP molecules may cocrystallize with PE molecules during the crystallization process of MPE resins, which is possibly due to the similarity in the molecular structure of CP and PE. Presumably, the heat of fusion for perfectly crystalline PE was then used as the source of the value for 100 crystallinity for CP. The 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 ±3 Jg^{-1}, which resulted in a ±1 error in estimating W_c. To observe the deformation structures of the MPA and PA resins in the PE/MPA and MPE/PA bottles, respectively, these bottles were fractured in liquid nitrogen and etched with formic acid. The etched samples were then gold-coated and examined using a scanning electron microscope (SEM).

Rheological Properties

All melt shear viscosities (η_s's) of the PE, PA, MPA, and MPE resins were measured at temperatures ranging from 225 to 250°C and shear rates ranging from 15 to 120 L/s using a Rosand Precision Advanced Capillary Extrusion Rheometer equipped with a capillary of 1-mm diameter. These η_s's measured at various temperatures and shear rates up to about 100 L/s were used to correlate with the deformation behavior of MPA in PE or PA in MPE matrices during the blow molding of PE/MPA and MPE/PA blends, respec-

tively. The shear rates of polymer melts during extrusion and blow molding are generally recognized to be less than 100 1/s.

RESULTS AND DISCUSSION

Thermal Properties of PE, PA, CP, MPE, and MPA Resins

The crystallinity values (W_c) and melting temperatures (T_m) of the PE, PA, CP, MPE, and MPA resins are summarized in Table III. The base PE exhibits a lower melting temperature but much higher crystallinity values than those of PA, and CP shows the lowest crystallinity value and melting temperature among the three base resins. On the other hand, the W_c and T_m of the MPE resins are lower than those of the base PE and decrease consistently with the CP content present in the MPE resins. The melting temperature and crystallinity values of each MPA sample is lower than those of PA. In fact, the W_c and T_m of the MPA resins decrease consistently with the increasing content of CP contained in the MPA resins. This decrease in the W_c can be attributed mainly to the reduced W_c caused by the reduction in the amounts of PA present in the MPA resins as the content of less crystallizable CP increases. In the meantime, the formation of CP-grafted PA copolymers during the preparation of MPA can also reduce the melting temperatures and crystallinity values of MPA as the CP contents contained in the MPA (Ccp's) resins increase, since these CP-grafted PA copolymers are less crystallizable polymers than is base PA, and the possibility of the formation of CP-grafted PA copolymers is higher as the Ccp's increase. In contrast, the carboxyl groups of CP are not expected to react with PE during the preparation of MPE resins, because no functional group is available on the PE molecules. In fact, the reduction in the W_c of the MPE resins can be attributed to the reduced W_c caused by decreasing amounts of PE present in the MPE resins as the contents of less crystallizable CP increase.

RHEOLOGICAL PROPERTIES OF PE AND MPA RESINS

The melt shear viscosities (η_s) of the PE, PA, CP, MPE, and MPA resins are summarized in Figures 1 and 2. The melt shear viscosities of the MPA
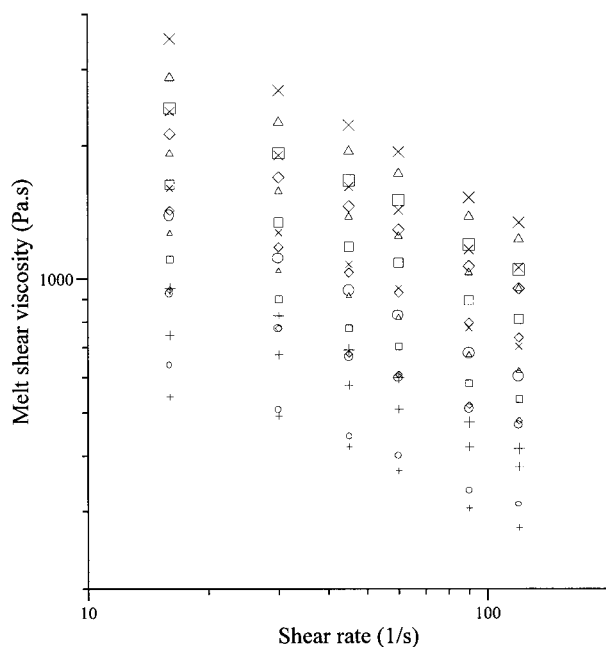
Figure 1 Melt shear viscosity of (×) PE, (+) PA, (○) MPA_{10}, (◇) MPA_{15}, (□) MPA_{20}, and (△) MPA_{40} resins at 225, 240, and 250°C.

