Effects of Composition of Modified Polyamide on Barrier Properties of Polyethylene/Modified Polyamide Blends

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ABSTRACT: A systematic study on the effects of types and contents of compatibilizer precursors (CPs) on degrees of crystallinity (W_c), melt shear viscosities (η_s), and permeation barrier properties of modified polyamides (MPAs) and on their corresponding morphology and barrier properties of bottles blow-molded from polyethylene (PE)/MPA blends is reported. Two alkylcarboxyl-substituted polyolefins were selected as CPs to modify PA and to improve its permeation resistance to xylene by the "reactive extrusion" process. The barrier improvements of MPAs prepared in this study depend significantly on the type and content of CP present in the MPA. A maximum improvement in barrier properties of each MPA series samples were found as the contents of CP reached an "optimum" value. On the other hand, it is interesting to note that bottles blow-molded from PE/MPA series samples exhibited better barrier properties because the MPAs used were associated with better permeation resistance to xylene. The melt shear viscosities of MPAs were found to depend on the type of CP used and increase with increasing CP contents. In contrast, the W_c of MPAs decreased with increasing CP contents. Further analysis of the fracture surfaces of bottles blow-molded from PE/MPA blends also indicated that the morphology of MPA laminas depended on the type of CP present in the MPA, and these MPA laminar structures became clearer as the contents of CPs increased. Possible mechanisms accounting for the interesting behaviors described above are discussed. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64**: 1531–1540, 1997

Key words: laminar structure; compatibilizer precursor; modified polyamide; permeation barrier property; viscosity ratio

INTRODUCTION

It is well known that organic liquids such as hydrocarbons and chlorinated solvents can easily permeate through polyethylene (PE). Polyamide 6 (PA), known for its outstanding permeation barrier properties of hydrocarbons, is often used as a complementary component for PE in the packaging industry. However, in contrast to PE, the physical properties of PA tend to deteriorate

because of high moisture susceptibility. As blending of PE with PA leads to a thermodynamically immiscible two-phase system, compatibilizer precursors (CPs) such as carboxylated PEs were, therefore, often used in PE/PA blends to improve the interfacial properties between PE and PA and the barrier as well as mechanical properties of PE/PA blends.[1–3] Further investigation indicated that the barrier properties of PE/PA/CP blends greatly depend on the mode of blending and on their corresponding morphology.[4–8] The heterogeneous blends of the PE/PA/CP system were prepared by melt processing the three components

under carefully controlled conditions, wherein the compatibilizer was believed to be present between the laminas and adhered them together. These heterogeneous blends contain laminar PA dispersed in PE matrix and have much better hydrocarbon barrier properties than homogeneous blends associated with finely dispersed PA in PE matrix.[4-8] Our latest study[9] reported on how PA was modified with different types of CPs at a fixed CP content and how these modified PAs (MPAs) affected the subsequent morphology and barrier properties of PE/MPA blends. It is not completely clear how the type of CP added affects the barrier properties of MPAs, whereas the level of barrier improvement of PE/MPA blends depends significantly on the barrier properties of MPA prepared and the extent of mixing PE and MPA before blow molding. As far as we know, very few investigations[4,5,9] reported on how the compositions of MPA affect its subsequent morphology and barrier properties of PE/MPA blends. In fact, Subramanian[4,5] only showed that the presence of CP and PA in PE/PA/CP blends might have a beneficial influence on the PE/PA/alkylcarboxyl-substituted polyolefin blends, because the containers blow-molded from the above blends exhibited significantly better barrier properties than those blow-molded from pure PE. However, the detailed mechanisms of how the compositions of CP and PA affect the barrier properties of PE/PA/CP blends were not described in their studies. In this study, MPAs prepared from varying the contents of two types of CPs were used to investigate the effects of MPA compositions on the barrier and rheological properties of MPAs and on their subsequent morphology and barrier properties of PE/MPA blends. The possible mechanisms accounting for how the compositions of CP present in MPA affect the barrier properties of MPA and its corresponding PE/MPA blends were discussed.

EXPERIMENTAL

Materials

Two types of CPs were selected to blend with PA in this study. CPa is a zinc-neutralized ethylene/acrylic acid copolymer and CPb is a high density PE grafted with maleic anhydride. The physical properties of PE, PA, and CPs used in this study are summarized in Table I.

