

The Barrier, Impact, Morphology, and Rheological Properties of Modified Polyamides and their Corresponding Polyethylene–Modified Polyamide Blends

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ABSTRACT: A systematic investigation of the effects of melt indices of polyamides (PAs) on the morphology, barrier, and impact properties of blow-molded polyethylene–polyamide and polyethylene-modified polyamide (PE–MPA) containers is reported. An appropriate alkyl carboxyl-substituted polyolefin was chosen as a compatibilizer precursor to modify PAs of varying melt indexes in a twin-screw extruder by the “reactive extrusion” process. The melt shear viscosities (η_s) of MPAs increased with decreasing melt indices of their corresponding PAs and were higher than those of their corresponding PAs, respectively. The barrier properties of MPAs were better than those of their corresponding PAs, and the level of barrier improvement of PAs and MPAs increased consistently with decreasing melt indices of their corresponding PAs. The values of total impact energy (E_t) of PAs and MPAs also improved with decreasing melt indices of PAs; however, MPAs exhibited lower values of E_t than their corresponding PAs. The barrier properties of PE–MPA bottles were much better than those of PE–PA bottles. The order of barrier improvement of these PE–MPA bottles corresponded approximately to the order of barrier improvement of pure MPA when the viscosity ratio of MPA to PE was about equal to or less than one. However, regardless of exhibiting the best barrier improvement in all MPAs, a significantly smaller barrier improvement of PE–MPA5 bottles was observed when the viscosity ratio of MPA to PE was significantly greater than one. Finally, it is interesting to note that PE–MPA sheets exhibited significantly higher E_t than their corresponding PE–PA sheets, although each PA was associated with a higher E_t than their corresponding MPAs. Possible mechanisms accounting for the interesting behaviors noted above are suggested in this study. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2517–2527, 1997

Key words: compatibilizer precursor; reactive extrusion; modified polyamide; barrier properties; total impact energy; viscosity ratio

INTRODUCTION

Rigid containers made of polyethylene (PE), especially of high-density polyethylene (HDPE), are widely used for packaging household and industrial chemicals. However, the relatively poor re-

sistance of PE to permeation by hydrocarbons and organic solvents compromises its ability to replace metal and glass for certain container applications. Some products such as agricultural chemicals, paint thinners, and gasolines can easily permeate PE containers; the results are pollution, safety, and health problems. Alternative technologies, such as surface treatment of PE by fluorination or sulfonation,^{1,2} multilayer coextrusion,^{1,2} and laminar-blend blow molding processes³ have been

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applied to try to improve this poor permeation resistance of PE. However, surface treatment technology is not widely used nowadays because of concern for environmental safety and health and because it requires substantial capital investment. An alternative to surface treatment, the coextrusion blow-molding process, is generally not available for with complex shapes products and requires specially designed equipment. Unlike the above-mentioned two barrier technologies, a laminar-blend process can form a layered structure containing dozens of discontinuous, overlapping plates of barrier resins, such as polyamide (PA) in PE matrix; and, at the same time, the process can lend itself to a wide variety of container designs and to processing convenience³ at a more competitive cost. It is, therefore, containers made by laminar processes that are widely used to package agricultural chemicals, paint thinners, industrial cleaners, and petroleum-based products.

As PE-PA blends are thermodynamically immiscible and mechanically incompatible, such compatibilizer precursors (CPs) as alkylcarboxyl-substituted polyolefins have often been used in PE-PA blends to improve the interfacial properties between PE and PA, as well as to enhance the barrier and mechanical properties of PE-PA blends.⁴⁻⁶ Further investigation has indicated that the barrier properties of PE-PA-CP blends depend greatly on the manner of blending and on the resulting morphology.⁷⁻¹¹ Heterogeneous blends of PE-PA-CP system are prepared by dry-blending the three components and then blow-molding under carefully controlled conditions wherein the compatibilizers are believed to be present among the laminars and to cause them to adhere. These heterogeneous blends contain PA laminars dispersed in a PE matrix and have much better hydrocarbon barrier properties than homogeneous blends associated with finely dispersed PA in the PE⁷⁻¹¹ matrix.

Very few investigations^{9,10,12,13} have reported on the effects of PE-PA-CP compositions on the morphology, barrier, and mechanical properties of the three-phase blends. Subramanian^{9,10} showed only that the presence of CP and PA in PE-PA-CP blends may have a beneficial influence since the containers blow-molded from the above blends exhibited significantly better barrier properties than those blow-molded from plain PE. However, the detailed mechanisms of the CP and PA compositions that affect the barrier properties of PE-PA-CP blends have not been described in those studies. The latest studies^{12,13} have indicated that

the type and content of CP present in modified polyamide (MPA) have a significant effect on the barrier, morphology, and rheological properties of MPAs and their corresponding PE-MPA blends. Possible mechanisms accounting for the above interesting results have also been discussed. In this study, the effects of melt indices of polyamides upon the morphology, barrier, rheological, and impact properties of MPAs and their corresponding PE-MPA blends were investigated.