and PA resins are much lower than those of PE, and the η_s's of the MPA resins are significantly higher than those of PA and increase consistently with the CP contents contained in the MPA resins (see Fig. 1). Somewhat surprisingly, as shown in Figure 2, the η_s's of the MPE resins are significantly lower than those of the PE resins and decrease consistently with increasing CP contents. As indicated in our previous investigations,[14,15] 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 the MPA resins. For instance, short CP chains may be dispersed into the PA matrix and grafted into several long PA molecules and they are presented as huge "crosslinked" CP/PA copolers in the PA matrix. Presumably, the η_s's of the CP-grafted-PA copolymers can be higher than those of CP and PA. As a consequence, the η_s's of the MPA resins increase with increasing contents of CP in the MPA resins because the possibility of the formation of CP-grafted-PA copolymers is higher as the content of CP in MPA increases. In contrast, the carboxyl groups of CP are not expected to react with the amine groups of PA during the preparation of the MPE resins. In addition, the melt shear viscosity of CP is much lower than that of PE (see Fig. 2). Therefore, the η_s's of the MPE resins decrease

significantly with increasing contents of CP in the MPE resins.

On the other hand, it is interesting to note that, at a given shear rate, the η_s's of the PE, PA, CP, MPA, and MPE resins decrease with increasing temperatures, wherein the decreased rates of the η_s's of the PE and MPE resins are slower than those of MPA and PA resins, respectively. These results show that the melt shear viscosity ratios of MPA to PE (or PA to MPE) decrease with increasing temperature (see Figs. 3 and 4). Similarly, the η_s's of the PE, PA, CP, MPA, and MPE resins decrease consistently with increasing shear rates, and the reduction rates of the η_s's of the PE and MPE resins, with increasing shear rates, are faster than those of the MPA and PA resins, respectively. These results show that the values of the melt shear VRs of MPA to PE (or PA to MPE) increase consistently with the shear rates (see Figs. 3 and 4).

Morphology of PE/MPA and MPE/PA Parisons and Bottles

The typical fracture surface morphology of the parisons and bottles of MPE/PA and PE/MPA are shown in Figures 5–7. As shown in Figure 5(a,b), almost no PA or MPA laminae were found on the fracture surfaces of the $MPE_{1.5}$/PA and PE/MPA_{15}
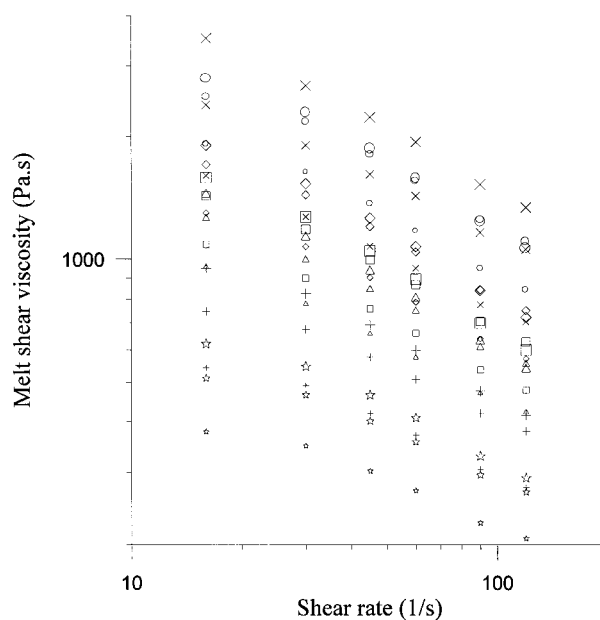

Figure 2 Melt shear viscosity of (×) PE, (+) PA, (☆) CP, (○) MPE_1, (◇) $MPE_{1.5}$, (□) MPE_2, and (△) MPE_4 resins at 225, 240, and 250°C.
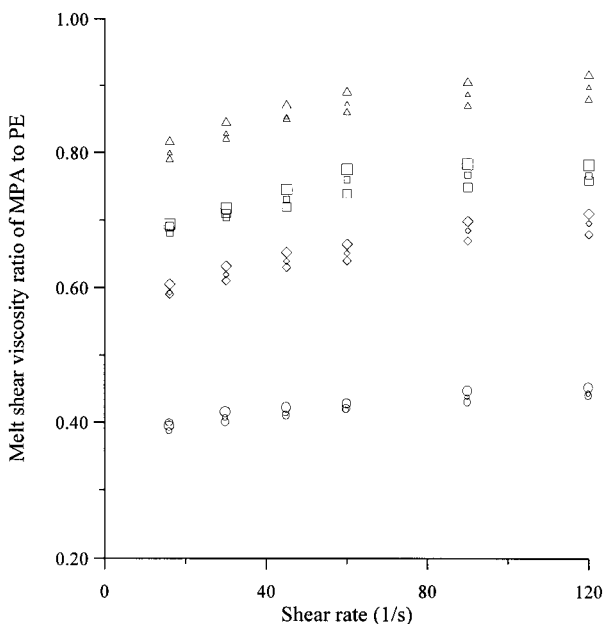
Figure 3 Melt shear viscosity ratios of PA to (○) MPA$_{10}$, (◇) MPA$_{15}$, (□) MPA$_{20}$, and (△) MPA$_{40}$ to PE at 225, 240, and 250°C.