The density values are cited from commercial

Table I Physical Properties of PE, PA, and CPs

| Properties | Type of Resins | | | |
| | PE | PA | CP | |
			CPa	CPb
Melt index (g/10 min)	0.36	2.40	9.20	0.80
Density (g/cm^3)	0.954	1.13	0.96	0.95
Melting temperature (°C)	136	224	95	135
Crystallinity (%)	71	41	17	32

catalogues. The detailed experimental procedures for determination of the other physical properties of PE, PA, and CPs shown in Table I will be described later. The antioxidant Irganox B225 was obtained from Ciba–Geigy Corporation.

Sample Preparation

Before melt blending, all CPs and PA were dried at 60°C for 8 h and 80°C for 16 h, respectively. The dried components of PA, CP, and 1500 ppm antioxidant were first dry blended thoroughly and then fed into a twin screw extruder. Table II summarizes the compositions of MPAs prepared in this study.

Some MPA specimens were dyed red for to better distinguish the morphology of MPA in blow-molded PE/MPA bottles. The extruder was operated at 215°C in the feeding zone and at 240°C toward the extrusion die at a screw speed of 1000 rpm. The MPAs obtained from twin screw extruder were quenched in cold water at about 15°C and cut into the form of pellet. These MPAs were then dried at 80°C for 16 h before mixing with PE. Various weight ratios of mixtures of PE and MPAs were blow-molded by a blow-molding machine operating at an extrusion temperature of 220°C and a screw speed of 25 rpm. The blow-molded bottles weighed about 100 g and had a capacity of about 1 L and a wall thickness of about 1 mm. For the purpose of comparison, bottles were also prepared from pure PE resin by using the same screw and blow-molding machine at a temperature of 190°C and a screw speed of 25 rpm.

Normalized Grafting Efficiency (NGE) of MPAs

The possible formation of CP-grafted PA copolymers through the reaction of carboxyl groups of

Table II Compositions of MPAs Prepared

	MPAa10	MPAa20	MPAa30	MPAb10	MPAb20	MPAb30	MPAb40
PA	90	80	70	90	80	70	60
CPa	10	20	30				
CPb				10	20	30	40

these CPs with the amide and terminal amine groups of PA during the preparation of MPA, were characterized by using the techniques of "solvent extraction" and Fourier transform infrared (FTIR).[10] Five grams of each MPA sample was suspended in 100 mL of formic acid at 80°C for 2 h. The soluble and insoluble fractions were then dried, weighed, and hot-pressed at 220°C and 20 MPa, respectively. The hot-pressed films with a thickness of about 0.1 mm were then used for FTIR analysis. The carboxyl groups of CPs and MPAs were identified by the presence of the $\delta(C=O)$ spectrum at about 1790 cm^{-1}. The normalized contents of carboxyl groups per backbone chain (NCC) of CP and the soluble and insoluble fractions of MPAs were defined to estimate the grafting efficiency of CP on PA and were calculated as follows:

NCC

$$= \frac{\substack{\text{area of peak of } \delta(C=O \text{ group}) \\ \text{integrated from 1760 to 1820 cm}^{-1}}}{\substack{\text{area of peak of } \delta(CH_2) \text{ group in CPs} \\ \text{integrated from 640 to 820 cm}^{-1}}} \quad (1)$$

The normalized contents of the carboxyl groups of the MPAs were then calculated by

$$\text{NCC}_{(\text{MPA})} = \text{wt \%}_{(\text{soluble fraction})}$$
$$\times \text{NCC}_{(\text{soluble fraction})} + \text{wt \%}_{(\text{insoluble fraction})}$$
$$\times \text{NCC}_{(\text{insoluble fraction})} \quad (2)$$

The NGE of CP into PA in each MPA was then estimated according to

$$\text{NGE} = 1$$
$$- (\text{NCC of MPA/NCC of pure CP}) \quad (3)$$

Crystallinity and Morphology

The crystallinities of PE, PA, CPs, and MPAs were determined by the differential scanning calorime-

try (DSC) method. The heat of fusion was measured at a heating rate of 10°C/min. The equilibrium heat of fusion cited for PE[11] and PA[12] are 293 and 190 J/g, respectively. The blow-molded bottles were fractured in liquid nitrogen and etched with formic acid. The etched samples were then gold-coated and examined using a scanning electron microscopy (SEM).