EXPERIMENTAL

Materials

Five polyamides 6 (PA) were used to prepare different MPAs by blending them with one type of CP in this study. The CP was a 40% zinc-neutralized ethylene-acrylic acid (89 : 11) copolymer. The physical properties of polyethylene (PE), PAs, and CP used in this study are summarized in Table I; the values of densities are cited from their commercial catalogues. The experimental procedures for determination of the other physical properties shown in Table I will be described later. The antioxidant used, with a trade name of Irganox B225, was obtained from Ciba-Geigy Corporation, Taiwan branch.

Sample Preparation

All PAs and CP were dried before melt blending at 80°C for 16 h and 60°C for 8 h, respectively. The dried components of PAs, CP, and 1500 ppm of antioxidant were first dry-blended and then fed into a twin-screw extruder. The weight ratio of each PA to CP is 80 : 20. The extruder was operated at 215°C in the feeding zone and at 240°C towards the extrusion die, at a screw speed of 1000 rpm. The MPA pellets prepared from twin-screw extruder were then dried at 80°C for 16 h before mixing with PE. PE-MPA blends fixed at a weight ratio of 90 : 10 were blow-molded by blow-molding machine operating at an extrusion temperature of 220°C and a screw speed of 25 rpm. The blow-molded bottles weigh about 100 g and have a capacity of about 1 L with a wall thickness of about 1 mm. For purposes of comparison, bottles were also prepared from pure PE resin by using a screw and blow-molding machine at a temperature of 190°C and a screw speed of 25 rpm.

Table I Physical Properties of PE, PAs, and CP

Properties	PA						CP
	PE	PA1	PA2	PA3	PA4	PA5	
Melt index (g 10 min)	0.360	29.1	14.3	2.4	2.1	1.5	9.20
Density (g cm ³)	0.954	1.14	1.05	1.13	1.12	1.14	0.96
Melting temperature (°C)	136.0	224.0	223.9	224.0	221.5	220.5	95.0
Crystallinity (%)	71.0	41.8	41.3	41.2	40.0	40.5	17.0

Crystallinity and Morphology

The crystallinity of PE, PAs, CP, and MPAs was determined by the differential scanning calorimetry (DSC) method. The heat of fusion was measured at a heating rate of 10°C min. The equilibrium heat of fusion cited for PE¹⁴ and PA¹⁵ are 293 and 190 J/g, respectively. The midsections of blow-molded bottles were used for morphology and crystallinity determinations. The 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 and shear viscosities of PE, PAs, CP, and MPAs were measured to correlate with their molecular weight (M_w) and extrusion properties during blow-molding. The melt indices were measured at 230°C per 2.16 kg for PE, PAs, CP, and MPAs, as suggested by ASTM D1238. The melt shear viscosities (η) 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 were measured at 230°C and a shear rate of 30 L/s. The melt shear viscosity ratio (VR) of MPAs to PE was used to correlate with the deformation behavior of the MPA dispersed phase during the process of blow-molding of PE-MPA blends.

Permeation Test

The barrier properties of the blow-molded bottles were evaluated by measuring the weight loss of the xylene filling in the bottles. The bottles were initially filled with 300 grams of xylene. The weight loss of xylene was determined after placing the filled bottles in a temperature controlled oven at 60 ± 1°C for 14 days. The relative humidity

(RH) was held at 35 ± 1% during each test. Presumably, steady-state permeation rates are required in order to compare barrier properties of various samples. It was found¹⁶ that the permeation rate of xylene through PE, PE-PA, and PE-MPA bottles at 60°C became steady only after a few days of testing. In fact, the steady-state permeation rates are very close to the average permeation rates obtained by dividing the cumulative weight loss of xylene by the testing time (i.e., 14 days), which has been widely used to evaluate the permeation resistance of various bottles to hydrocarbon solvents.⁷⁻¹² Therefore, the average permeation rates were used to evaluate the permeation barrier properties of all samples used in this study. On the other hand, the barrier properties of pure PE, PAs, and MPAs were determined based on their hot-pressed sheets because it is well known that pure PAs and various MPAs are difficult to process by blow-molding because of their poor melt strength. The pellets of PE, PA, and MPA were hot-pressed into about 1 mm thick sheets and cut into circles of a diameter of 14 cm. The circular sheets were sealed as lids on the top of test flasks filled with 300 grams 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 ± 1°C and 35 ± 1% RH for 14 days. The barrier improvement was defined as weight loss of pure PE sample over those of the other samples. The value of barrier index was calculated as one minus the inverse value of barrier improvement. Both barrier improvement and barrier index were calculated to compare the barrier properties of all samples.

Impact Properties

All falling-weight impact experiments were performed at 25°C according to ASTM D3029, on a Hung-sun Impact Tester Model 208. The impact

Table II The Normalized Grafting Efficiencies and Soluble Fractions of MPAs

MPA Properties	MPA1	MPA2	MPA3	MPA4	MPA5
Normalized grafting efficiency	0.92	0.93	0.92	0.93	0.93
Soluble fraction (%)	93.6	94.2	94.9	95.2	96.3

energy was calculated by determining the area under force versus the displacement graph. The blow-molded bottles and hot-pressed sheets used for permeation test were cut as sheet specimens and were supported by an annular anvil with an internal diameter of 37.5 mm.

