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Barrier Property and Morphology of Polypropylene/Polyamide Blend Film

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Abstract−The barrier property of polypropylene (PP)/polyamide (PA) blend film produced by the extrusion casting film process was studied by investigating the effects of rheological properties of each components, compatibilizer content, screw rpm, and the absorbed moisture, and by performing morphological analysis and permeability modeling. The oxygen barrier property of blend film with ellipsoidal structure of PA dispersed phase was significantly improved by a factor of 5.4 with the addition of only 20 wt% PA, when compatibilizer was added by the content of 7 phr and the PP matrix resin and process condition was selected to induce lower viscosity ratio less than unity. Using Fricke's model with the value of 19.6 of aspect ratio of the ellipsoid, the permeabilities of blend films as a function of PA content could be predicted and exhibited a good agreement with the experimental results. The absorbed moisture had a significant influence on the barrier property of the PP/PA blend system, suggesting that the hygroscopic PA resin should be incorporated with the high water barrier PP resin by the amount below about 20 wt% to minimize the deterioration of the barrier property in the humid atmosphere.

Key words: Polypropylene/Polyamide Blends, Barrier Property, Permeability Modeling

INTRODUCTION

Conventionally, polymeric films with good oxygen and moisture barrier properties for the application of food and medical packaging have been produced with multilayered structures using coextrusion and lamination process. In this film manufacturing process, a layer of ethylene-vinyl alcohol copolymer (EVOH) or polyamide (PA) resin having high barrier property is usually positioned as a middle layer and a polyolefin resin as outer layer covers this barrier layer to exclude the moisture effect of EVOH or PA resin [Finlayson, 1989]. However, these processing techniques have some drawbacks such as high investment cost of equipment and difficulty in process control resulting from requirements for multiple extruders and dies, adhesives between layers, and multi-step operations. In addition, multilayer composite films have a limitation of recyclability since resins with different characteristics adhere together. Currently, diverse techniques such as sol-gel silica coating [Azuta et al., 1999; Lee et al., 1999], plasma coating [Agres et al., 1996], and blending [Faisant et al., 1998; Lee and Kim, 1997] have been proposed to overcome these shortcomings. Among these techniques, blending approach for improving barrier property has been recognized as attractive methodology because existing extrusion processing systems can be used without further investment of equipment. In this polymer blend system, the improvement in barrier property is achieved through the formation of elongated morphology of the dispersed phase due to orientation effect during extrusion processing, resulting in an increase of tortuous paths [Yeo et al., 2001; Kim and Chun, 1999; Subramanian and Mehra, 1987; Kamal et al., 1995; Holsti-Meittinen et al., 1995; Lee and Kim, 1997].

The first successful attempt to produce blow molded high barrier containers with developed laminar morphology was reported by Subramanian [1985]. The results showed that PA6, the barrier resin, could be distributed as large and thin sheets in the HDPE matrix by extruding the blends under special extrusion conditions. Recently, we have demonstrated that a high increase in toluene barrier properties of LLDPE/EVOH blends could be achieved by producing laminar structure with more elongated morphology of the dispersed phase through drawing and blowing operation in the extrusion blown film process [Kim and Chun, 1999]. In addition, PP/EVOH blend film with higher barrier property could be obtained by generating a laminar structure having larger area using a biaxial orientation film process [Yeo et al., 2001]. Although EVOH exhibits excellent gas barrier property and transparency, it has some drawbacks of high cost, low toughness, and difficult processing [Finch, 1993]. On the other hand, PA that is inexpensive relative to EVOH exhibits high resistance to the permeation of hydrocarbons as well as good toughness [Lee and Kim, 1998]. Thus, polypropylene and Polyamide have been blended to improve the thermal and mechanical properties of polypropylenes. Furthermore, addition of polyamide to polypropylene results in improvement in barrier properties as well as mechanical properties. Polypropylene exhibits excellent barrier properties to moisture, but it has a poor barrier property with respect to O_2 or CO_2. On the other hand, polyamide has high barrier properties to gases such as O_2 and CO_2, and high resistance to hydrocarbons [Holsti-Meittinen et al., 1995]. However, compatibilizer must be used to enhance the interphase adhesion and phase stability in immiscible blends of PP and PA [Holsti-Meittinen et al., 1992]. The ultimate barrier property of the polymer blend depends on the morphological structure of the dispersed phase, the intrinsic barrier property of each component, and the nature of the interface between the two phases [Lohfink and Kamal, 1993; Kit et al., 1995; Subramanian and Mehra, 1987]. Recently, it has been reported that injection-molded PP/PA blends with improved barrier property could be pro-

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duced by generating laminar morphology of polyamide dispersed phase induced by shear and elongational flow [Jarus et al., 2002].