Rheological Properties

The melt indices (MIs) and shear viscosities (η_s) of PE, PA, CPs, and MPAs were measured to correlate with their molecular weights (MWs) and extrusion properties during blow-molding. The MIs were measured at 230°C/2.16 kg for PE, PA, CPs, and MPAs as suggested by ASTM D1238. The η_s of the blends and pure components were characterized using a Rosand Precision Advanced Capillary Extrusion Rheometer equipped with a capillary of 1-mm diameter. All η_s were measured at 230°C and a shear rate of 30 L/s. The melt shear viscosity ratios (VRs) of MPAs to PE measured at 30 L/s were used to correlate with the deformation behavior of the MPA dispersed phase during the blow-molding process of MPA/PE blends.

Permeation Test

The barrier properties of the blow-molded bottles were evaluated by measuring the weight loss of the xylene filled in the bottles. The bottles were initially filled with 300 g of xylene. The weight loss of xylene was determined after placing the filled bottles at 60°C for 14 days. On the other hand, the barrier properties of pure PE, PA, and MPAs were determined based on their hot-pressed sheets, because it is well known that pure PA and various MPAs are difficult to process by blow molding due to their poor melt strength. The pellets of PE, PA, and MPAs were hot-pressed into about 1-mm thick sheets and cut into circles of 14-cm diameter. The circular sheets were sealed

Table III   Normalized Grafting Efficiency of MPAs, Normalized Contents of Carboxyl Groups of CPs, and Soluble and Insoluble Fractions of MPAs

MPA	NCC in Soluble Fraction	Soluble Fraction (%)	NCC in Insoluble Fraction	Insoluble Fraction (%)	NCC of MPA	NCC of Pure CP	Normalized Grafting Efficiency
a10	7.25×10^{-4}	98.5	8.13×10^{-4}	1.5	7.26×10^{-4}	8.35×10^{-3}	0.913
a20	6.38×10^{-4}	94.9	6.85×10^{-4}	5.1	6.40×10^{-4}	8.35×10^{-3}	0.923
a30	4.26×10^{-4}	56.2	4.69×10^{-4}	43.8	4.45×10^{-4}	8.35×10^{-3}	0.947
b10	2.59×10^{-3}	95.6	8.33×10^{-3}	4.4	2.84×10^{-3}	3.50×10^{-2}	0.919
b20	1.98×10^{-3}	82.0	1.13×10^{-3}	18.0	1.83×10^{-3}	3.50×10^{-2}	0.948
b30	1.65×10^{-3}	45.5	1.48×10^{-3}	54.5	1.56×10^{-3}	3.50×10^{-2}	0.955
b40	1.53×10^{-3}	32.3	1.44×10^{-3}	67.7	1.47×10^{-3}	3.50×10^{-2}	0.958

as lids on the top of a test flask filled with 300 g of xylene. The barrier properties of the circular sheets were then determined by measuring the weight loss of xylene after placing the flasks at 60°C for 14 days. The barrier improvement is defined as the weight loss of pure PE sample over those of the other samples. The value of the barrier index is calculated as one minus the inverse value of barrier improvement. Barrier improvement and barrier index were calculated to compare the barrier properties of all samples.

RESULTS AND DISCUSSION

Normalized Grafting Efficiency of MPAs, Normalized Contents of Carboxyl Groups of CPs, and Soluble and Insoluble Fractions of MPAs

As shown in Table III, the NGE of MPAs and insoluble fraction of MPAs in formic acid solution increased as CP contents increased.

As reported by Serpe et al.,[10] the soluble fraction of MPA in formic acid solution was suggested to consist of pure PA or long PA sequences with shorter grafted CP chains. The insoluble fraction supposedly consisted of pure CPs or long CP sequences with shorter grafted PA chains, because the CPs are insoluble in formic acid solution. Based on these premises, it is reasonable to suggest that the possibility of formation of CP-grafted PA copolymers in PA molecules through the reaction of carboxyl groups of CPa and/or CPb with the terminal amine and amide groups of PA increases as the contents of CPs increase. Therefore, the NGE of MPA increased significantly with increasing CP contents. On the other hand, the

amounts of CPs unreacted or long CP sequences with shorter grafted PA chains can also increase as CP contents increase, hence increasing the amounts of insoluble fraction of MPA in formic acid solution.