parisons, respectively. Similar morphology was found on the fracture surfaces of other MPE/PA or PE/MPA parisons. After blow molding, many clearly defined PA and MPA laminae were found on the fracture surfaces of the MPE$_{1.5}$/PA and PE/MPA$_{15}$ bottles, respectively (see Figs. 6 and 7). In fact, more layers of demarcated PA and MPA laminae were found in the MPE$_{1.5}$/PA and PE/MPA$_{15}$ bottles, respectively, when they were prepared from higher screw speeds. However, some of these MPA and PA laminae broke into segmented obscure laminae when PE/MPA$_{15}$ and MPE$_{1.5}$/PA bottles were prepared from screw speeds higher than about 400 rpm [see Fig. 6(c,d) and 7(c,d)]. Similar phenomena were found on the fracture surfaces of other MPE/PA and PE/MPA bottles. The underlying mechanisms accounting for these interesting phenomena are not completely clear at this point. Presumably, MPA or PA can be dispersed into more segments in PE or MPE matrices during extrusion, when PE/MPA or MPE/PA blends, respectively, were extruded at a higher screw speed. The dispersed MPA or PA segments can then be stretched by PE or MPE matrices into laminae, as long as the interfacial adhesion between MPA and PE or PA and MPE is high enough during the blow molding of the PE/MPA or MPE/PA parisons, respectively. As a consequence, more layers of demarcated MPA (or PA)

laminae were found for PE/MPA (or MPE/PA) bottles prepared at a higher screw speed, wherein MPA (or PA) were well dispersed in their parisons. However, some of the MPA (or PA) segments became too small to be stretched by PE (or MPE) into continuous and demarcated laminae if they were too well dispersed at high screw speeds during the extrusion process. This is probably the reason that some segmented and broken MPA (or PA) laminae were found on the fracture surfaces of PE/MPA (or MPE/PA) bottles prepared at screw speeds higher than the optimum value of about 400 rpm.

On the other hand, it is worth noting that, at a fixed screw rate of 400 rpm, more clearly defined MPA laminae were found on the fracture surfaces of the PE/MPA bottles prepared at an extrusion temperature near 230°C than for those prepared at extrusion temperatures of 195, 215, or 250°C (see Fig. 8). Presumably, MPA can be stretched by PE into laminar structures as long as it adheres well to the PE matrix and is not too hard to draw during the blow-molding process of the PE/MPA bottles. However, some of the MPA present in the PE/MPA parison extruded at 195 and 215°C may be too difficult to draw into clearly defined MPA laminae because this extrusion temperature is well below the melting temperature of MPA. Therefore, much more clearly defined MPA lami-
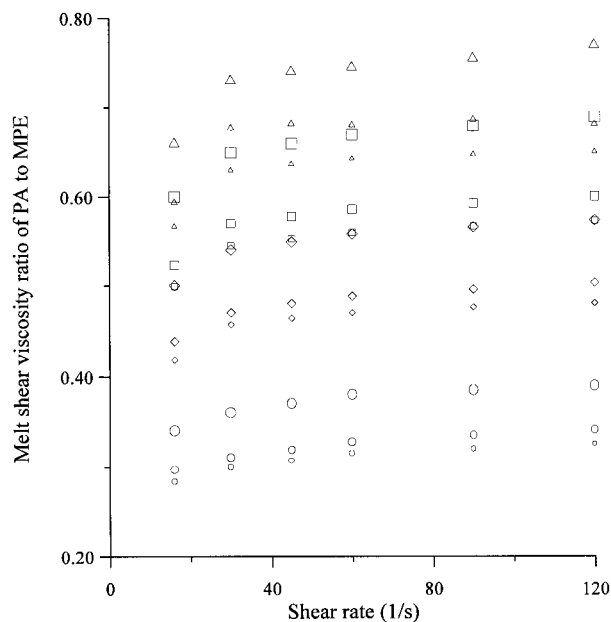

Figure 4 Melt shear viscosity ratios of PA to (○) MPE$_1$, (◇) MPE$_{1.5}$, (□) MPE$_2$, and (△) MPE$_4$ at 225, 240, and 250°C.

