Oxygen Barrier Properties of Polypropylene/Polyamide 6 Blends

R. M. HOLSTI-MIETTINEN,* K. P. PERTTILÄ, J. V. SEPPÄLÄ, and M. T. HEINO

Helsinki University of Technology, Department of Chemical Engineering, Kemistintie 1, FIN-02150 Espoo, Finland

SYNOPSIS

Effects of composition, compatibilization, and blending procedure on oxygen barrier properties of injection-molded polypropylene/polyamide 6 blends were investigated. The main attention was paid to the relationships between oxygen permeability, mechanical properties, and blend morphology. The effect of the polypropylene/polyamide 6 ratio was evident in blends with a homogeneous dispersion type of morphology. After the phase inversion, when polyamide became the continuous phase, the barrier properties of the blends were significantly improved and approached those of polyamide 6. Increasing the amount of the compatibilizer, maleic anhydride grafted polypropylene, was found to increase the permeability of the blend. The blending procedure had a significant effect on the permeability of the blends. The injection-molded blend exhibited a laminar type of morphology when polyamide 6 and the compatibilizer were preblended in a twin-screw extruder, and polypropylene was added later as a dry-blend before injection molding. The dispersed polyamide phase formed thin elongated platelets in the polypropylene matrix. This laminar morphology resulted in significant improvement of oxygen barrier properties approaching the level of the theoretical values calculated for corresponding coextruded structures. Moreover, both the tensile and impact properties of this particular blend were exceptionally good. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Good oxygen barrier properties are vital in many packaging applications as a means of achieving a long shelf life for the product. Polymers have many advantages in packaging including strength, transparency, flexibility, and heat sealability. However, many of them also have limited or specific barrier properties. A polymer with good oxygen barrier properties may show poor water barrier properties, and vice versa. Such problems can sometimes be avoided by coextrusion. The permeability of a coextruded structure can be calculated from the following equation:

$$1/P_c = \Sigma(\phi_i/P_i) \qquad (1)$$

where P_c is the permeability of the composite, ϕ_i the

volume fraction of the component i, and P_i the permeability of the individual layer i.[1]

The permeability of a polymer depends on many internal factors, such as the interchain forces of polymer molecules, crystallinity, and orientation. Many external factors, including nature of the penetrant, temperature, and moisture, also affect the permeability.[2-4] Our particular concern in this work was oxygen permeability, which is reduced by strong intermolecular forces in a polymer. Chemical groups that lead to such high attractive forces include esters, amides, hydroxyls, and cyano groups. Thus, examples of polymers that are good barriers against oxygen are ethylene–vinyl alcohol copolymer, polyethylene terephthalate, polyvinylchloride, and polyamide 6.

Blends of polyolefins with polyamides have been of interest to many research groups.[5-9] The primary target of the research and development of polypropylene/polyamide blends has been to improve the thermal and mechanical properties of polypropylenes. However, if polyamides (PA) are added to

---

polypropylenes (PP), in addition to the improvement of mechanical properties, also some functional properties like paintability or barrier properties may be improved as well.

Polyolefins exhibit excellent moisture barrier properties but poor oxygen barrier properties. Although polyamides, in turn, normally have good oxygen barrier properties, water acts as a plasticiser, weakening the strong interchain forces so that, in the presence of moisture, oxygen molecules can more easily penetrate through them.

In polymer blends, the barrier properties are strongly dependent on morphology. In most immiscible polymer blends the morphology is more or less homogeneous, with the second polymer dispersed as spherical particles in the matrix polymer. In this case, the incorporation of the dispersed polymer does not significantly change the barrier properties of the matrix polymer. The permeability of a homogeneous polymer blend has been expressed by Barrer et al.[1] as

$$P_c/P_m = \phi_m/\tau \tag{2}$$

where P_m is the permeability of the matrix, ϕ_m the volume fraction of the matrix, and τ the tortuosity, which can be approximated from the volume fraction of the dispersed phase (ϕ_d) as

$$\tau = 1 + \phi_d/2 \tag{3}$$

Subramanian et al.[10,11] report that blends with nonuniform heterogeneous dispersion of a condensation polymer in a polyolefin matrix show improved solvent barrier properties. The solvents they tested were xylene and mixtures of aliphatic and aromatic hydrocarbons. The permeability of the blends approached that of the coextruded structures. The preferred laminar morphology was observed in blow-molded containers.

The object of our work was to study how oxygen barrier properties depend on the composition and on the blending procedure in polypropylene/polyamide 6 blends. The efficiency of mixing during the extrusion was varied. Injection-molded test specimens were used for the evaluation of mechanical properties. Because polypropylene/polyamide blends always require a compatibilizer for bridging the dissimilar polymers and stabilization of the morphology, the effect of a compatibilizer on oxygen permeability was investigated as well. Barrier properties of the blends were compared with those calculated for corresponding coextruded structures.