The normalized grafting efficiencies of MPAa series samples were slightly lower than those of MPAb series samples, but were approximately equal to one. This suggested that the reactivity of the possible formation of CP/PA copolymers in PA molecules through the reaction of carboxyl groups of CPa and/or CPb with the terminal amine and amide groups of PA was very high. However, MPAa series samples were associated with a significantly higher soluble fraction in formic acid solution than MPAb series samples at each fixed CP content. In addition, the NCC of MPAa and MPAb series samples in the insoluble fraction were significantly lower than those of pure CPa and CPb, respectively (see Table III). As will be discussed later (see Table IV), CPa is associated with a much higher MI than CPb, which indicates the average molecular weight and/or the average length of CPb molecules are larger than those of CPa.

As suggested in our previous study,[9] the fact that MPAa series samples having higher soluble fractions than MPAb series samples at each fixed CP content possibly indicated that CPb was associated with longer CP chains than CPa, and a significant part of these long CPb sequences were grafted into shorter PA chains during reactive extrusion of MPAb. In contrast, most of the CPa chains were possibly grafted into long PA sequences during the preparation of MPAa, which was dissolved in formic acid solution during solvent extraction.

**Table IV   Rheological Properties of PE, PA, CPs, and MPAs**

| | Sample | | | | | | | | | | |
| | | | CP | | MPA | | | | | | |
Properties	PE	PA	CPa	CPb	a10	a20	a30	b10	b20	b30	b40
Melt indices											
(g/10 min)	0.36	2.4	9.2	0.8	2.4	1.7	1.5	3.5	2.2	1.9	1.7
η_{30} (Pa s)	2437	751	529	1966	1090	1808	1937	824	957	1215	1733
VR	1.0	—	—	—	0.400	0.742	0.795	0.389	0.393	0.424	0.711

Degrees of Crystallinity of PE, PA, CPs, and MPAs

The W_c of PE, PA, and CPs are summarized in Table I. As expected, the W_c of PE is higher than that of PA, and the W_c of PE and PA are significantly higher than those of CPa and CPb. In addition, the W_c of MPAs were found to decrease with increasing contents of CP in the MPAs (see Fig. 1). This decrease in W_c can be mainly due to the reduced W_c caused by reducing the amounts of PA in the MPA as the content of less crystallizable CP increases. In the meantime, the possible formation of CP-grafted PA copolymers during preparation of MPA may also reduce the W_c of MPA.

Rheological Properties of PE, PA, CPs, and MPAs

The MIs, η_s, and VRs of PE, PA, CPs, and MPAs to PE VRs are summarized in Table IV. As expected, the η_s of CPs and MPAs tend to increase with decreasing MI. It is interesting to note that
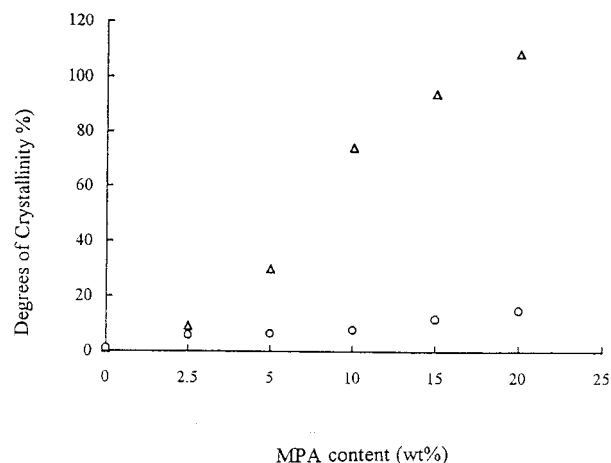
Figure 1   The degrees of crystallinity of (△) MPAa and (○) MPAb series samples plotted against contents of CPs added.

