Effects of compatibilizer precursors on the barrier properties and morphology of polyethylene/polyamide blends

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Summary

A systematic investigation on the effects of type of compatibilizer precursors (CP) upon the barrier properties and morphology of PE/PA blends was reported. Three alkyl carboxyl-substituted polyolefins were selected to modify PA in a twin screw extruder by "reactive extrusion" process. The barrier property of the modified PA (MPA) was better than pure PA, and the amount of barrier improvement of the blend of PE and MPA depended significantly on the barrier property of the MPA prepared. The extent of mixing PE and MPA before blow-molding has a significant effect on its corresponding barrier properties. Further analysis of the fracture surfaces indicated that a more demarcated laminar structure of MPA dispersed in PE matrix is essential for better barrier properties of PE/MPA blends. It is not completely clear how the type of CP added affects the barrier properties of MPAs. However, it is suggested that long PA sequence with shorter grafted CP chain and high normalized grafting efficiency of MPA are essential for preparing a clear laminar structure of MPA, and a good barrier properties of PE/MPA blends.

Introduction

Polyethylene (PE) is one of the most prevailing and suitable materials for packaging various liquids, because of its easy processing, good resistance to moisture permeation, excellent chemical inertness, low temperature flexibility. However, organic liquids such as hydrocarbons and chlorinated solvents have high permeability through PE. In contrast to PE, polyamide (PA) is known for its outstanding barrier properties of hydrocarbons and very often used as a complementary component in the packaging industry. However, PA and PE polymers are immiscible, compatibilizer precursors (CPs) such as carboxylated polyethylenes were often used to improve the interfacial properties of PE

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and PA resins. In fact, it has been reported that the hydrocarbon permeability and mechanical properties of PE/PA blends improved significantly by the addition of CPs as compatibilizer[1-3]. Further investigation indicated that the barrier properties of PE/PA/CP blends depend strongly on the way of blending and on their corresponding morphology. Subramanian P. M.[4-7] and Diluccio R. C. [8] disclosed heterogeneous laminar PA dispersed in a PE matrix, containing a compatibilizer, which has very good hydrocarbon barrier properties than those of homogeneous blends associated with finely dispersed PA in PE. The heterogeneous blends of PE/PA/CP system were prepared by melt processing the three components under carefully controlled conditions, wherein the compatibilizer is believed to be present between the laminars and adhere them together. However, as far as we know, no further detailed investigation was reported on how PA was modified with different types of CPs and how these modified PA (MPA) affect its subsequent morphology and barrier properties of PE/MPA blends. A systematic study on the barrier properties of MPAs prepared from different CPs and its subsequent barrier properties and morphology of PE/MPA blends were reported in this study.

Experimental
Materials
The densities and melt indexes of the polyethylene (PE), polyamide (PA) and compatibilizer precursors (CPs) used in this study were summarized in Table 1, wherein PA is a blend of 75% polyamide 6 (PA6) and 25% semi-aromatic polyamide (SAPA), CPa is a 40% zinc neutralized ethylene/acrylic acid (89/11) copolymer, CPb is a high density polyethylene grafted with 0.4% of maleic anhydride, and CPc is a 70% zinc neutralized ethylene/methylacrylic acid (96/4) copolymer. These properties were cited from their commercial catalogues. The antioxidant with a trade name of Irganox B225 was obtained from Ciba-Geigy.

Sample preparation
Before blending, all CPs and PA were dried at 60°C for 8 hrs and 80°C for 16 hrs, respectively. The dried components of 80% PA / 20% CP and 1500 ppm of antioxidant were first dry-blended thoroughly and then fed in a twin screw extruder. The extruder was operated at 215°C in the feeding zone and at 240°C towards the extrusion die, and at a screw speed of 1000 rpm. The CP modified polyamide (MPA) 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 hrs before mixing with PE. Various weight ratio of mixtures of PE and MPAs were blow-molded by a blow molding machine,

Table 1. Melt indexes and densities of PE, PA and CPs.