The relationship between the observed morphology and permeability properties is discussed.

EXPERIMENTAL

Materials

The polypropylene used in the experiments was an isotactic homopolymer VC12 33B, supplied by Borealis Polymers. It is an injection molding grade with density 0.900 kg/dm³ and melt flow index 12 (230°C, 2.16 kg). The polyamide 6 was Ultramid B3 S produced by BASF, which is also an injection molding grade, with density 1.13 kg/dm³. Maleic anhydride grafted polypropylene, Exxelor PO X1 1015, from Exxon Chemicals, was used as the compatibilizer. The amount of the grafted maleic anhydride was 0.4 wt %. The density of the polymer was 0.910 kg/dm³, and the melt flow index 120 (230°C, 2.16 kg).

Blends and Mixing

Before processing, polyamide 6 was predried overnight at 80°C in a dehumidifying dryer. The materials were dry mixed before melt blending in a Bergstorff ZE 25x33D corotating twin-screw extruder at an average melt temperature of 245°C. The screw rotating speed was 200 rpm. The screw configuration was especially designed for reactive blending.

In a first series of tests, the effect of the composition was studied by changing the PP/PA ratio from 100/0 to 0/100. The compatibilizer content was kept constant at 10 wt % of the amount of polyamide 6. Because the compatibilizer was a modified polypropylene, the amount of PP was reduced by the amount of compatibilizer. All materials were dry mixed and melt blended with the twin-screw extruder.

The effect of the amount of compatibilizer was investigated with one PP/PA composition (70/30), and the content of compatibilizer was varied from 0, 1.5, 3.0, to 4.5 wt %, with appropriate reductions being made in the PP phase. The mixing and melt blending were done as described above.

The effect of blending procedure was studied by mixing one model composition (PP/PA/compatibilizer 67/30/3 in wt %), in four different ways. The first sample was melt blended in a twin-screw extruder as above. The second sample was melt blended in the same extruder but using a very "mild" screw configuration consisting mainly of conveying elements. The third sample was only dry mixed, and

not melt blended at all before injection molding. In the fourth sample polyamide 6 and the compatibilizer were melt blended normally, as in the first case, and polypropylene was then added to the mixture as dry blend. This sample was then fed directly to the hopper of the injection molding machine. These blends are referred to below as I to IV, respectively.

Testing and Characterization

After blending, the materials were dried for 16 h at 80°C in a dehumidifying dryer. All samples were injection molded into test plates and tensile test bars. The thickness of the plates (100 × 100 mm) was 1 mm. The test bars for mechanical testing with the dimensions as in ISO R527 6A were injection molded according to ISO 294 standard. Before testing, the samples were again dried for 16 h at 80°C and preserved in a desiccator before measurement. The effect of moisture on the mechanical properties was, thus, minimized.

Oxygen transmission rate was measured according to standard ASTM D3985. Two parallel tests were made on each sample. Tensile strength and modulus were measured according to standard ISO R527 and Izod notched impact strength according to standard ISO 180/1A, both at 23°C. A minimum of five samples were tested in each case, and the standard deviation was less than 10%.

The morphologies were evaluated by scanning electron microscopy (SEM) JEOL JSM-820. Micrographs were taken of injection-molded tensile test bars. Samples were prepared by fracturing the parts at liquid nitrogen temperature, and the fracture surfaces were coated with a layer of gold.

Melt viscosities of polypropylene, polyamide 6, and the polyamide/compatibilizer (90/10) preblend were measured with a Göttfert Rheograph 2002 capillary rheometer. The measurements were made at the processing temperature (245°C) to be able to determine the viscosity ratio between PA and PP related to different blending procedures. A die with length to diameter ratio of 30/1 was used, and Rabinowitch correction was made to the results.

RESULTS AND DISCUSSION

Effect of Composition

Compositions and oxygen permeabilities in the first series of tests are presented in Table I, and the measured and calculated permeabilities are compared in Figure 1. The permeabilities for the corresponding coextruded structures were calculated from eq. (1). The permeabilities for homogeneous dispersions were calculated from eqs. (2) and (3), on the assumption that the phase inversion takes place roughly at 50/50 composition.

In these tests, where all components were fed into the twin-screw extruder simultaneously, morphologies with homogeneous dispersions were achieved, as shown by SEM micrographs recorded from the samples. A typical example of such morphology is shown in Figure 5(a) for the composition PP/PA/Comp 67/30/3. So long as the polypropylene provided the matrix, the oxygen permeability was close to that of polypropylene; but after phase inversion, the barrier properties approached those of polyamide 6. As can be seen in Figure 1, the measured values were close to those calculated for homogeneous dispersions.