In this study, the barrier property and morphology of PP/PA blend film prepared by casting film process were studied by investigating the effects of compatibilizer contents, rheological property of each phase, screw rpm, and the absorbed moisture. In addition, permeability modeling was performed to predict the oxygen permeability of PP/PA blend system as a function of PA content.

EXPERIMENTAL

1. Materials

Polypropylene (grade name: HF21AGT) supplied by Samsung General Chemicals was chosen as a basic matrix resin. It is a film grade with density 0.910 g/cc, and melt flow index (M.I.) 2.0 g/10 min (230 °C, 2.16 kg). Other PP film grades of HF301AGT (M.I.= 4.0) and HF411AGT (M.I.=6.0) were also used as continuous phases to examine the effects of rheological properties of matrix resin on the variation of oxygen permeability of the blend film. The three kinds of PP resins with different values of M.I. are designated as PP1 (M.I.=2.0), PP2 (M.I.=4.0), and PP3 (M.I.=6.0), respectively. For the dispersed phase as a barrier resin, PA (grade name: 2835TF, T_m=191.5 °C, T_c=143.9 °C) obtained from Hyosung Co, which is a copolymer of PA 6 and PA 6,6, was used because PA copolymer having melting point lower than that of homopolymer was expected to be easily deformed into layer structure during extrusion processing due to reduced melting point discrepancies between two phases. Since PP and PA are incompatible, PP resin with 0.3 wt% grafted maleic anhydride (PP-g-MAH) as a compatibilizer was used to improve the interfacial adhesion between two resins. This is a PO1015 resin provided by Exxon Co.

2. Blend Film Preparation

Before processing, PA was predried at 60 °C overnight in a vacuum dryer because of the hygroscopic behavior of PA. In all blends, the weight ratio of PP/PA blend was fixed at 80/20, while the concentration of compatibilizer was 0, 1, 2, 4, 7, and 10 phr (parts per hundred resin). Cast films of compatibilized PP/PA were prepared by first mixing the dried resins with a pellet shape, followed by melting blending in a Hakke Rheomix 252 single screw extruder with a 10 cm×0.14 cm slit die and a take-up system. The temperature profiles for the three heating sections of the extruder barrel and die were set at 190, 205, 220, and 230 °C. The standard conditions for the compatibilizer composition and cast film processing, which are summarized in Table 1, were used in all experiments except the variable to be examined.

3. Rheological Property Measurements

Rheological properties of pure resins in the low range frequency from 0.1 to 100 rad/sec were measured by a Rheometrics Mechanical Spectrometer (RMS 800) fitted with a parallel plate geometry. The plate diameter was 25 mm and the gap between two plates was set to 2.0 mm. All experiments were conducted under nitrogen gas blanket to prevent degradation. The shear viscosities of the molten PP and PA in the high shear rate range between 0.8×10^2 and 10^5 sec^{-1} were also measured by using a Rosand capillary rheometer (RH720) with a capillary die (L/D=16). The measurements were made at 230 °C and 240 °C for considering the actual temperature conditions in the extrusion process.

Table 1. Standard conditions for the compatibilizer content and film processing of PP/PA blend films

Compatibilizer content	PP matrix	Screw rpm	Draw ratio	Die temperature
4.0 phr	PP1	60	5.8	230 °C

4. Morphological Analysis

The morphology of the blend films was observed by a scanning electron microscope (SEM, JSM-T200). The morphological structure of the dispersed phase deformed by casting film extrusion could be analyzed by observing the cross-sections of blend film samples cut parallel to both machine and transverse directions. The blend samples were prepared by fracturing the samples frozen for enough time in liquid nitrogen, followed by coating the fractured surfaces with a thin layer of gold.