(a)   (b) $\overline{}$
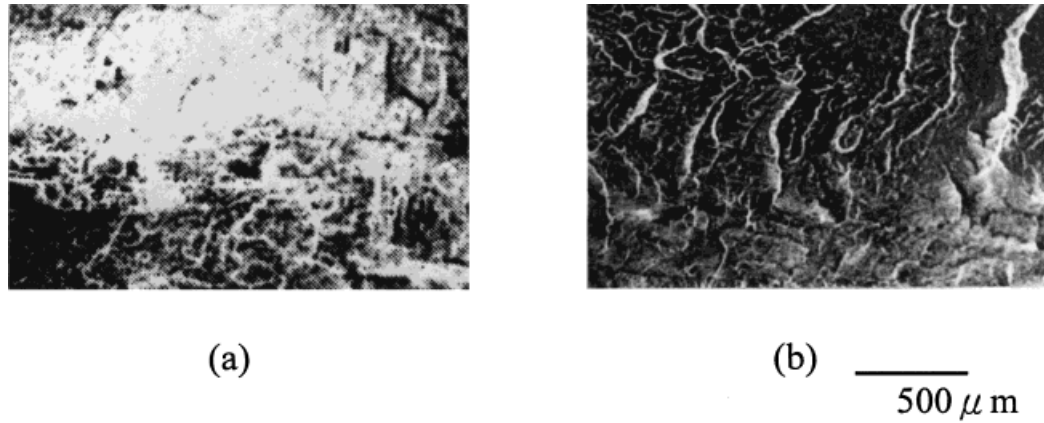 $500\,\mu\mathrm{m}$

Figure 5 Fracture surfaces of (a) $MPE_{1.5}/PA$ and (b) PE/MPA_{15} extruded at 230°C and a screw speed of 400 rpm.

nae were found on the fracture surfaces of PE/MPA bottles only when they were prepared at an extrusion temperature of about 230°C. However, as mentioned in the previous section, the η_s's of MPAs are much lower than those of PE and de-

crease faster than those of PE as the temperatures increase from 225 to 250C. At an extrusion temperature of 250°C, MPA resins may become too soft to be stretched by the PE matrix and can be easily pulled apart by PE during the molding of
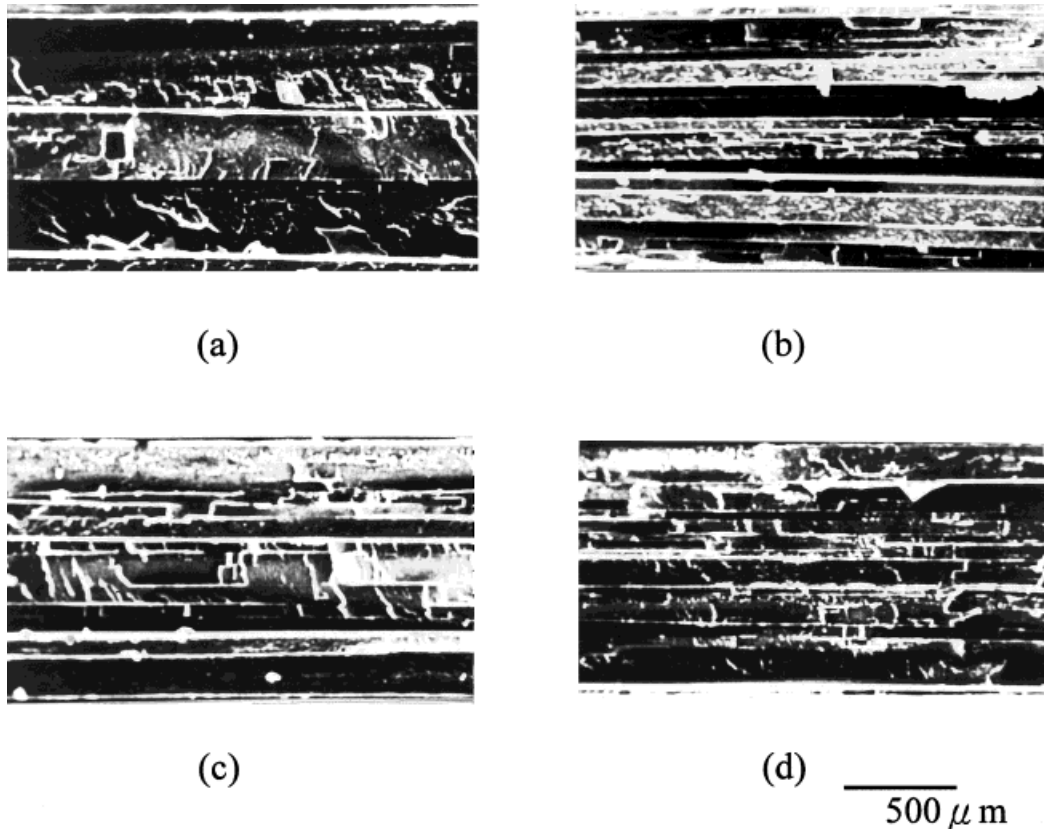

(a)   (b)

(c)   (d) $\overline{}$
                  $500\,\mu\mathrm{m}$

Figure 6 Fracture surfaces of $MPE_{1.5}/PA$ bottles prepared at an extrusion temperature of 230°C and a screw speed of (a) 200 rpm, (b) 400 rpm, (c) 600 rpm, and (d) 800 rpm.