Properties	PE	PA		CP		
		PA6	SAPA	CPa	CPb	CPc
Melt index (g/10min)[1]	0.27	8.8	32.3	0.8	0.6	5.0
Density (g/cm^3)	0.944	1.13	1.19	0.96	0.95	0.94

[1]: 190°C and 2.16kg for PE and CPs, 240°C and 2.16kg for PA.

operated at an extrusion temperature of 220°C and a screw speed of 100 rpm. The blow-molded bottles weigh about 100 grams and have a capacity of about 1 liter with a wall thickness of about 1mm. In contrast to the above samples, other samples were prepared by pre-blending the above mixtures of PE and MPAs in a twin screw extruder before feeding into the blow molding machine. These samples will be referred to as the samples of "homogeneous 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 grams 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 basic barrier properties of pure PE, PA and MPA were determined based on their hot-pressed sheets, because it is well known that pure PA and various MPAs were difficult to be processed by blow-molding. 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 a test flask 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°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 barrier index is calculated as one minus the inverse value of barrier improvement. Both the properites of barrier improvement and barrier index were calculated to compare the barrier properites of all samples.

Morphology

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).

Normalized grafting efficiency (NGE) of MPAs

The possible formation of CP-grafted-PA copolymers through the reaction of carboxyl groups of these CPs with the terminal amine groups of PA during the preparation of MPA, were characterized by using the techniques of "solvent extraction" and Fourier Transform Infrared (FTIR) method[9]. Five grams of each MPA sample was suspended in 100 ml of formic acid at 80°C for 2 hrs. 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 0.1mm were then used for FTIR analysis. The carboxyl groups of CPs and MPAs were indentified by the presence of $\delta(C=O)$ 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 :

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

.... (1)

The normalized contents of carboxyl groups of MPA were then calculated by equation (2)

$$NCC_{(MPA)} = \text{weight percent}_{(\text{soluble fraction})} \times NCC_{(\text{soluble fraction})} +$$
$$\text{weight percent}_{(\text{insoluble fraction})} \times NCC_{(\text{insoluble fraction})} \quad \dots\dots\dots\dots\dots (2)$$

The normalized grafting efficiency (NGE) of CP on PA in each MPA was then estimated according to equation (3).

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

Results and Discussion

Barrier properties of MPA, PE, PA sheets and blow-molded bottles of PE/MPA blends

As shown in Table 2, all MPAs exhibited good barrier properties than that of pure PE, wherein MPAa performed the best, MPAc the second, and MPAb the worst. In fact, it is worth noting that the barrier properties of the MPAs are even better than that of pure PA. The barrier properties of the blow-molded bottles of the mixtures of 90% PE and 10% various MPAs were summarized in Table 3, which performed better than those of pure PE sample (i.e. C1) and sample prepared from the mixture of 90% PE and 10 % unmodified PA (i.e. C2). In addition, it is interesting to note that the order of barrier improvement of these samples is approximately corresponding to the order of barrier improvement of pure MPA before blending with PE. These results clearly suggested that CP modified PA and made its barrier property better than pure PA, and the amount of barrier improvement of the blend of PE and MPA depended significantly on the barrier property of the MPA prepared. Further investigation indicated that the amounts of MPA mixed with PE had a significant effect on their barrier properties. As shown in Table 4, the barrier property of the PE/MPA blend increased with increasing the content of MPA. These barrier properties are much better than those blow-molded from "homogeneous blends" of the same composition (i.e. samples 2-3H and 2-5H), where PE and MPA were pre-blended in a twin screw extruder rather than dry blending before blow-molding. These results clearly suggest that the extent of mixing PE and MPA before blow-molding has a significant effect on its corresponding barrier properties. However, it is not completely clear what is the underlying mechanism accounting for this difference.

Morphology of blow-molded bottles

The fracture surfaces of the blow-molded bottles of samples prepared from the mixture of 90% PE and 10% pure PA exhibited "marblized structures". (see Fig. 1a) In contrast, after adding CPs, the fracture surfaces of the blow-molded samples of 90% PE and 10%

Table 2. Barrier properties of hot-pressed MPA, PA and PE sheets

	MPA			PA	PE
	MPAa	MPAb	MPAc		
Permeability(g/day)	0.036	0.071	0.057	0.10	1.90
Barrier Improvement	52.8	26.8	33.3	19.0	1.0
Barrier Index	0.981	0.963	0.970	0.947	0

Table 3. Barrier properties of blow-molded bottles of pure PE and PE/MPA mixtures.