Normalized Grafting Efficiency of MPAs

The possible formation of CP-PA copolymers through the reaction of carboxyl groups of CP with the amide and terminal amine groups of PAs during the preparation of MPA were characterized by using the techniques of solvent extraction and the Fourier transform infrared (FTIR) method.¹⁷ 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 CP and MPAs were identified by the presence of the δ (C=O) spectrum at about 1790 cm⁻¹. The normalized contents of carboxyl groups per backbone chain (NCC) of CP, the soluble and insoluble fractions of MPAs, were defined to estimate the grafting efficiency of CP on PA and were calculated as follows:

$$\text{NCC} = \frac{\text{the area the peak of } \delta \text{ (C=O) integrated from 1760 to 1820 cm}^{-1}}{\text{the area the peak of } \delta \text{ (CH}_2\text{)}_{n>4} \text{ integrated from 640 to 820 cm}^{-1}} \quad (1)$$

The normalized content of carboxyl groups of MPA was then calculated by eq. (2), as follows:

$$\begin{aligned} \text{NCC}_{(\text{MPA})} = & \text{weight percent}_{(\text{soluble fraction})} \\ & * \text{NCC}_{(\text{soluble fraction})} + \text{weight percent}_{(\text{insoluble fraction})} \\ & * \text{NCC}_{(\text{insoluble fraction})} \quad (2) \end{aligned}$$

The normalized grafting efficiency (NGE) of CP on PA in each MPA was then estimated according to eq. (3), as follows:

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

RESULTS AND DISCUSSION

Normalized Grafting Efficiency of MPAs and Soluble and Insoluble Fractions of MPAs in Formic Acid

As shown in Table II, the NGEs of MPAs prepared from PAs of various melt indices were more than 0.9 and remained approximately the same at about 0.92–0.93, which indicated the

Table III Rheological Properties and Crystallinity of PE, CP, PAs, and MPAs

Properties	PE	CP	MPA1	MPA2	MPA3	MPA4	MPA5	PA1	PA2	PA3	PA4	PA5
Melt index (g 10 min)	0.36	9.2	14.5	11.5	1.7	1.2	0.47	29.1	14.3	2.4	2.1	1.5
Shear viscosity (Pa s)	2437	529	352	829	1808	2481	4411	187	581	752	1686	2183
Shear viscosity ratio (VR)	1.0	—	0.14	0.34	0.74	1.02	1.81	0.08	0.24	0.31	0.69	0.89
Crystallinity (%)	71	17	29	28	27	27	29	41	41	41	40	41