Mechanical properties of the blends are depicted in Table II and Figure 2. The tensile modulus and

Table I   Compositions of the Blends in Weight Percent, and Their Oxygen Permeability

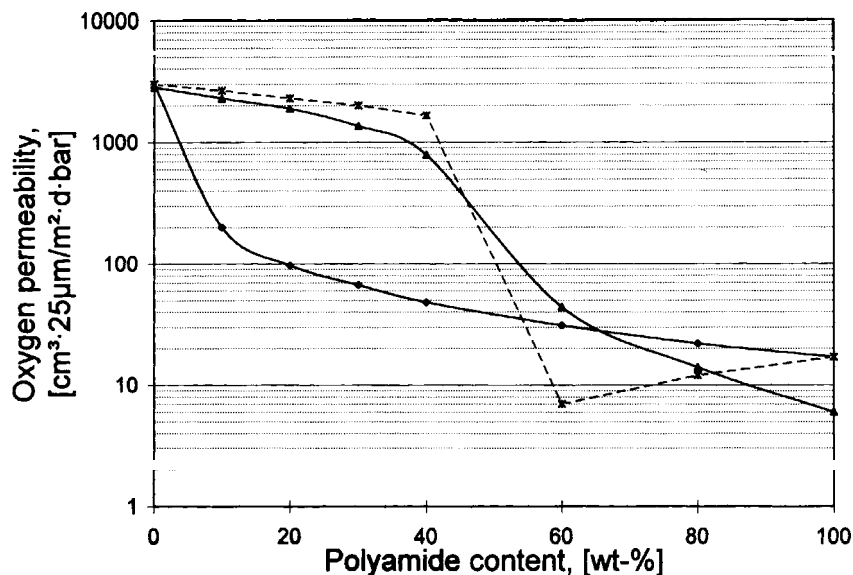| Sample	PP wt %	PA 6 wt %	Compatibilizer wt %	Oxygen Permeability $(cm^3 \cdot 25~\mu m/m^2 \cdot d \cdot bar)$
1	100	0	0	2820
2	89	10	1	2290
3	78	20	2	1880
4	67	30	3	1360
5	56	40	4	790
6	34	60	6	44
7	12	80	8	14
8	0	100	0	6

Figure 1   Oxygen permeabilities as a function of polyamide content: ▲ is the measured permeability, ◆ the calculated permeability for corresponding coextruded structures, and x the calculated permeability for homogeneous dispersions.

tensile strength increased with the polyamide content. Slight improvement also occurred in the Izod notched impact strength. The level of impact strength, nevertheless, is low because the samples were dried before measurement reducing the plasticizing effect of water in polyamide 6.

Effect of Compatibilizer Content

In these tests, the amount of the compatibilizer in blends was varied while the polyamide 6 content was kept constant at 30 wt %. Thus, polypropylene always formed the matrix, and polyamide 6 the dispersed phase. The melt blending was done in the twin-screw extruder by feeding all the components into the hopper simultaneously.

The compatibilization reaction between amine end groups of polyamide 6 and maleic anhydride groups has been reported[5] to lead to a finer and more homogeneous dispersion than in noncompatibilized blends. In our work, the size of the dispersed polyamide particles diminished with increasing compatibilizer content. At the same time, the barrier effect of the polyamide phase clearly decreased, as can be seen in Figure 3. Thus, minimizing the amount of compatibilizer needed is important for good barrier properties. However, without compatibilization, blends of polypropylene and polyamide

Table II   Mechanical Properties of the Blends of Different Composition (codes as in Table I)

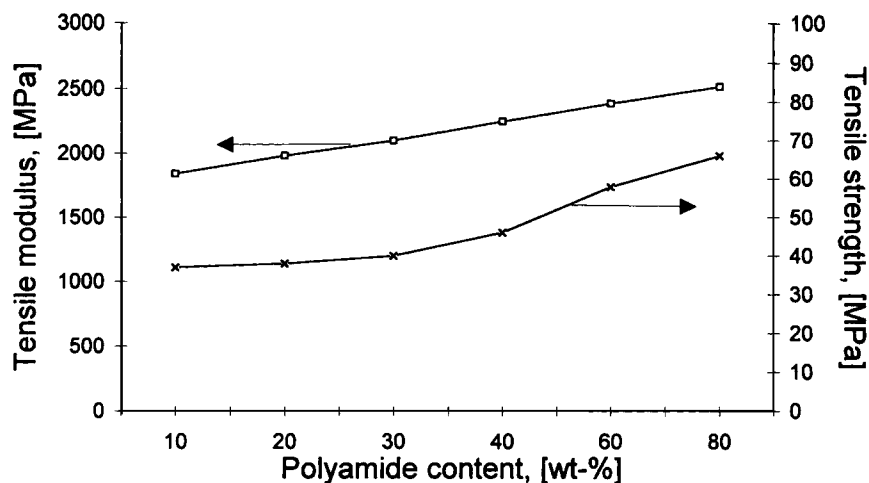| Sample	Tensile Modulus MPa	Tensile Strength MPa	Notched Izod Impact Strength kJ/m^2
2	1840	37	2.3
3	1980	38	2.6
4	2100	40	2.4
5	2250	46	3.0
6	2390	58	4.7
7	2520	66	4.9

Figure 2   Tensile modulus and strength as a function of polyamide content.

do not show stable morphology or interesting properties.