the η of CPa is significantly smaller than that of CPb, which indicates that the average molecular weight and the average length of CPa molecules are significantly lower than those of CPb. The η_s of MPAs increase with the increasing contents of CPs in the MPAs and the η_s of MPAa series samples are higher than those of MPAb series samples at each fixed CP content, although the η of CPa is significantly lower than that of CPb. It is not completely clear what the underlying mechanisms accounting for these behaviors is. Presumably, the shear viscosities of the CP-grafted PA copolymers can be higher than those of CP and PA, because the structures of CP-grafted PA copolymers can be quite huge and complex compared to those of CPs and PA. For instance, short CP chains may be dispersed into PA matrix and grafted into several long PA molecules and present as huge "crosslinked" CP/PA copolymers in the PA matrix. Therefore, the η_s of MPAs increase with the increasing contents of CPs in the MPAs, because the possibility of formation of CP-grafted PA copolymers is higher as the content of CP in MPA increases. In contrast, as discussed earlier, CPb is possibly associated with longer CP chains than CPa. A significant part of these long and huge CPb sequences might be difficult to disperse into PA matrix and were grafted into shorter PA chains during reactive extrusion of MPAb series samples. These long CPb sequences with shorter grafted PA chains are associated with a much smaller dimension than crosslinked CPa/PA copolymers formed by grafting short CPa chains into long PA sequences. The η_s of MPAa series samples are, therefore, higher than those of MPAb series samples at each fixed CP content.

Barrier Properties of PE, PA, and MPA Sheets

The barrier properties of PE, PA, and MPA sheets are summarized in Table V. As expected, PA ex-

Table V   Barrier Properties of Hot-Pressed PE, PA, and MPA Sheets

| | | | Sample | | | | | | |
| | | | | MPA | | | | | |
	PE	PA	a10	a20	a30	b10	b20	b30	b40
Permeability (g/day)	1.829	0.100	0.042	0.039	0.047	0.093	0.082	0.080	0.099
Barrier									
Improvement	1	18.3	43.5	46.9	38.9	19.7	22.3	22.9	18.5
Index	0	0.95	0.98	0.98	0.97	0.95	0.96	0.96	0.95

hibited better barrier properties than pure PE, in which the barrier improvement of PA was 18.3. It is not completely clear why PA restricts the mobility of permeant xylene molecules more efficiently than PE, and MPA exhibits significantly better xylene barrier properties than pure PA. 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, therefore, reasonable to suggest that the molecular composition and configuration 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 can barely allow the nonpolar xylene molecules to enter into and permeate through the amorphous regions of PA as compared to nonpolar PE molecules. As a consequence, the barrier properties of PA against nonpolar xylene are significantly better than those of PE, although the W_c of PE is higher than that of PA.

It is surprising to note that MPAs prepared from any content of CPs showed significantly improved barrier properties than pure PA, wherein MPAs prepared from the CPa series performed better than those prepared from CPb series. On the other hand, it is interesting to note that the barrier properties of MPAs improved initially with the contents of CPa or CPb present in MPAs. However, this beneficial effect of CP content on the barrier properties of MPAs disappeared as the contents of CPa and CPb present in the MPAs were more than 20 and 30 wt %, respectively. In fact, as shown in Figure 2, the barrier improvements of these MPAs reduced significantly as the amounts of CPs added were more than 20 and 30 wt % for MPAa and MPAb series samples, respectively.

It is not completely clear what the underlying mechanisms accounting for these behaviors is. As mentioned previously, short CP chains may 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. The possibility of formation of these crosslinked structures increases as CP content increases. Presumably, these crosslinked structures of CP/PA copolymers can significantly reduce the free volume of MPA and further prohibit the nonpolar xylene molecules from entering into and permeating through the amorphous regions of MPA. Therefore, the barrier properties of MPAa and MPAb series samples improve initially with the contents of CPa or CPb present in the MPAs. In contrast, as mentioned earlier, CPb is possibly associated with longer CP chains than CPa, and a significant portion of these long CPb sequences are grafted into shorter PA chains. These long CP sequences with shorter grafted PA chains may be immiscible
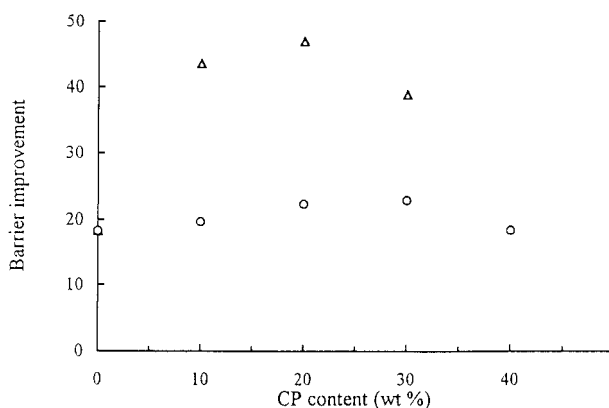
Figure 2   Barrier improvements of (△) MPAa and (○) MPAb series samples prepared from different contents of CPs.
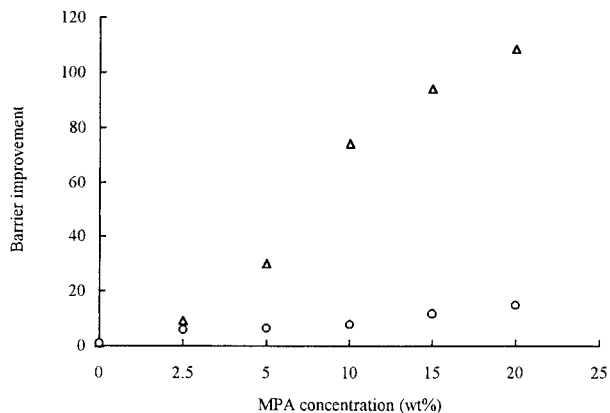
Figure 3 Barrier improvements of bottles blow-molded from (△) PE/MPAa20 and (○) PE/MPAb20 blends.