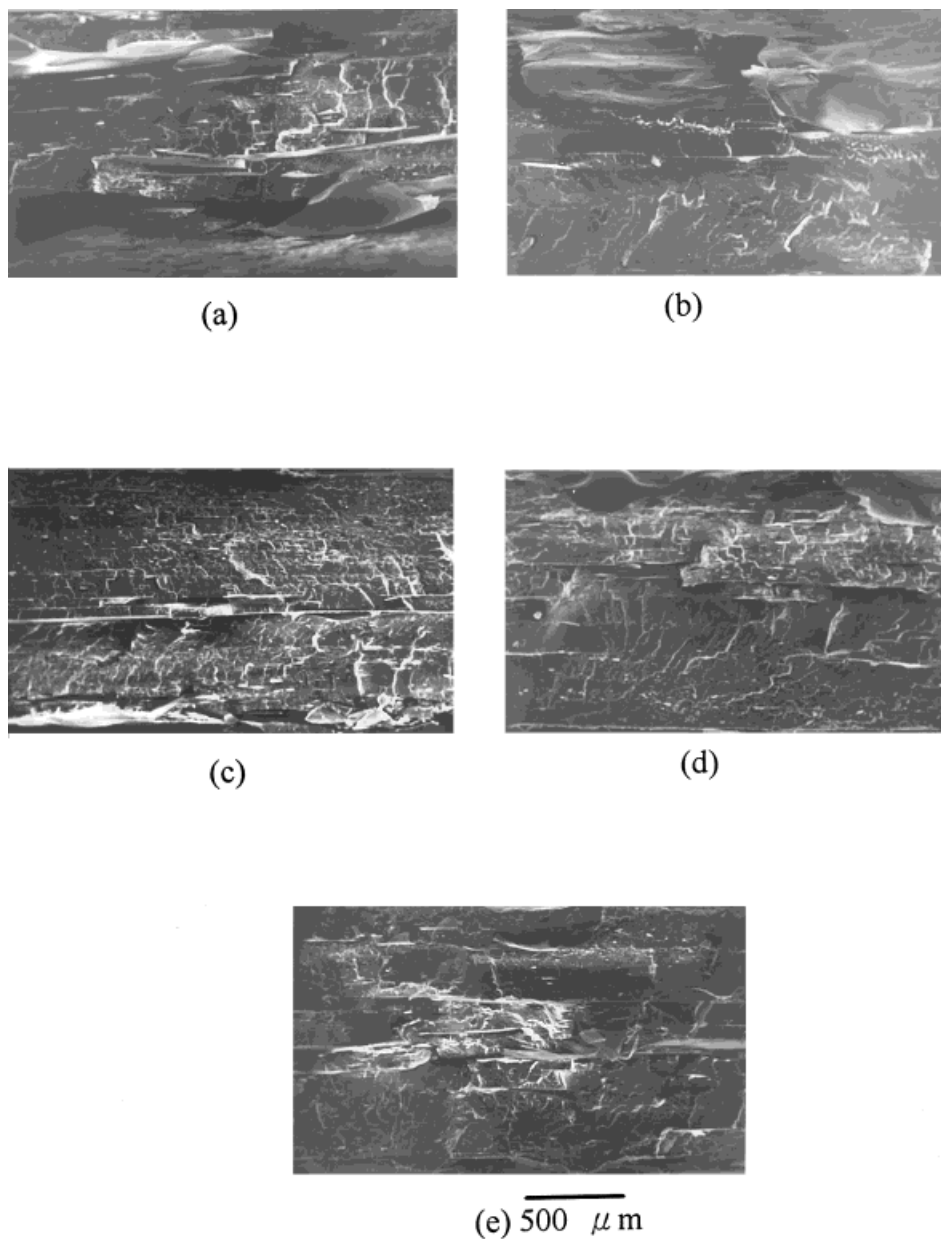


Figure 1 Morphologies of bottles blow-molded from (a) PE-PA1 (b) PE-PA2, (c) PE-PA3, (d) PE-PA4, and (e) PE-PA5 blends (weight ratio of PE to PA is 90 : 10).

reactivity between amide-terminal amine groups of PA and carboxyl groups of CP is very high. In addition, soluble fraction of MPAs in formic acid solution increased consistently with decreasing melt indices of their corresponding PAs. As reported by Serpe et al.,¹⁷ 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, and the insoluble fraction to consist of unreacted pure

CP or long CP sequences with shorter grafted PA chains since CP is insoluble in formic acid solution. Based on the above premises, it is reasonable to suggest that the possibility of formation of long PA sequences with shorter grafted CP chains will be higher with increasing lengths of PA molecules; hence, higher soluble fractions of MPAs in formic acid solution were found when MPAs were prepared from PAs of lower melt indices.