5. Oxygen Permeability Measurements

Oxygen permeability of the sample was measured according to the method based on ASTM D3985. The permeation cell consisted of a stainless steel short cylinder divided into an upper and lower part. The sample with a diameter of 4.4 cm was inserted into this permeation cell separated by O-ring for sealing. The permeation system was evacuated at 10^{-3} torr for about one hour, and then oxygen (760 torr) was introduced to the upstream side. The permeated pressure as a function time on the downstream side was monitored by an MKS-Baratron transducer (MKS-627B). The temperature was controlled by water bath and maintained at 25 °C during each measurement. Two cylinders were connected to both upstream and downstream side to minimize the fluctuation of pressure with time by increasing the volume. The oxygen permeability could be determined from the slope in the plot of permeated pressure variation with time.

6. Water Absorption

The amount of water absorbed by the blend films containing various contents of PA was measured according to ASTM D-570 method. The blend samples were dried for 12 hr in a vacuum dryer to eliminate the moisture existing within the samples, and then wetted samples were obtained by immersing in distilled water at 25 °C for 24 hr. Water absorption percentage (%) was calculated by the following relation.

$$\text{water absorption percentage (\%)} = \frac{\text{wt of wetted sample} - \text{wt of dried sample}}{\text{wt of dried sample}} \times 100$$

RESULTS AND DISCUSSION

1. Rheological Properties

In the compatibilized binary blend system, the rheological properties of each component consisting of blends and the viscosity ratio of the dispersed phase to the matrix resin have been recognized as significant factors affecting the ultimate morphology of blend product [Favis and Chalifoux, 1987; Wu, 1987]. Therefore, obtaining information for the rheological property with shear rate and temperature corresponding to actual processing conditions is very essential in establishing extrusion processing window for fabricating high barrier blend films by generating a stable and homogeneous mor-

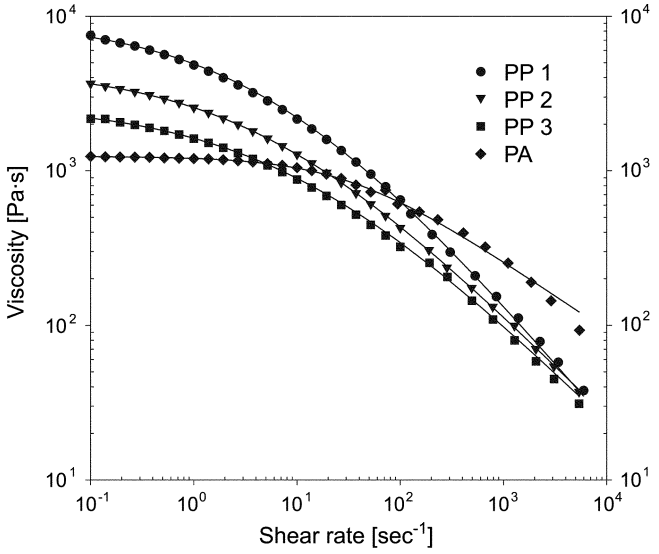

Fig. 1. Shear viscosity of PA and three kinds of PP as a function of shear rate at 230 °C.

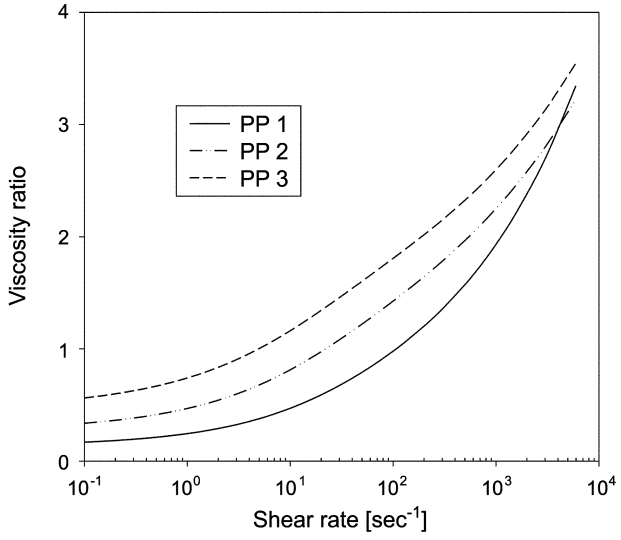

Fig. 2. Viscosity ratio as a function of shear rate for the PP resin having different M.I. at 230 °C.

phological structure of the dispersed phase in the matrix.