Figure 7 Fracture surfaces of PE/MPA$_{15}$ bottles prepared at an extrusion temperature of 230°C and a screw speed of (a) 200 rpm, (b) 400 rpm, (c) 600 rpm, and (d) 800 rpm.
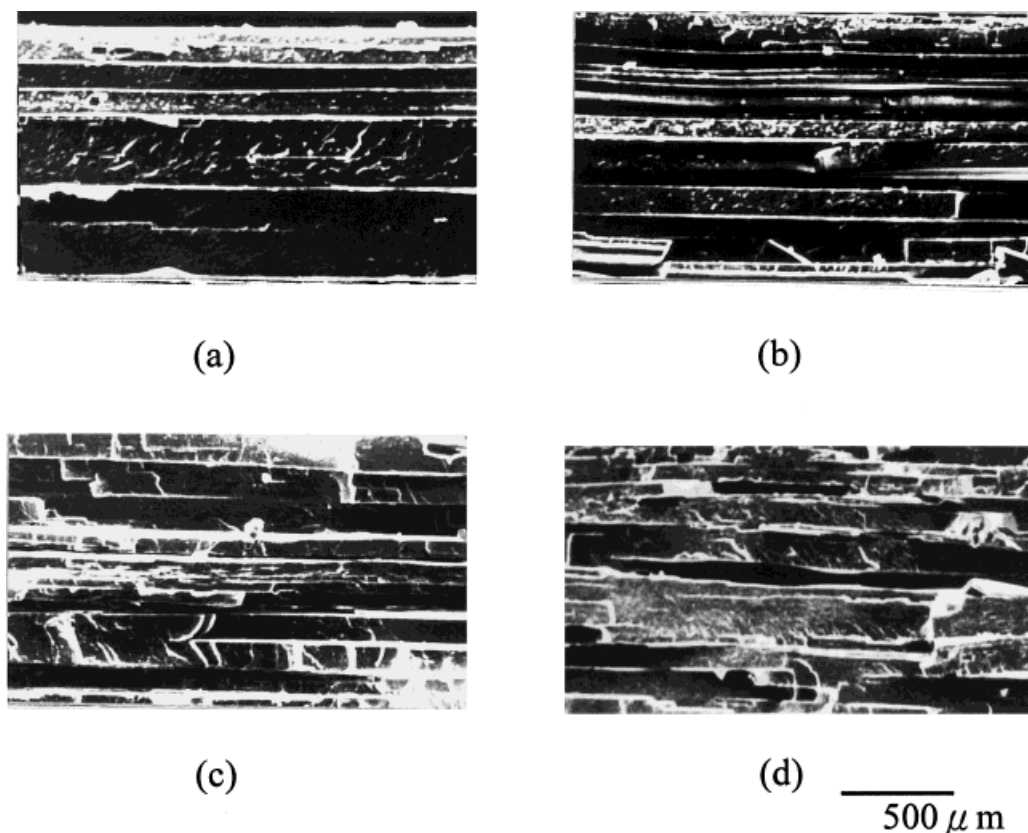
the PE/MPA parisons. As a consequence, more obscure MPA laminae were found on the fracture surfaces of PE/MPA bottles produced at an extrusion temperature of 250°C.

Permeation Barrier Properties of PE, PA, CP, MPA, and MPE Sheets

The permeation barrier properties of hot-pressed sheets of PE, PA, CP, MPE, and MPA resins are summarized in Table III. As expected, the xylene permeation resistance of the base PA sheet is significantly better than that of the base PE, in which the barrier improvement of PA is 15.8 as compared to that of the base PE sheet. Among the three base PE, PA, and CP sheets, CP exhibits the worst permeation resistance. Somewhat surprisingly, the permeation resistance of the MPE sheets is worse than that of the base PE sheet and becomes even worse as the amounts of CP present in the MPE sheets increase. In contrast, the xylene permeation barrier properties of all MPA