Effect of Blending Procedure

The morphology of all immiscible blends strongly depends on the melt-blending process. The applied mixing intensity (shear forces), temperature, and residence time are important parameters. In polypropylene/polyamide blends the size of the dispersed particles has been found to depend on the applied screw configuration.[12] We studied the effect of blending procedure on oxygen barrier and me-

chanical properties with one model blend composition: PP/PA/Comp 67/30/3 (wt %). The influence of processing on the oxygen permeability is depicted in Figure 4, where the oxygen permeabilities are also compared with the theoretical values calculated for layered and homogeneous blend structures [eqs. (1) and (2)]. The oxygen permeabilities of the blends made in a twin-screw extruder in normal (Sample I) or in mild shearing conditions (Sample II) as well as that of the dry-mixed blend (Sample III) were about at the same level as that calculated for homogeneous dispersions. The oxygen permeability of sample IV, in turn, was significantly
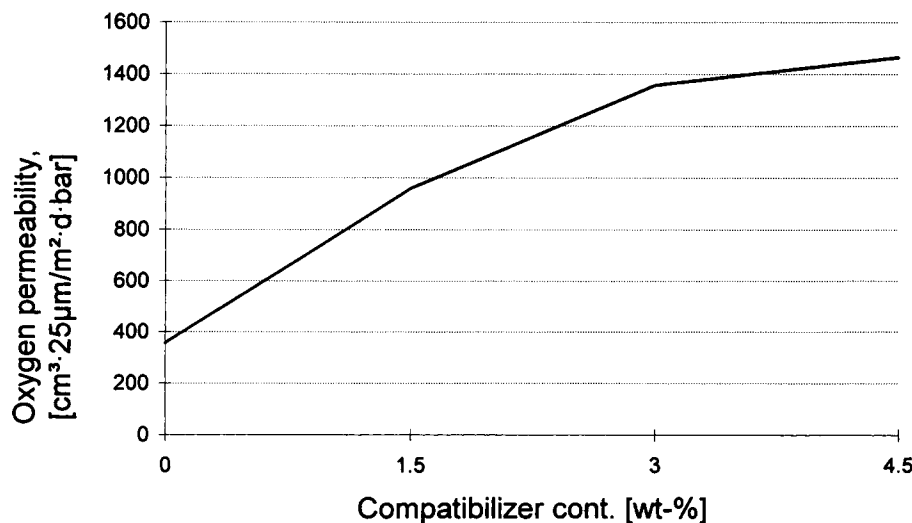

Figure 3   Effect of the compatibilizer content on oxygen permeability of blends with 30 wt % PA.
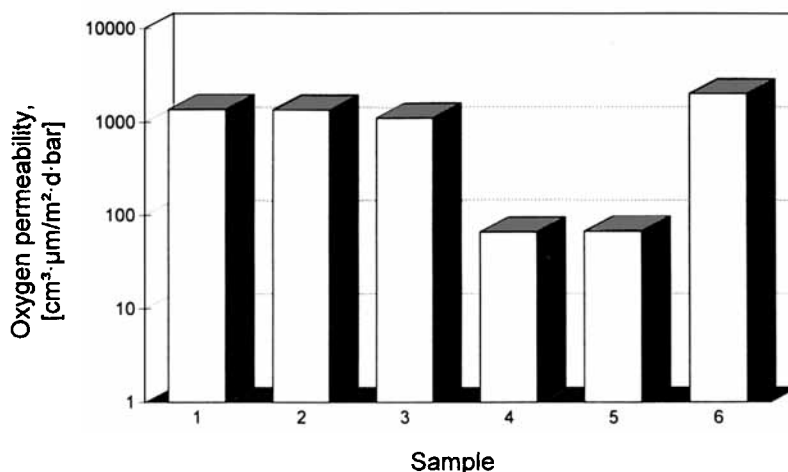
Figure 4 Effect of blending procedure on oxygen permeability. 1. Sample I, normally mixed in the twin-screw extduder. 2. Sample II, mildly mixed in the twin-screw extruder. 3. Sample III, polymers only dry mixed before injection molding. 4. Sample IV, PA + Comp. mixed in the twin-screw extruder, PP added as dry blend before injection molding. 5. Permeability calculated for corresponding coextruded structure [eq. (1)]. 6. Permeability calculated for corresponding homogeneous dispersion [eqs. (2) and (3)].

lower approaching the theoretical value calculated for a coextruded PP/PA structure. This remarkable improvement was achieved through formation of a special morphology.