with and phase-separated from the "PA" matrix, and hence cannot significantly improve the barrier properties of PA as much as those improved by long PA sequences with shorter grafted CP chains. As a consequence, the barrier properties of MPAa series samples are better than those of MPAb series samples at a fixed CP content. In addition to the amounts of crosslinked molecules of CP/PA copolymers present in the amorphous phase of PA matrix, the W_c of the MPAs can also significantly affect the barrier properties of MPAs. The W_c of MPAa and MPAb series samples decreased significantly as the contents of CPa and CPb increased, respectively. This reduction in W_c may significantly shorten the permeant path of xylene molecules as the contents of CP increase and compromise the beneficial effect of crosslinked CP/PA molecules on the barrier properties of MPA. As a consequence, the barrier improvements of MPAa and MPAb samples series decrease as the contents of CPa and CPb reach about 20 (MPAa20) and 30 (MPAb30) wt %, respectively.

Barrier Properties of Blow-Molded Bottles of PE/MPA Blends

As shown in Figure 3, all bottles blow-molded from PE/MPAa and PE/MPAb blends exhibited significantly better barrier properties than bottles blow-molded from pure PE. This improvement continued with increasing MPA concentrations in

PE/MPAa and PE/MPAb series samples, respectively. In addition, bottles blow-molded from PE/MPA blends exhibited better barrier properties as the MPAs used were associated with better barrier properties. For instance, the barrier improvements of PE/MPAa bottles are much better than those of bottles blow-molded from PE/MPAb blends at each fixed MPA concentration, and the bottles blow-molded from PE/MPAa20 and PE/MPAb30 exhibited better barrier improvement than bottles blow-molded from other CPa and CPb contents, respectively (see Fig. 4). These results clearly suggested that CP-modified MPA and enhanced its barrier properties ever better than pure PA, and the level of barrier improvements of PE/MPA blends depended significantly on the content of CP present in the MPA and the barrier properties of the MPA prepared.