sheets are better than those of the base PA sheet, and the barrier improvements of the MPA sheets reach the maximum value as the amounts of CP contained in the MPA (Ccp) approaches 15 wt %. As mentioned previously, CP is highly unlikely to react with PE during the preparation of the MPE resins, wherein CP exhibited an even worse permeation resistance than that of the base PE. Therefore, it is reasonable to believe that the permeation resistance of the MPE sheets can be reduced consistently with increasing amounts of CP present in the MPE sheets. In contrast, formation of the crosslinked structures of CP/PA copolymers during reactive extrusion can significantly reduce the free volumes of MPA resins and further prohibit the nonpolar xylene molecules from entering into and permeating through the amorphous regions of the MPA resins. Moreover, the crystallinity values of the MPA resins were found to decrease significantly with increasing Ccp (see Table III), which can also significantly affect the barrier properties of the MPA resins. This reduc-
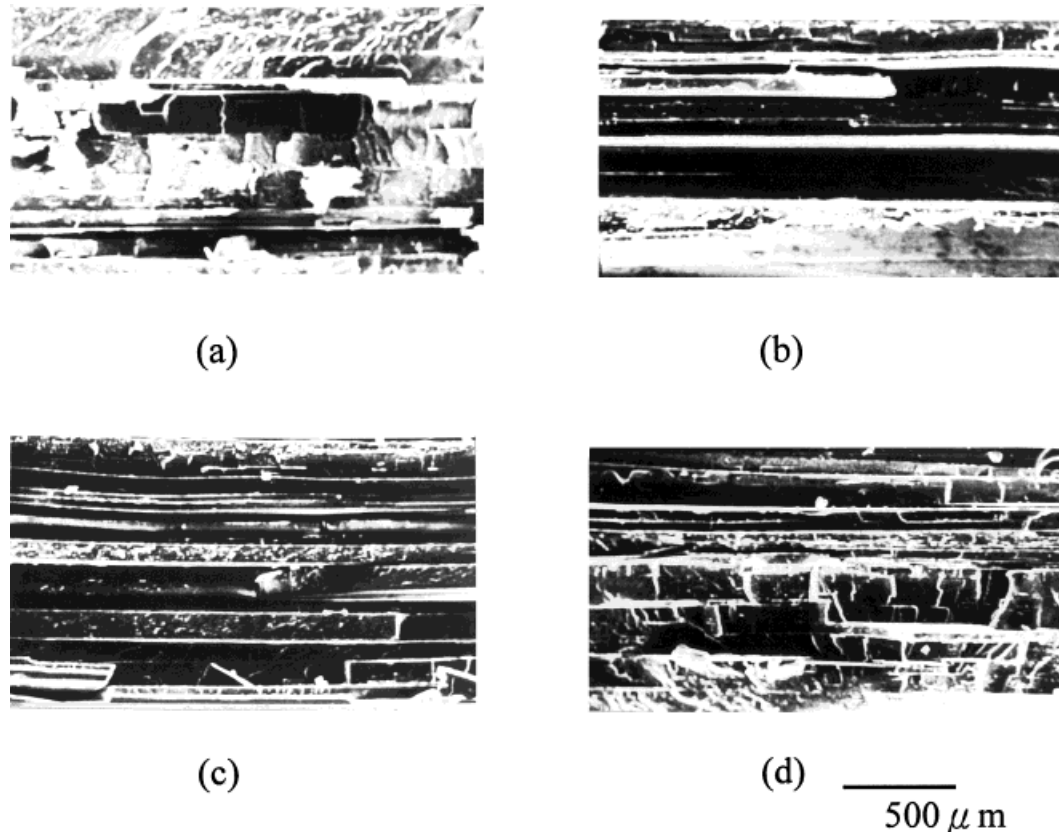
Figure 8   Fracture surfaces of PE/MPA$_{15}$ bottles prepared at a screw speed of 400 rpm and an extrusion temperature of (a) 195°C, (b) 215°C, (c) 230°C, and (d) 250°C.

tion in W_c may significantly shorten the permeant path of the xylene molecules as Ccp increases and compromise the beneficial effect of "crosslinked" CP/PA molecules on the barrier properties of the MPA resins. As a consequence, the the MPA sheet exhibits the best xylene permeation resistance as it contains the optimum amount of CP.

Permeation Barrier Properties of PE, MPE, PE/MPA, and MPE/PA Bottles

Table IV summarizes the permeation barrier properties of PE, MPE, PE/MPA, and MPE/PA bottles prepared at a screw speed of 400 rpm, wherein PE and MPE were extruded at a temperature of 190°C and PE/MPA and MPE/PA were extruded at 230°C. Similar to the hot-pressed sheets, the xylene permeation resistance of the MPE bottles is worse than that of the base PE bottle and decreases consistently as MPE contains more CP. However, after adding PA in MPE during blow molding, the xylene permeation barrier properties of the MPE/PA bottles improve

significantly. In fact, it is worth noting that the permeation barrier properties of the MPE/PA bottles improve consistently as the MPE contains more CP, although the permeation resistance of MPE is consistently reduced as it contains more CP (see Table IV). For example, the xylene permeation rates of the MPE/PA bottles are reduced from 0.524 to 0.218 g/day when the amounts of CP contained in MPE increase from 1.1 to 4.26 wt % (see Tables I and IV). In contrast, the PE/MPA bottles exhibit dramatically better permeation barrier properties than those of the MPE/PA and PE bottles, wherein the PE/MPA and MPE/PA bottles were prepared from the same compositions of PE, CP, and PA. For instance, the xylene permeation rate of the MPE$_{1.5}$/PA bottle is about 13 times faster than that of the PE/MPA$_{15}$ bottle (0.476 versus 0.037 g/day).