Variation in the blending procedure resulted in different morphologies in the final injection-molded samples, which well explains the oxygen permeability results obtained. The SEM micrographs reproduced in Figures 5 and 6 show a variation from homogeneous (Sample I) to laminar-type morphology (Sample IV). In samples I and II, enhanced interactions through the amine/anhydride reaction caused a fine dispersion of polyamide in the polypropylene matrix. The average particle size of the dispersed phase was about 1–2 μm. The structures of Samples I and II were closely similar, indicating that the screw configuration of the twin-screw extruder is not a critical parameter. By contrast, for Sample III, where components were merely dry mixed before injection molding, the residence time and mixing intensity in the injection molding machine were not sufficient for compatibilization reactions to take place. The morphology of Sample III was nonhomogeneous and the adhesion between the components was poor.

A significantly different morphology can be observed for Sample IV, where the polyamide 6 phase formed extended thin platelets. The dispersed polyamide domains were strongly deformed and elongated during the injection molding, resulting in a laminar-type morphology. This morphology of

Sample IV explains its very good oxygen barrier property. Because of the long polyamide platelets, the penetrating oxygen has a longer path to travel through the material. The morphology resembles that obtained by Subramanian[10] in blow-molded containers made of polyamide/polyethylene blends.

The blending procedure also had a clear effect on the morphology of the skin regions of the specimen. Figure 6 depicts the structures of Samples II and IV. Sample II has also a somewhat more layered structure in the skin region than in the middle of the specimen. The effect is much more pronounced in Sample IV, however.

In Sample IV, the melt-blending of polyamide with the compatibilizer, maleic anhydride grafted polypropylene, enables the amine anhydride reaction to take place, but the compatibilizer is not mixed with the polypropylene phase. Probably the compatibilizer is dispersed after the melt blending in the polyamide phase.[9] The amine/anhydride reaction results in a polypropylene-polyamide graft copolymer that acts as the final compatibilizer. The copolymer is probably located at the interface between the dispersed compatibilizer and polyamide matrix. When polypropylene is then later added, the polyolefinic segments of the compatibilizer are free to provide sufficient miscibility between the compatibilizer and polypropylene during the injection molding.

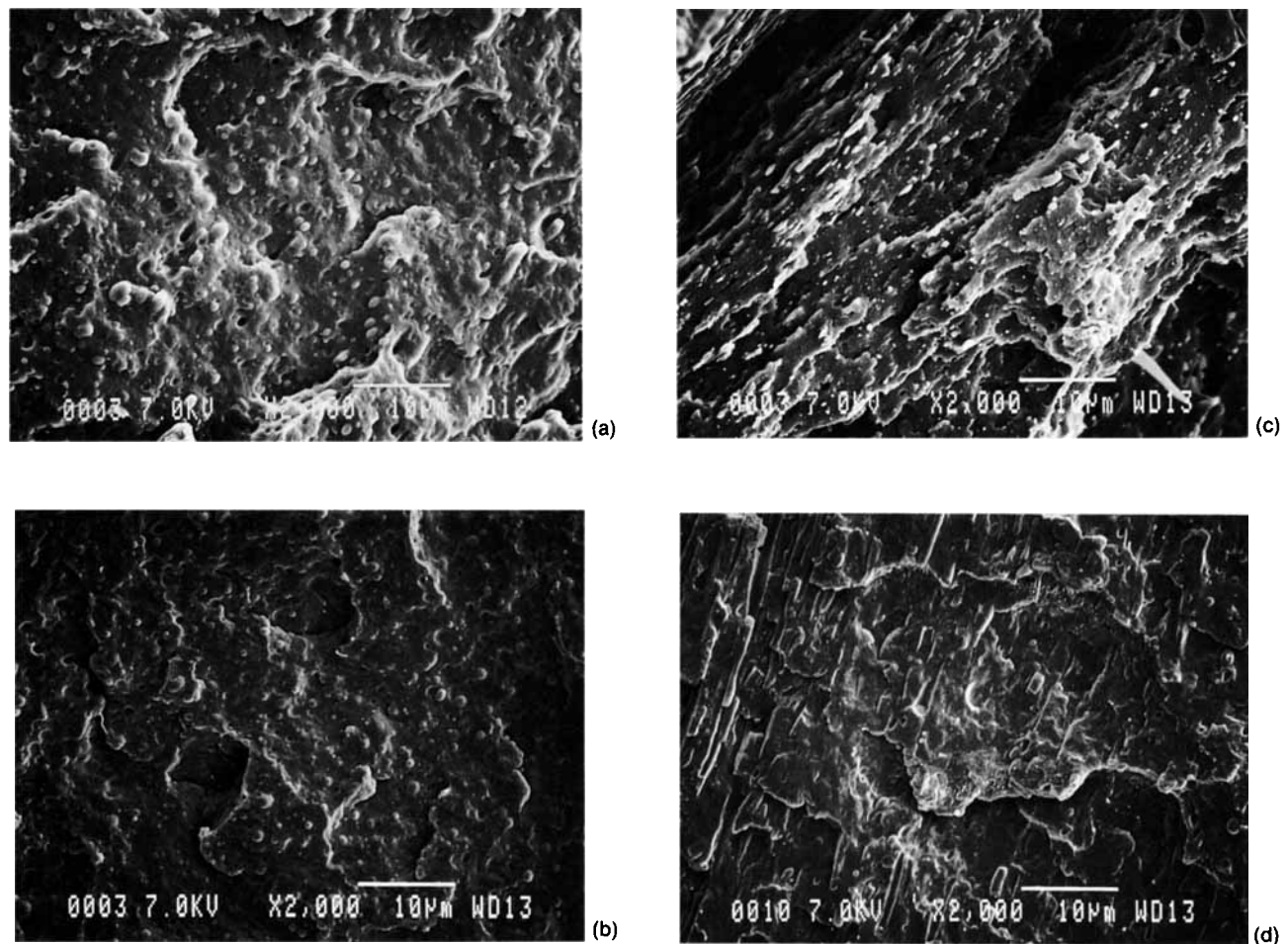In addition, preblending of the compatibilizer and polyamide affected also the melt rheology, which is