Morphology of Blow-Molded Bottles of PE/MPA Blends

As shown in Figures 5 and 6, the fracture surfaces of the bottles blow-molded from mixtures of MPAs and PE at various compositions exhibited MPA laminas distributed across the wall thickness direction of the bottles. In fact, it is worth noting that the laminar structures of MPAa series samples are essentially clear, elongated, and layered platelets, while the laminar structures of MPAb series of low CP contents become relatively "obscure" and "broken" for bottles blow molded from the PE/MPAb sample series [see Figs. 5(a,b) or 6(a,b)]. In addition, the MPA laminar structures of PE/MPA bottles become clearer as the contents
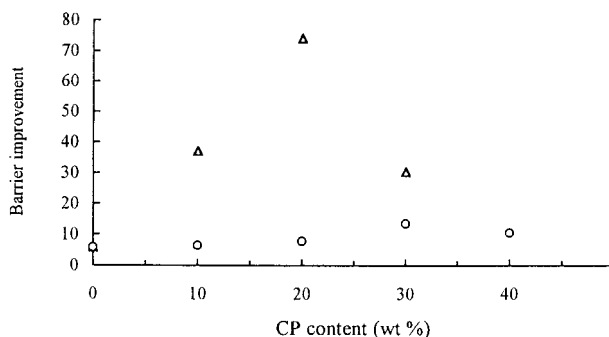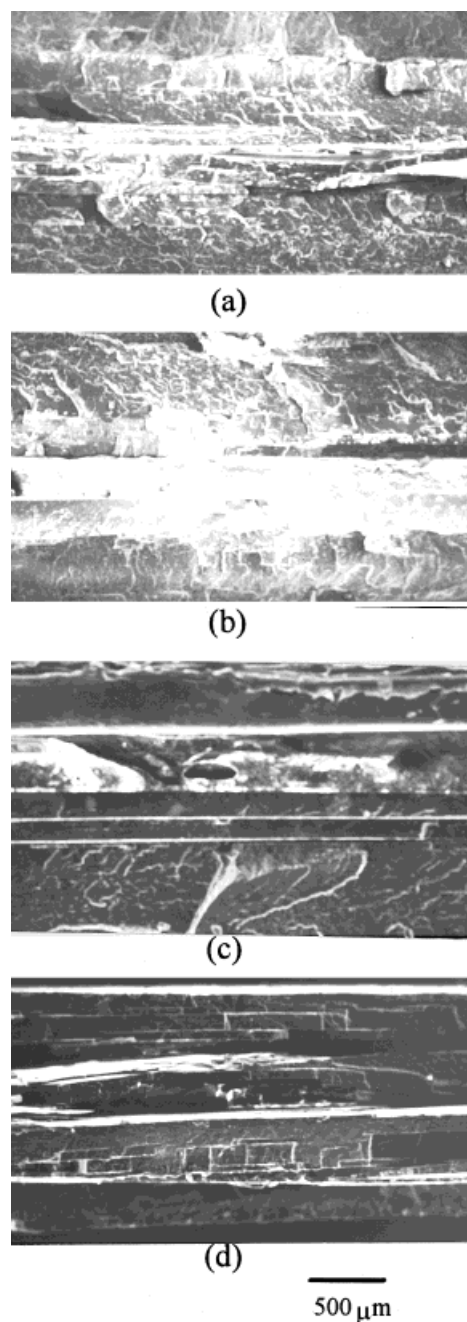

Figure 4 Barrier improvements of bottles blow-molded from (△) PE/MPAa and (○) PE/MPAb blends, in which the weight ratio of PE/MPA is 90/10.
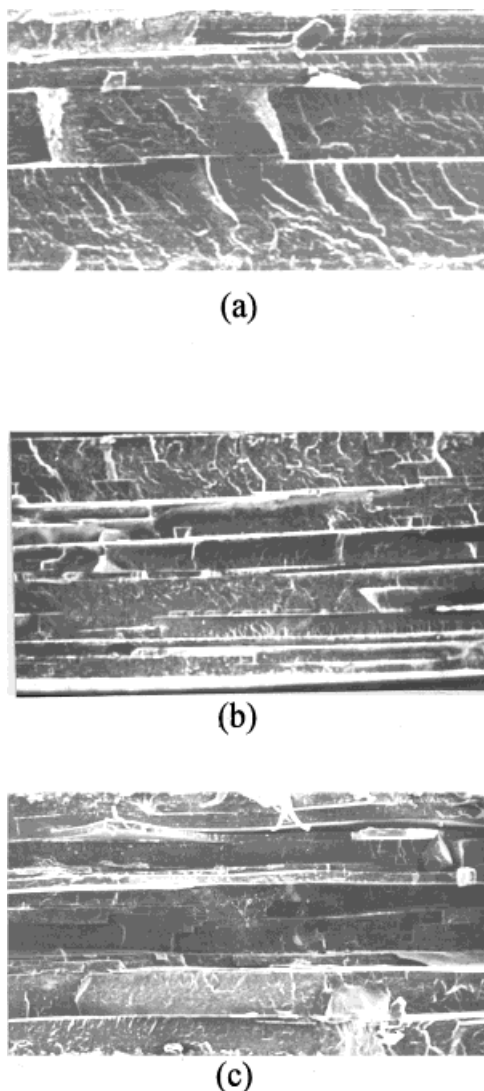
Figure 5 Morphologies of bottles blow-molded from PE/MPAa blends, in which the weight ratio of PE/MPA is 90/10: (a) PE/MPAa10, (b) PE/MPAa20, (c) PE/MPAa30.