The measured melt shear viscosities of three kinds of PP and PA as a function of shear rate at 230 °C are shown in Fig. 1. The data below 100 sec^{-1} were obtained from complex viscosity according to Cox-Merz rule, because no steady shear viscosity data at low shear rate were available. Fig. 2 exhibits the viscosity ratio ($\lambda=\eta_d/\eta_m$) calculated from the viscosity data shown in Fig. 1. The viscosity ratio less than unity induces easier deformation and breakup of the minor phase domains because of efficient stress transfer from the continuous phase to the dispersed phase. Whereas, the degree of deformation of dispersed phase is reduced as viscosity ratio beyond unity increases. It can be seen that because of shear sensitivity of viscosity of PP, the viscosity ratio increases gradually with increase of shear rate, falling into the range of 0.3 to 1.3 for PP1 and 0.8 to 2.2 for PP2 and 1.2 to 2.5 for PP3 in the practical shear rate range between 10^1 and 10^3 sec^{-1}.

The apparent shear rate in the slit die used for extrusion casting film processing can be expressed as follows [Tadmor and Gogos, 1979],

$$\dot{\gamma}=\frac{6Q}{BH^2} \tag{1}$$

where Q is the volumetric flow rate (cc/s); B is the width of die gap (cm); H is the height of the die gap. In this casting film processing, the apparent shear rate in the die with dimension of 10.0×0.14 cm was estimated to be 18-47 sec^{-1} according to processing conditions.

2. Modeling of Permeability

In polymer blend systems, the barrier property depends only on the morphological structure of the dispersed phase if the permeability of the each component is given, and permeation does not occur through interfacial microvoids between two phases due to poor interfacial adhesion. In order to predict the permeability of a blend system, various model equations have been proposed by applying the model developed for describing the conductivity of two phase system. For a composite film with two layers stacked in series produced by coextrusion process, the permeability is given by

$$\frac{1}{P_c}=\frac{\phi_1}{P_1}+\frac{\phi_2}{P_2} \tag{2}$$

Here, ϕ, P are volume fraction and permeability, respectively. A subscript denotes the each layer.

In a homogeneous blend system containing low-permeability spherical particles dispersed in a high permeability matrix, the Maxwell's model expression below has been used to predict the permeability of the blend [Lohfink and Kamal, 1993].

$$P=\frac{P_m[P_d+2P_m-2\phi_d(P_m-P_d)]}{P_m[P_d+2P_m+\phi_d(P_m-P_d)]} \tag{3}$$

where P, P_d, P_m are the permeabilities of the blend, dispersed phase, and matrix, respectively. ϕ_d is the volume fraction of the dispersed phase.

In current, the following Fricke's model expression that extends Maxwell's model has been used to describe the permeability of the blend system containing low permeable dispersed phase with an ellipsoidal shape [Kit et al., 1995].

$$P=\frac{P_m+GP_d}{1+G} \tag{4a}$$

where

$$G=\frac{\phi_d}{1-\phi_d}\left[\frac{1}{1+(1-K)(P_d/P_m-1)}\right] \tag{4b}$$

$$K=\frac{\cos\alpha}{\sin^3\alpha}\left(\alpha-\frac{1}{2}\sin 2\alpha\right) \tag{4c}$$

$$\cos\alpha=\frac{W}{L} \tag{4d}$$

In this expression, W is the dimension of the axis of the ellipsoid parallel to the direction of permeation, L the dimension of the axis tranverse to the direction of permeation. G can be considered a weighting factor responsible for the aspect ratio of the ellipsoid, volume fraction of dispersed phase, and the ratio of permeability of each phase.