Figure 5 SEM micrographs of fractured surfaces for samples of composition PP/PA/ Comp 67/30/3. (a) Sample I, normally mixed in the twin-screw extruder. (b) Sample II, mildly mixed in the twin-screw extruder. (c) Sample III, polymers only dry mixed before injection molding. (d) Sample IV, PA + Comp. mixed in the twin-screw extruder, PP added as dry blend before injection molding (taken from the middle part of the injection-molded specimen). Magnification: scale bar 10 μm.

crucial for the morphology. As seen from Figure 7, the melt viscosity of the PA/compatibilizer (90/ 10) preblend was clearly higher than that of PP at all shear rates studied. According to our earlier studies,[13,14] this means that the more viscous component (PA) tends to form relatively large domains in the matrix (PP) instead of a fine dispersion. Especially at higher shear rates applied in injection molding the viscosity ratio ($\eta_{PA}/\eta_{PP} \approx 2$) led to the formation of larger PA domains, which were deformed into extended platelets due to shearing. In case III, where all three polymers were only dry mixed, the conditions were slightly similar, but the poor mixing led to a more unhomogeneous morphology and lack of interfacial adhesion. In cases I

and II, instead, where all three polymers were blended in the twin-screw extruder (maximum shear rates about 300–500 1/s), the viscosity ratio was near unity and a fine dispersion of PA in PP matrix was obtained.

The stable, more laminar morphology achieved with the fourth blending procedure resulted also in better mechanical properties than obtained with other blending procedures. Although the recipe was the same in all four cases, a significant improvement in tensile modulus, tensile stress at yield, and Izod notched impact strength was evident with the fourth mixing procedure, as seen in Figure 8. Evidently this improvement is due to the special morphology formed, i.e., elongation of the dispersed polyamide
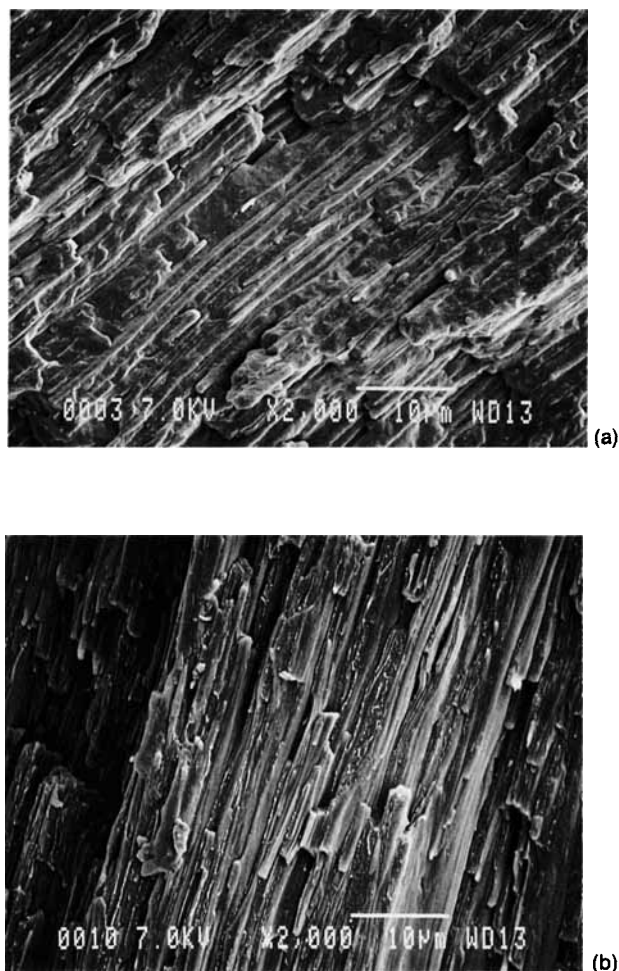
Figure 6 Morphology of the skin region of the injection-molded samples. (a) Sample II, mildly mixed in the twin-screw extruder. (b) Sample IV, PA + Comp. mixed in the twin-screw extruder, PP added as dry blend before injection molding. Magnification: scale bar 10 μm.