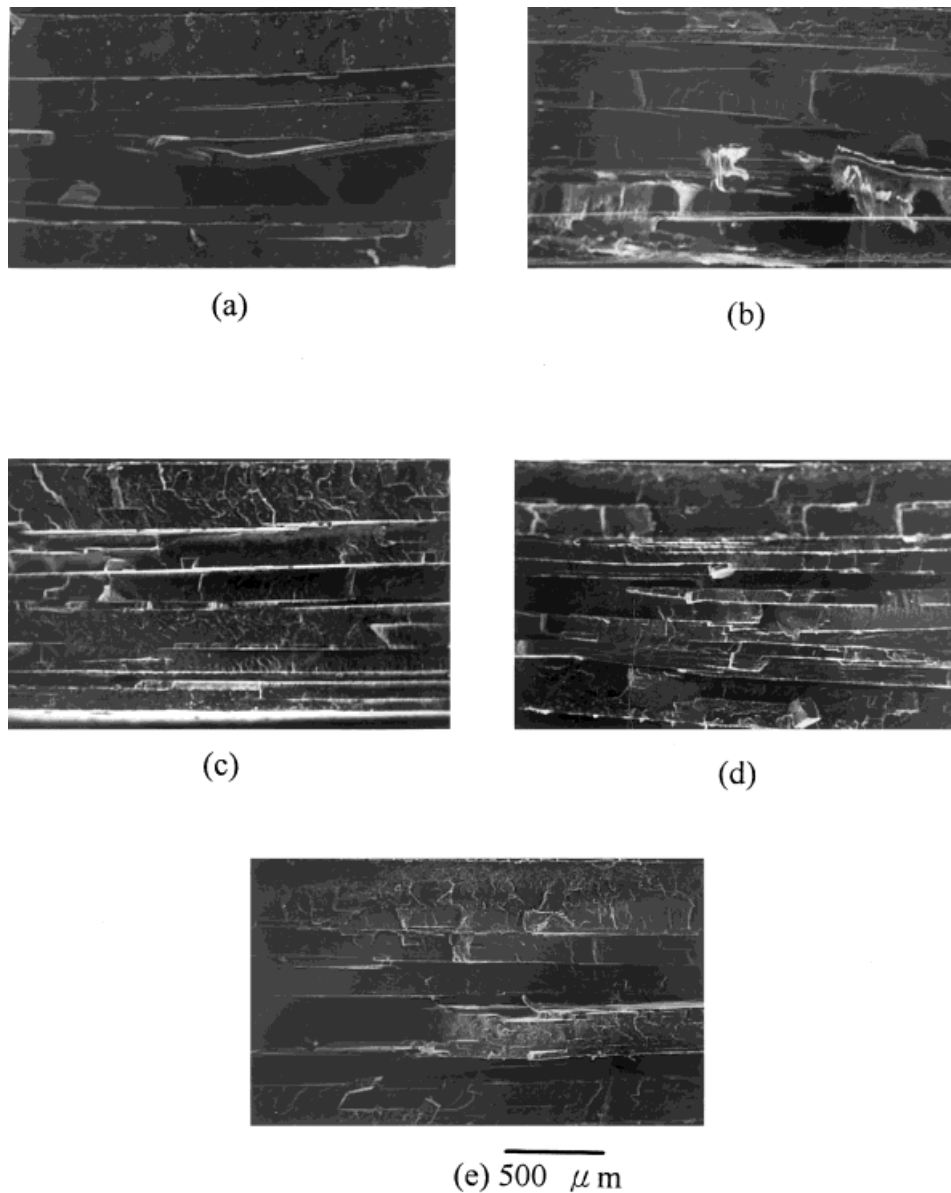


Figure 2 Morphologies of bottles blow-molded from (a) PE-MPA1, (b) PE-MPA2, (c) PE-MPA3, (d) PE-MPA4, and (e) PE-MPA5 blends (weight ratio of PE to MPA is 90 : 10).

Rheological Properties and Crystallinity of PE, PAs, CP, and MPAs

The melt indices (MI) and melt shear viscosities (η_s) of PE, PAs, CP, and MPAs and viscosity ratios (VR) of PAs and MPAs to PE are summarized in Table III. As expected, the melt shear viscosities of PAs and MPAs increased with decreasing melt index. On the other hand, it is worth noting that η_s of MPAs are significantly higher than those of their corresponding PAs. The underlying

mechanisms accounting for these behaviors are not completely clear. Presumably, η_s of the CP-grafted PA copolymers can be higher than those of CP and PAs since the structure of CP-grafted PA copolymer can be quite huge and more complex than those of CP and PAs. For instance, short CP chains may be dispersed into PA matrix and reacted with PA molecules as the huge crosslinked CP-PA copolymers in the PA matrix. In addition, the dimension and shear viscosities of crosslinked CP-PA copolymers can be made

Table IV Barrier and Impact Properties of Hot Pressed PE, PA, and MPA Sheets

Properties	PE	PA ₁	PA ₂	PA ₃	PA ₄	PA ₅	MPA ₁	MPA ₂	MPA ₃	MPA ₄	MPA ₅
Permeability (g day)	1.83	0.11	0.102	0.098	0.095	0.086	0.058	0.044	0.039	0.033	0.032
Barrier improvement	1	16.7	17.8	18.5	19.2	21.3	31.5	41.6	46.9	55.4	57.2
Barrier index	0	0.94	0.94	0.95	0.95	0.95	0.97	0.98	0.98	0.98	0.980
Total impact energy (J)	4.97	15.79	16.00	16.7	17.11	18.04	8.61	9.26	9.84	10.65	11.48

larger by increasing CP-PA copolymers and can also be made larger by increasing the lengths of the PA molecules. Therefore, the shear viscosities of MPAs were significantly higher than those of their corresponding PAs and increased consistently with decreasing melt indices of PAs.

The degrees of crystallinity (W_c) of PE, CP, PAs, and MPAs are summarized in Table III. As expected, W_c of PE is higher than those of PAs which are associated with W_c higher than that of CP. Regardless of the various melt indices of PAs and MPAs, W_c of PAs and MPAs remained approximately the same within the series. However, it is interesting to note that the W_c of MPAs (ca. 28%) are significantly low than those of their corresponding PAs (ca. 41%). This decrease in W_c can be caused mainly by the reduced amounts present in MPAs, as CP is a less-crystallizable component. In addition, the possible formation of CP-grafted PA copolymers during the preparation of MPAs may also reduce the W_c of MPAs.

Morphology of Blow-Molding Bottles of PE-PA and PE-MPA Blends

The fracture surface of the blow-molded bottles of PE-PA blends exhibit a marbilized surface when prepared from PAs with various melt shear viscosities [see Figs. 1(a) and 1(e)]. Only obscure, broken laminar structures were found across the wall thickness direction of PE-PA bottles. In contrast, the fracture surfaces of the blow-molded bottles prepared from mixtures of various MPAs and PE exhibited clear MPA laminas across the wall thickness direction of the bottles [see Figs. 2(a)-(e)]. These laminar structures of MPAs are essentially two-dimensional, continuous, long, thin, and layered platelets. However, these MPA laminar structures became less clear as the viscosity ratio of MPA to PE was significantly larger than one [see Fig. 2(e)]. It is recognized that poly-

mer melts of high shear viscosities exhibit high melt strength during processing. As mentioned previously, the melt shear viscosities of MPAs are significantly larger than their corresponding PAs, and the interfacial adhesion between MPA and PE is better than that between PA and PE. Only obscure laminar structures of PAs were therefore observed on fracture surfaces of PE-PA bottles. In contrast, MPAs with higher shear viscosities and good adhesion to PE were drawn as more demarcated long laminar structures without lack of adhesion to PE or being drawn apart by PE of relatively high η during the blow-molding process. However, this drawing of MPAs into demarcated laminar structures becomes difficult as the melt shear viscosities of MPAs are significantly larger than that of PE, at which PE melt is too soft to draw the hard MPA melt, even though they adhere quite well to PE during the blow-molding process. As a consequence, the MPA5 laminar structures are less clear than the other MPA laminar structures shown on the fracture surfaces of PE-MPA bottles.