Samples	C1	C2	1	2	3
Composition(wt%)					
PE	100	90	90	90	90
PA		10			
MPA	0				
MPAa(PA/CPa=90/10)			10		
MPAb(PA/CPb=90/10)				10	
MPAc(PA/CPc=90/10)					10
Permeability(g/day)	9.82	8.09	1.23	5.73	4.94
Barrier improvement	1.0	1.2	8.0	1.7	2.0
Barrier Index	0	0.176	0.875	0.416	0.497

Table 4. Effect of the content of MPAb upon the barrier properties of blow-molded bottles of PE/MPAb mixtures and blends

Samples	C1	2-1	2	2-2	2-3	2-3H	2-4	2-5	2-5H	MPAb Sheet
Composition(wt%)										
PE	100	95	90	85	80	80	75	70	70	0
MPAb	0	5	10	15	20	20	25	30	30	100
Permeability(g/day)	9.82	7.99	5.73	4.09	2.80	4.11	1.39	0.90	3.17	0.071
Barrier Improvement	1.0	1.2	1.7	2.4	3.5	2.4	7.1	10.9	3.1	26.8
Barrier Index	0	0.186	0.416	0.583	0.715	0.581	0.858	0.908	0.677	0.963

various MPAs exhibited MPA laminars distributed across the wall thickness direction of the bottles as essentially two dimensional, discontinuous, multiple, thin and overlapping layered platelets. In fact, it is worth noting that MPA samples exhibited more clearly laminar structures for samples associated with better barrier properties. (see Table 2 and Fig. 1) The laminar structures of MPA became clearer as the content of MPA increased. The typical fracture surfaces of the blow-molded bottles prepared from the PE/MPAb mixtures with increasing contents of MPAb were shown in Fig. 2. However, the laminar structure of MPA can not be clearly observed if PE and MPAb are pre-blebded in a twin screw extruder before blow molding (see Fig. 3). These results suggested that a more demarcated laminar structure of MPA dispersed in PE matrix is essential for better barrier properites of PE/MPA blow-molded blends, and the type of MPA and the extent of mixing of MPA and PE before blow-molding have a significant effect on the morphology of MPA/PE blow-molded blends.

Normalized grafting efficiency of MPAs and contents of normalized contents of carboxyl groups of CPs, soluble and insoluble fractions of MPAs

It is interesting to note that sample MPAa with a higher normalized grafting efficiency (NGE) (0.937) exhibited better barrier properties than that of sample MPAc of lower NGE (0.626) (see Tables 2 and 5). However, sample MPAb with 22% insoluble fraction in formic acid solution exhibited a poor barrier property than those of samples MPAa and MPAc with approximate 100% soluble fraction, although sample MPAb was
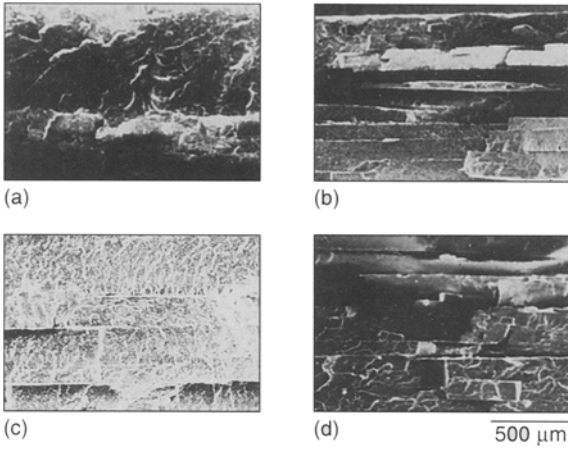
Fig. 1. Fracture surfaces of the blow-molded bottles of samples with a composition of 90% PE and 10% (a) PA, (b) MPAa, (c) MPAb, (d) MPAc.
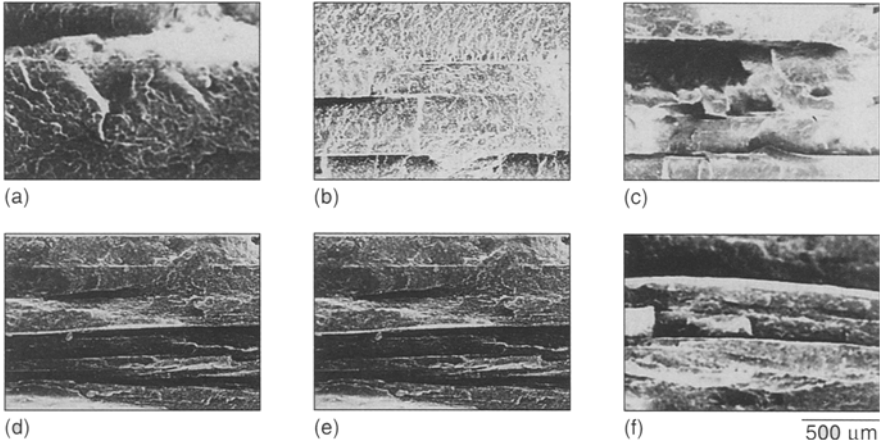

Fig. 2. Fracture surfaces of the blow-molded bottles of samples prepared from the blends of PE and (a) 5%, (b) 10%, (c) 15%, (d) 20%, (e) 25%, (f) 30% MPAb.