phase in the matrix. The oxygen permeability of the blends followed that of the continuous phase, and a dramatic improvement in barrier properties was achieved after phase inversion, when polyamide 6 became the continuous phase.

In the study of the effect of compatibilizer concentration, polypropylene was the major phase (70–65.5 wt %), polyamide the minor phase (30 wt %), and maleic anhydride-grafted polypropylene the compatibilizer (0–4.5 wt %). Increasing the amount of the compatibilizer caused the size of the dispersed polyamide particles to become smaller and the oxygen permeability increased. Thus, minimizing the amount of compatibilizer needed is important for good barrier properties.

The blending procedure was found to have a great influence on the oxygen permeability. The best oxygen barrier and mechanical properties were associated with the laminar type of morphology where the dispersed polyamide phase formed thin elongated platelets in the polypropylene matrix. This special morphology was obtained when polyamide and compatibilizer were melt blended separately in a twin-screw extruder and polypropylene was added later, as a dry blend, to the hopper of the injection molding machine. The reduction of oxygen permeability was significant compared to the normal procedure where all components were blended in a twin-screw extruder before processing. Moreover, the measured oxygen permeability of the blend was even as low as the theoretical value calculated for a coextruded PP/PA structure. Formation of the laminar morphology is based on a favorable viscosity ratio between PA and PP phases and the amine/anhydride reaction during preblending of PA and the compatibilizer.
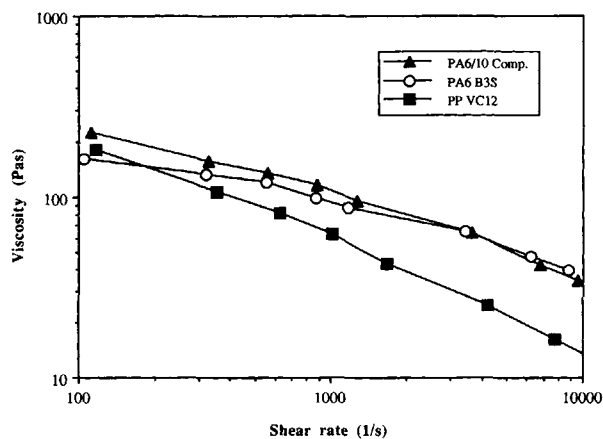
particles and adequate interfacial adhesion achieved through the compatibilization.

CONCLUSIONS

The aim of this study was to improve the oxygen barrier property of polypropylene by blending with polyamide. The effects of blend composition, compatibilizer content, and blending procedure on oxygen permeability of injection molded polypropylene/polyamide 6 blends were studied and the results were compared with morphology and mechanical properties of the blends.

Mixing of polypropylene, polyamide 6, and the compatibilizer in the twin-screw extruder resulted in a fairly homogeneous dispersion of the minor