Barrier Properties of PE, PA, and MPA Sheets

The barrier properties of hot-pressed sheets of PE, various PAs, and MPAs are summarized in Table IV. As expected, all PAs exhibited better barrier properties than pure PE. 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 penetrating primarily 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 property. On the other hand, the presence of polar amide, terminal amine groups, and intermolecular hydrogen bonding in PA can barely allow nonpolar xylene mole-

Table V Barrier and Impact Properties of Blow-Molded Bottles of Pure PE, PE-PA, and PE-MPA Blends

Properties	PE	PE-PA1	PE-PA2	PE-PA3	PE-PA4	PE-PA5	PE-MPA1	PE-MPA2	PE-MPA3	PE-MPA4	PE-MPA5
Permeability (g day)	10.80	3.35	1.95	1.71	1.49	1.92	0.46	0.22	0.14	0.11	0.33
Barrier improvement	1	3.2	5.5	6.3	7.2	5.6	23.5	48.7	77.1	98.2	32.7
Barrier index	0	0.69	0.82	0.84	0.86	0.82	0.96	0.98	0.99	0.99	0.97
Total impact energy (J)	3.56	1.14	1.33	2.61	2.84	3.01	4.89	5.15	5.45	6.02	5.37

cules to enter into and permeate through the amorphous regions of PA as compared to the amorphous regions of nonpolar PE molecules. As a consequence, PA exhibits better barrier properties of nonpolar xylene than PE, although the percentage of crystallinity of PE is higher than that of PA. In contrast, CP-modified polyamides (MPAs) exhibited even better barrier properties than those of pure PAs (see Table IV). Similar results were found in our previous investigations.^{12,13} This improved barrier property of MPA was attributed to the possible formation of the cross-linked structure of CP-PA copolymers during reactive extrusion, which can significantly reduce the free volume of MPA and prohibit xylene molecules from entering into and permeating through the amorphous region of MPA. On the other hand, the barrier improvements of MPAs and PAs increased consistently with the decreasing melt indices of their corresponding PAs. For instance, the barrier improvements of MPAs increased from 31.5 to 57.2 as the melt indices of their corresponding PAs reduced from 29.1 to 1.5 g/10 min, respectively (see Table IV). The underlying mechanisms accounting for the above behaviors are not completely clear. However, it is generally accepted that free volume reduces with increasing molecular weight (i.e., decreasing melt index) of polymers. In addition, the degrees of crystallinity of PAs and MPAs remain approximately the same regardless of varying melt indices of their corresponding PAs. Based on these premises, it is reasonable to suggest that the improved barrier properties of PAs and MPAs with decreasing melt indices are attributable to the decrease in free volume of PAs and MPAs, which prohibits xylene molecules from entering into and permeating through the amorphous regions of PAs and MPAs.

Barrier Properties of Blow-Molded Bottles of PE, PE-PA, and PE-MPA Blends

The barrier properties of blow-molded bottles of the mixtures of 90% PE and 10% various PAs or MPAs are summarized in Table V, which performed better than those of pure PE bottles. It is interesting to note that the barrier improvements of blow-molded bottles of PE-PA mixtures are in an order of magnitude lower than those of bottles blow-molded from their corresponding PE-MPA mixtures. Except for PE-MPA5 bottles, it is interesting to note that the order of barrier improvement of these PE-MPA bottles approximately corresponded to the order of barrier improvement