Figures 9 and 10 summarize the permeation barrier properties of the MPE/PA and PE/MPA bottles prepared at various screw speeds and extrusion temperatures, respectively. It is worth noting that the permeation resistance of the

Table III   Crystallinity Values and Melting Temperatures of PE, PA, CP, MPA, and MPE Resins and Xylene Permeation Barrier Properties of Hot-pressed Sheets of PE, PA, CP, MPA, and MPE Resins

Parameter	Sample						
	PE	PA	CP	MPA_{10}	MPA_{15}	MPA_{20}	MPA_{40}
Permeation rate (g/day)	1.105	0.070	1.980	0.030	0.026	0.027	0.035
Barrier improvement[a]	1	15.8	0.6	36.8	42.5	40.9	31.6
Melting temperature (°C)	136.4	223	95.0	220.8	220.5	220.3	219.7
Crystallinity (%)	70	38	17	31	29	26	24
				MPE_1	$MPE_{1.5}$	MPE_2	MPE_4
Permeation rate (g/day)				1.217	1.243	1.295	1.366
Barrier improvement[a]				0.91	0.89	0.85	0.81
Melting temperature (°C)				133.3	130.7	128.2	124.5
Crystallinity (%)				65	63	62	60

[a] Barrier improvement = (permeation rate of hot-pressed sheet of PE)/(permeation rate of hot-pressed sheet of each sample).

MPE/PA bottles improved consistently when they were prepared at higher extrusion temperatures (see Fig. 9). In contrast, at a fixed screw speed, the best permeation resistance of each PE/MPA bottle series is always obtained when prepared at an extrusion temperature around 230°C (see Fig. 10). With extrusion temperatures higher than 230°C, their xylene permeation resistance decreased significantly. It is not completely clear what accounts for these interesting phenomena. Presumably, the carboxyl groups of CP contained in MPE may react with the amine groups of PA and form CP/PA copolymers, when the temperatures used in the extrusion and blow-molding pro-

Table IV   Xylene Permeation Rates of PE, MPE, MPE/PA, and PE/MPA Bottles

	Sample				
	PE	MPE_1	$MPE_{1.5}$	MPE_2	MPE_4
Permeation rate (g/day)	4.58	4.65	4.71	4.88	5.25
		MPE_1/PA	$MPE_{1.5}$/PA	MPE_2/PA	MPE_4/PA
Permeation rate (g/day)		0.524	0.476	0.241	0.218
		PE/MPA_{10}	PE/MPA_{15}	PE/MPA_{20}	PE/MPA_{40}
Permeation rate (g/day)		0.129	0.037	0.063	0.311

PE and MPE bottles prepared at an extrusion temperature of 190°C and a screw speed of 400 rpm. MPE/PA and PE/MPA bottles prepared at an extrusion temperature of 230°C and a screw speed of 400 rpm.
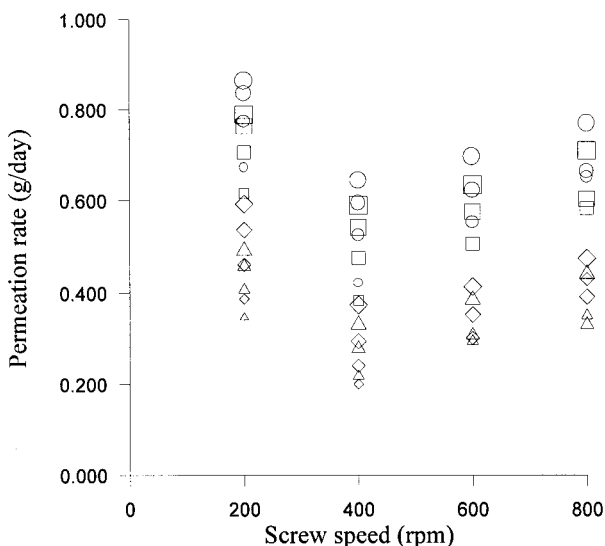
Figure 9 Xylene permeation rates of (○) MPE$_1$/PA, (□) MPE$_{1.5}$/PA, (◇) MPE$_2$/PA, (△) MPE$_4$/PA bottles at 195, 215, 230, and 250°C. Nos. are the extrusion temperatures used to prepare the MPE/PA bottles.

cess are high enough. As mentioned earlier, the crosslinked CP/PA copolymers can reduce the free volume of PA and prohibit the nonpolar xylene molecules from entering into and permeating through the amorphous regions of PA in the MPE/PA bottles. Moreover, the possibility of the formation of CP/PA copolymers and the permeation resistance of the MPE/PA bottles can increase as the temperatures used in extrusion and blow molding of MPE/PA increase. However, the extent of reaction between CP and PA in the MPE/PA bottles cannot be as high as those obtained in the PE/MPA bottles, wherein the carboxyl groups have extensively reacted with the amine groups of PA during the prior reaction extrusion of the MPA resins. Therefore, the xylene permeation resistance of the PE/MPA bottles is much better than the corresponding MPE/PA bottles and does not improve consistently with the extrusion temperatures.