Figure 7 Melt viscosities vs. shear rate for PP, PA, and PA/compatibilizer (90/10) preblend measured at 245°C.
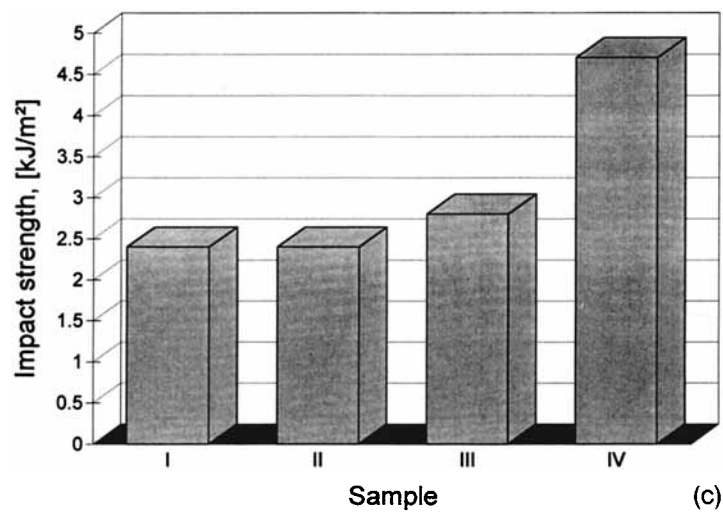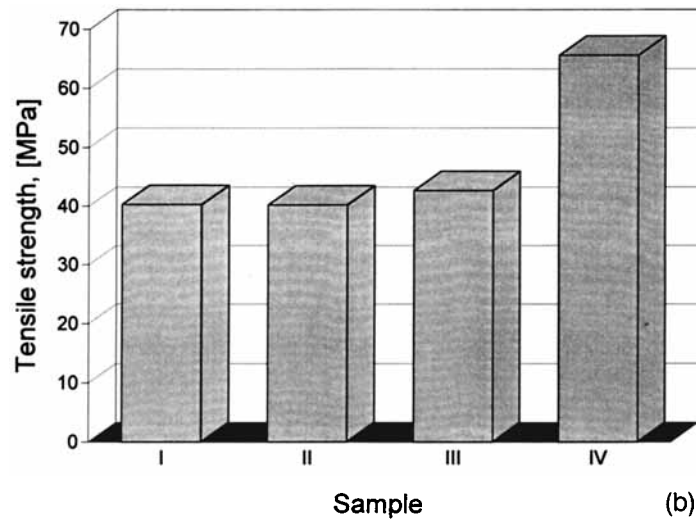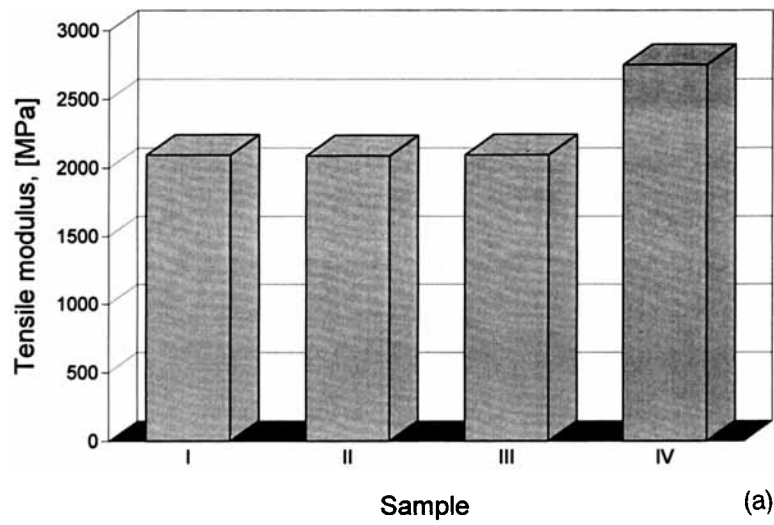
Figure 8 Effect of blending technique on (a) tensile modulus, (b) tensile strength, and (c) notched Izod impact strength: Sample I, normally mixed in the twin-screw extruder; Sample II, "mildly" mixed in the twin-screw extruder; Sample III, polymers only dry mixed before injection molding; and Sample IV, PA + Comp. mixed in the twin-screw extruder, PP added as dry blend before injection molding.

REFERENCES

1. R. M. Barrer, J. A. Barrie, and M. G. Rogers, *J. Polym. Sci., Part A,* **1,** 2565 (1983).
2. D. H. Weinkauf and D. R. Paul, in *Barrier Properties and Structures,* W. J. Koros, Ed., ACS Symposium Series 423, Washington, DC, 1989.
3. J. H. Briston, *Converter,* **26,** 14 (1989).
4. W. J. Koros, in *Barrier Properties and Structures,* ACS Symposium Series 423, Washington, DC, 1989.
5. F. Ide and A. Hasegawa, *J. Appl. Polym. Sci.,* **18,** 963 (1974).
6. G. Fairley and R. E. Prud'Homme, *Polym. Eng. Sci.,* **27,** 1495 (1987).
7. J. M. Willis and B. D. Favis, *Polym. Eng. Sci.,* **28,** 1416 (1988).
8. R. Holsti–Miettinen, J. Seppälä, and O. Ikkala, *Polym. Eng. Sci.,* **32,** 868 (1992).
9. S. Schlag, J. Rösch, and Chr. Friedrich, *Polym. Bull.,* **30,** 603 (1993).
10. P. M. Subramanian and V. Mehra, *Polym. Eng. Sci.,* **27,** 663 (1987).
11. J. D. Booze and P. M. Subramanian, *EP 0 090 554,* Du Pont (1983).
12. T. Vainio and J. Seppälä, *Polym. Polym. Compos.,* **1,** 427 (1993).
13. P. Hietaoja, R. Holsti–Miettinen, J. Seppälä, and O. Ikkala, *J. Appl. Polym. Sci.,* **54,** 1613 (1994).
14. M. Heino, P. Hietaoja, T. Vainio, and J. Seppälä, *J. Appl. Polym. Sci.,* **51,** 259 (1994).