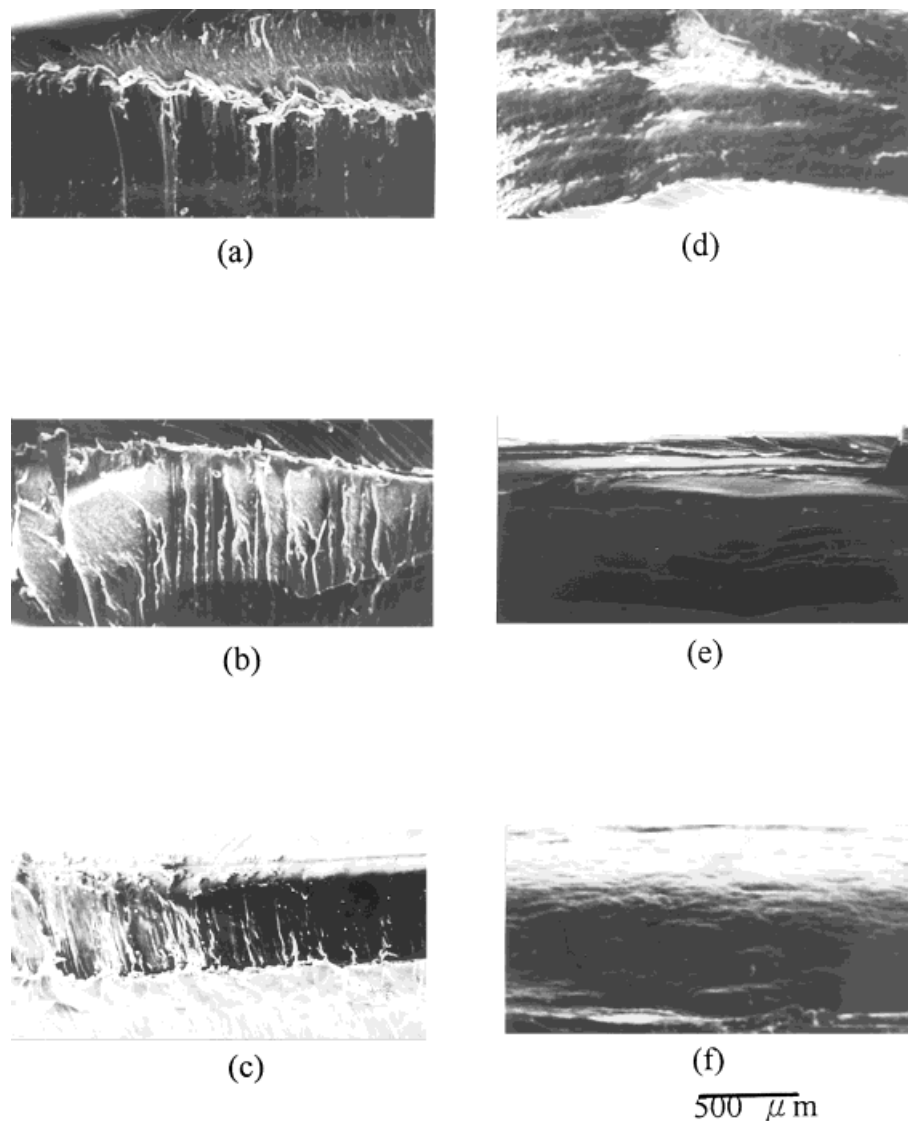


Figure 3 The fracture surfaces of (a) PA1, (b) PA3, (c) PA5, (d) MPA1, (e) MPA3, and (f) MPA5 sheets after impact testing.

of pure MPA before blending with PE. On the other hand, it is surprising to find that PE-MPA5 bottles exhibited smaller barrier improvement than PE-MPA2, PE-MPA3, and PE-MPA4 bottles (see Table V), although the original MPA5 exhibited the best barrier properties of all MPAs. As mentioned previously, PE-MPA5 bottles exhibited the least clear MPA laminar structures among all PE-MPA bottles because the melt shear viscosity of MPA5 was significantly larger than that of PE. This made PE melt too soft to draw hard MPA5 melt into clear laminar structures during the blow-molding process. These results clearly suggested that CP modified PA and made its barrier property better than PA, and that

the level of barrier improvement of PE-MPA blends depended significantly on the barrier property of the MPA prepared. In addition to the barrier properties of MPA itself, demarcated laminar structure of MPA is another key factor controlling the barrier properties of PE-MPA bottles. However, this demarcated laminar structure of MPA cannot be obtained as the melt shear viscosity of MPA is significantly higher than that of PE.

Impact Properties of PE, PAs, MPAs, PE-PA, and PE-MPA Sheets

As shown in Table IV, the total impact energy (E_t) of PA sheets improved slightly with decreas-