laminar structures, while those MPAs with lower η_s can barely remain in the elongated laminar structures because PE melt with relatively high η tends to deteriorate MPAs of lower melt

Figure 6 Morphologies of bottles blow-molded from PE/MPAb blends, in which the weight ratio of PE/MPA is 90/10: (a) PE/MPAb10, (b) PE/MPAb20, (c) PE/MPAb30, (d) PE/MPAb40.

of CP increase (see Figs. 5 and 6). It is generally recognized that polymer melts exhibit higher melt strength during processing as their viscosities increase. As mentioned previously, the η_s of all MPAs prepared in this study are lower than that of PE wherein the η of MPAa at each fixed CP content is higher than that of MPAb. In addition, the viscosity ratios of these MPAs to PE increase with increasing CP contents. These results clearly suggest that MPAs with higher η_s exhibit higher melt strength and clearer as well as elongated

strength into broken and obscure laminar structures during the controlled blow-molding process.

As mentioned in our previous study,[9] clearer MPA laminar structures dispersed in PE matrix are essential for obtaining better barrier properties of PE/MPA blends. However, one must keep in mind that the barrier properties of MPA itself are other key factors in determining the barrier properties of PE/MPA blends. The barrier properties of MPAa30 are significantly worse than those of MPAa20, which can compromise the beneficial effect of clear laminar structures of MPAa30 on the barrier properties of bottles blow-molded from PE/MPAa30 blend [see Fig. 5(c)]. Therefore, PE/MPAa30 bottles exhibited worse barrier properties than PE/MPAa20 bottles.

CONCLUSION

A maximum improvement in barrier properties of MPAa and MPAb series were found as the contents of CPa and CPb reached an optimum value of 20 and 30 wt %, respectively. The increasing formation of huge and crosslinked structures of long PA sequences with short grafted CP chains during reactive extrusion is suggested to be responsible for the initial improvement of the barrier properties of the MPA samples, because the crosslinked molecules of CP/PA copolymers are possibly present in the amorphous regions of the PA matrix during crystallization of PA, which can significantly reduce the free volume of MPA and prohibit the nonpolar xylene molecules from entering into and permeating through the amorphous regions of MPA. On the other hand, the decreasing degrees of crystallinity of MPAs with increasing CP contents can compromise the beneficial effect caused by the presence of crosslinked molecules of CP/PA copolymers in the amorphous regions of the PA matrix because the reduction in W_c can significantly shorten the permeant path of xylene molecules in the amorphous regions of MPA matrix. As a consequence, the barrier improvements of MPAa and MPAb series decrease significantly because the contents of CPa and CPb are larger than their optimum values. The fact that the barrier improvements of the MPAa series are better than those of the MPAb series at a fixed CP content is possibly attributed to the presence of much more crosslinked molecules of CP/PA copolymers in the amorphous regions of the MPAa

series than in those of the MPAb series, wherein many of these CP/PA copolymers are long CP sequences with short grafted PA chains that tend to become immiscible with or even phase separated from the PA matrix. The study of the η_s of MPAs and fracture surface analysis of PE/MPA bottles suggests that PE melt with relatively high η_s tends to deteriorate MPAs with low η_s (i.e., low melt strength) into obscure and broken laminar structures. And only MPAs with high η_s are strong enough to be drawn by PE into elongated and clear laminar structures during the controlled blow-molding process. Finally, it is important to conclude that the barrier properties of PE/MPA bottles significantly depend on the permeation resistance of MPA itself, although clearer laminar structures of MPAs dispersed in PE matrix are also essential for obtaining good barrier properties of PE/MPA bottles.

NOMENCLATURE

CP	compatibilizer precursor
CPa	zinc-neutralized ethylene/acrylic acid copolymer
CPb	high density polyethylene grafted with maleic anhydride
MI	melt index
MPA	modified polyamide
MPAa	modified polyamide by CPa
MPAb	modified polyamide by CPb
MPAa20	MPAa with 20 wt % of CPa
MPAb30	MPAb with 30 wt % of CPb
NCC	normalized contents of carboxyl groups per backbone chain of CP
NGE	normalized grafting efficiency
PA	polyamide 6
PE	polyethylene
VR	melt shear viscosity ratio of MPA to PE
W_c	degrees of crystallinity

Greek Letters

η_s	melt shear viscosity

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