Fig. 3. Fracture surfaces of the blow-molded bottles of PE/MPAb samples pre-blended in a twin screw extruder before blow-molding with (a) 10%, (b) 20%, (c) 30% of MPAb.

associated with a high NGE of 0.923. As reported by Serpe et al[9], 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 consists of pure CPs or long CP sequences with shorter grafted PA chains, since the CPs are insoluble in formic acid solution. As indicated in Tables 1 and 5, CPb is associated with the lowest melt index than those of CPa and CPc, and the normalized contents of carboxyl groups (NCC) of MPAb in the insoluble fraction is significantly lower than that of pure CPb (see Table 5). These results suggested that CPb was associated with more long CP chains than those of CPa and CPc, and most of these long CPb sequences grafted with shorter PA chains during reactive extrusion of MPAb. In contrast, most of the CPa and CPc chains were possibly grafted with long PA sequences during the preparation of MPAa and MPAc, which was dissolved in formic acid solution during "solvent extraction". It is not completely clear how these CP/PA copolymers improve the barrier properties of MPAs over those of pure PA. Presumably, the possible formation of CP/PA copolymers through the reaction of carboxyl groups of these CPs with the terminal amine groups of PA was suggested to be responsible for this improvement, since it has been reported that the free amine and amide groups of PA are susceptible to water[10] and tend to reduce its corresponding barrier properties[11]. It is, therefore, sample MPAa with a higher grafting efficiency exhibited a better barrier properties than that of sample MPAc. However, the barrier properties of MPA depend not only on grafting efficiency of CP but also on how these CPs copolymerized with PA. For instance, long PA sequences with shorter grafted CP chains may be well dispersed in the amorphous region of PA matrix during crystallization of PA, and significantly improve the barrier properties of PA than those improved by long CP sequences with shorter grafted PA chains, because these copolymers may be immiscible and become phase-separated with the PA matrix.

It is reasonable to believe that the barrier properties of samples of PE/MPA blends improve with the barrier properties of MPAs prepared. In addition to the type of MPA prepared, however, the interfacial interaction between PE and MPA should also have a significant effect on the barrier properties and morphology of PE/MPA blends. As suggested by several authors[12-15], CP/PA copolymers can act as compatibilizer or interfacial agent and improve the interfacial properties on the boundary of PE and PA. As mentioned previously, PE/MPA samples of better barrier properties are associated with more clear laminar structures of MPA. Based on these premises, it is reasonable to suggest that long PA sequence with shorter grafted CP chain and high NGE of MPA are

Table 5. The normalized grafting efficiency of MPAs and normalized contents of carboxyl groups of CPs, soluble and insoluble fraction of MPAs.

	NCC in soluble fraction	Soluble Fraction (%)	NCC in insoluble fraction	Insoluble Fraction (%)	NCC of MPA	NCC of Pure CP	normalized grafting efficiency
MPAa	5.27×10^{-4}	99.6	6.12×10^{-4}	0.4	5.27×10^{-4}	8.35×10^{-3}	0.937
MPAb	3.26×10^{-3}	78.0	7.29×10^{-4}	22.0	2.70×10^{-3}	3.50×10^{-2}	0.923
MPAc	3.35×10^{-3}	90.2	-	0.8	3.32×10^{-3}	8.89×10^{-3}	0.626

essential for preparing a clear laminar structure of MPA, which is beneficial to the barrier properties of PE/MPA blends. However, these laminar structures can become invisible if the extent of mixing between PE and MPA become too vigorous, because MPA may be too well dispersed to retain the laminar structure under this condition.

Conclusion

Compatibilizer precursors modified PA and made its barrier property better than pure PA, and the amount of barrier improvement of the blend of PE and MPA depended significantly on the barrier property of the MPA prepared. The extent of mixing PE and MPA before blow-molding has a significant effect on its corresponding barrier properties. Further analysis of the fracture surfaces indicated that a more demarcated laminar structure of MPA dispersed in PE matrix is essential for better barrier properties of PE/MPA blends. It is not completely clear how the type of CP added affects the barrier properties of MPAs. However, it is suggested that long PA sequence with shorter grafted CP chain and high normalized grafting efficiency of MPA are essential for preparing a clear laminar structure of MPA, and a good barrier properties of PE/MPA blends.

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