On the other hand, it is interesting to note that the xylene permeation rates of each MPE/PA and PE/MPA bottle series prepared at a fixed extrusion temperature reached a minimum for each bottle series prepared at an optimum screw speed around 400 rpm (see Figs. 9 and 10). The xylene permeation rates of each MPE/PA and PE/MPA bottle series then increased consistently with the screw speeds when prepared at screw speeds higher than the optimum screw speed. For instance, the xylene permeation rate of the PE/

MPA$_{15}$ bottle series extruded at 230°C was merely 0.037 g/day when prepared at a screw speed of 400 rpm. The permeation rate then significantly increased to 0.096 g/day for the PE/MPA$_{15}$ bottles prepared at a higher screw speed of 800 rpm. Similar phenomena were found for other PE/MPA or MPE/PA bottle series prepared at various extrusion temperatures. As mentioned previously, more layers of continuous and demarcated MPA or PA laminae were found on the fracture surfaces of the PE/MPA and MPE/PA bottles prepared near the optimum screw speed of about 400 rpm, respectively. However, some segmented and broken MPA (or PA) laminae were found on the fracture surfaces of PE/MPA (or MPE/PA) bottles prepared at screw speeds higher than the optimum value. It is generally recognized that more layers of continuous MPA (or PA) laminae can further prolong the permeation period of the nonpolar xylene molecules through the PE/MPA (or MPE/PA) bottles over those bottles with fewer layers of continuous or with broken laminae. Based on these premises, it is reasonable to suggest that the maximum improvement in the permeation resistance of each PE/MPA and MPE/PA bottle series mentioned above is attributed to more layers of continuous but not broken MPA (or PA) laminae present in the PE/MPA (or MPE/PA) bottles prepared at an optimum screw speed near 400 rpm.
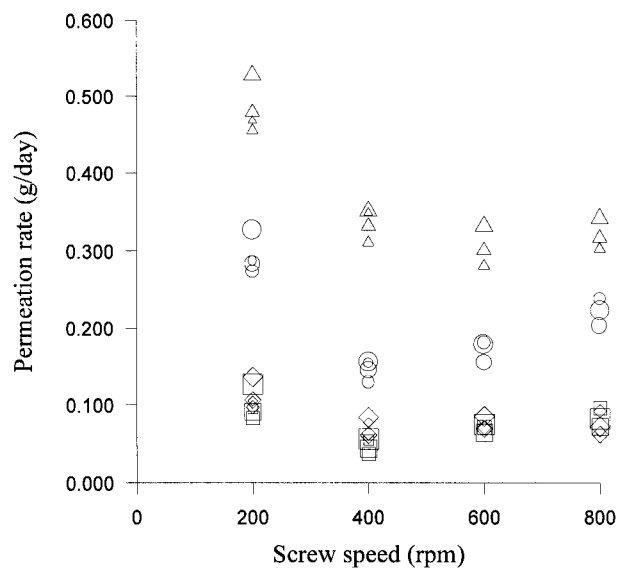

Figure 10 Xylene permeation rates of (○) PE/MPA$_{10}$, (□) PE/MPA$_{15}$, (◇) PE/MPA$_{20}$, and (△) PE/MPA$_{40}$ bottles at 195, 215, 230, and 250°C. Nos. are the extrusion temperatures used to prepare the PE/MPA bottles.

CONCLUSIONS

The xylene permeation resistance of the MPE bottles is worse than that of the base PE bottle and is reduced consistently as MPE contains more CP. After adding PA to MPE during blow molding, the xylene permeation barrier properties of the MPE/PA bottles are significantly better than those of the base PE bottle. In fact, the permeation barrier properties of the MPE/PA bottles improve consistently as MPE contains more CP. In contrast, at the same blow-molding conditions, the PE/MPA bottle exhibits dramatically better barrier properties than those its corresponding MPE/PA bottle with the same compositions of CP, PA, and PE. Apparently, the processing sequence of CP with PA has a significant effect on the barrier properties of the PE/MPA and MPE/PA bottles, in which each MPA was formed by reacting CP with PA before blow molding with PE, but PE is not expected to react with CP during the preparation of MPE.

On the other hand, it is interesting to note that the xylene permeation rates of each MPE/PA and PE/MPA bottle series prepared at a fixed extrusion temperature reached a minimum for each bottle series when prepared at an optimum screw speed around 400 rpm. This permeation improvement is attributed to more layers of continuous but not broken MPA (or PA) laminae present in the PE/MPA (or MPE/PA) 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 it was prepared at an optimum extrusion temperature of about 230°C.

Further morphological investigations indicated that more clearly defined MPA laminae were found on the fracture surfaces of the PE/MPA bottles prepared at an extrusion temperature near 230°C than those prepared at other temperatures. In contrast, the xylene permeation resistance of each MPE/PA bottle improved consistently when prepared at the higher extrusion temperatures used in this study. These results clearly suggest that the processing conditions used in the blow-molding process have a significant influence on the morphology and barrier properties of the PE/MPA and MPE/PA bottles.

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