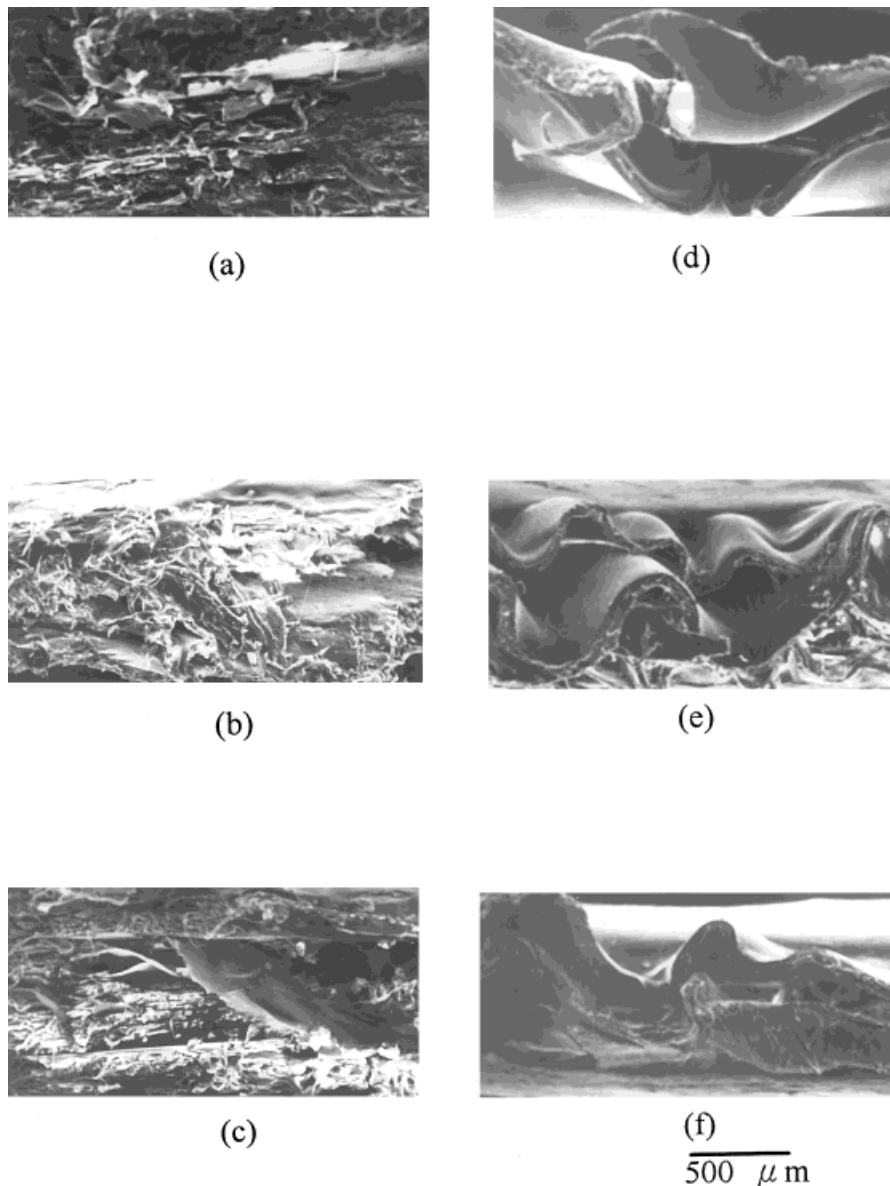


Figure 4 The fracture surfaces of bottles blow-molded from (a) PE-PA1, (b) PE-PA3, (c) PE-PA5, (d) PE-MPA1, (e) PE-MPA3, and (f) PE-MPA5 blends after impact testing.

ing melt indices and was significantly better than that of PE. Similarly, E_t of MPAs improved slightly with decreasing melt indices of their corresponding PAs, whereas the CP modified polyamides exhibited a much lower E_t than their corresponding PAs (see Table IV). The fracture surfaces of PA and MPA sheets are shown in Figure 3. The fibrils observed on fracture remnants of MPAs were considerably less drawn than those of their corresponding PAs, which indicated a more brittle type of fracture behavior. It is not completely clear what accounts for this interesting

behavior. However, formation of the crosslinked structure of CP-PA copolymers during reactive extrusion cannot only reduce the free volume but also restrict the deformation of MPAs during impact testing. It is therefore a more brittle type of fracture surface, and a much lower E_t was found for MPA sheets. The total impact energies of PE-PA and PE-MPA sheets are summarized in Table V. It is interesting to note that PE-MPA sheets exhibited significantly higher values of E_t than their corresponding PE-PA sheets, although each PA was associated with a higher E_t than its corre-

sponding MPA. Further investigation showed less drawn fibrils on the interfaces between PE and PAs than those between PE and MPAs (see Fig. 4), indicating that the adhesion and compatibility between PE and MPAs during the blow-molding was better than that between PE and PAs. Therefore, PE-MPA sheets performed better E_t than PE-PA sheets.

CONCLUSION

Compatibilizer precursor modification of PAs made their barrier properties better than PAs, and the level of barrier improvement of PAs and MPAs increased consistently with decreasing melt indices of their corresponding PAs. These significantly improved barrier properties of PAs and MPAs with decreasing melt indices of PAs could be attributed to the decrease in free volume of PAs and MPAs, which prohibits xylene molecules from entering and permeating through the amorphous regions of PAs and MPAs. Total impact energies of MPAs and PAs also improved with decreasing melt indices of PAs; however, MPAs exhibited lower values of E_t than their corresponding PAs. The results of morphology and barrier properties of PE-PA and PE-MPA bottles suggest that the level of barrier improvement of PE-MPA bottles depends significantly on the barrier properties of the MPAs prepared. Further investigation on the morphology of PE-PA and PE-MPA bottles suggested that the demarcated laminar structure of MPA is another key factor controlling the barrier properties of PE-MPA. However, bottles cannot be obtained, as the melt shear viscosities of MPAs are significantly higher than that of PE; so the PE melt becomes too soft to draw hard MPA melt into clear laminar structures during the blow-molding process. Finally, it is interesting to note that PE-MPA sheets exhibited significantly higher values of E_t than the corresponding PE-PA sheets, although each PA was associated with a higher E_t than its corresponding MPA. This behavior is attributed mainly to better adhesion and compatibility between PE and MPAs than those between PE and PAs during the blow-molding process.

NOMENCLATURE

CP	compatibilizer precursor
MI	melt index
MPA	modified polyamide
NCC	normalized contents of carboxyl groups per backbone chain of CP
NGE	normalized grafting efficiency
PA	polyamide 6
PE	polyethylene
VR	melt viscosity ratio of MPA to PE
W_c	degrees of crystallinity
η	melt shear viscosity

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