In this study, since uniaxial elongation to the machine direction

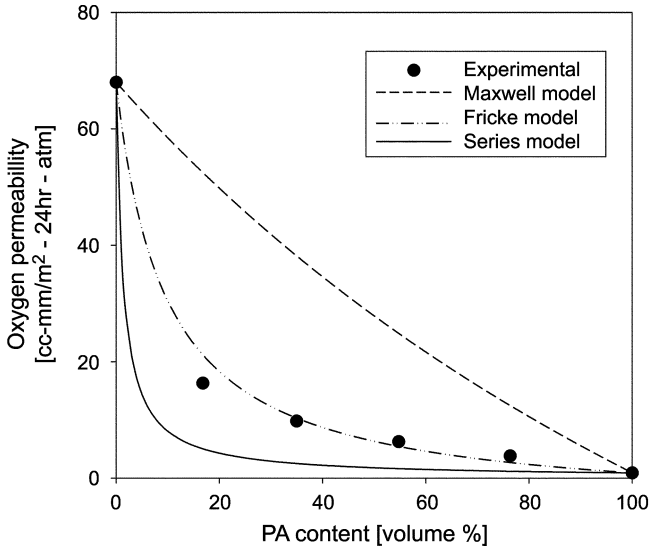

Fig. 3. Comparison of measured permeabilities of the PP/PA blend film as a function of PA contents with the predicted values obtained from various permeability models.

was expected to be dominant over the stretching to the transverse direction in the casting film process employed for producing PP/PA blend film, the Fricke's model appropriate for the blend system with ellipsoidal structure of the dispersed phase was used to predict the permeability of the blend film and to compare the experimental results.

In Fig. 3, the measured permeabilities of the blend film as a function of PA contents are compared with those predicted by several models of Fricke, Maxwell, and series. It can be seen that the oxygen barrier property of the blend can be enhanced significantly by adding small amount of PA resin with high barrier property up to about 20 volume%. In particular, when the amount of dispersed phase exceeds about 55 volume%, the permeability of the blend film approaches that of pure PA resin due to phase inversion. Among these models, the permeabilities predicted by Fricke's model were in excellent agreement with measured values when the value of 19.6 for L/W of a ellipsoid of dispersed PA phase was used in this modeling. This value of L/W was found to be a reasonable value from morphological analysis of the dispersed phase as shown in Fig. 4. In addition, It was confirmed from these SEM micrographs that the casting film process used in this study produced blend films with ellipsoidal structure of dispersed phase due to dominant stretching effect only in the machine direction.

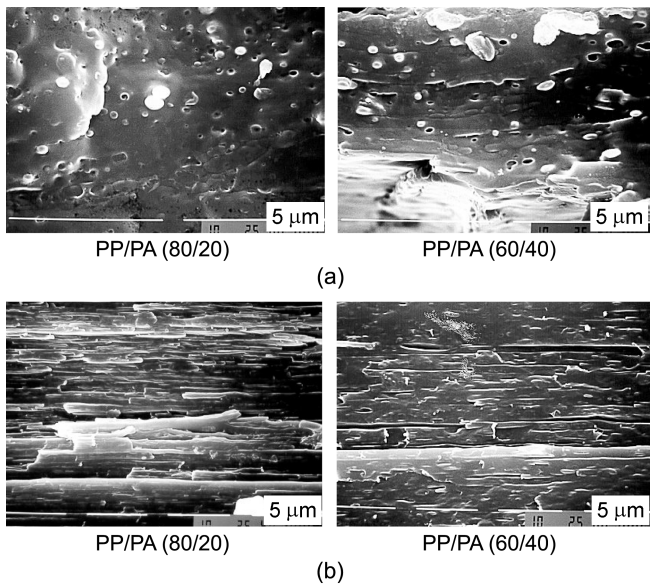

Fig. 4. SEM micrographs of PP/PA blend films containing 20 and 40 wt% of PA in (a) transverse and (b) machine directions.

3. Effect of Compatibilizer Content

Since the blend of PP and PA forms immiscible mixture due to different polar characteristic, the addition of compatibilizer into this blend system is required to improve the interfacial adhesion between dispersed phase and matrix and to obtain finer and more homogeneous morphology, which is attributed to the compatibilization reaction between amine groups of polyamide and maleic anhydride groups of PP-g-MAH. Furthermore, it has been known that the addition of compatibilizer into immiscible blends can prevent coalescence of the dispersed particles by reducing interfacial tension between two phases during melt flow through a die after dispersed domains are crushed by high shear stress induced by screw rotation within the extruder.

Fig. 5 shows the effect of compatibilizer content on the oxygen permeability of PP/PA blend films. As shown in the figure, the permeability decreases with increasing of compatibilizer content, but is almost invariant above 7 phr of compatibilizer content. This result is conflicting with our previous result exhibiting optimum level of compatibilizer content for obtaining high barrier property, which has been reported for the biaxially oriented PP/EVOH blend film [Yeo et al., 2001]. This contradictory result may be attributed to the fact that for the PP/EVOH blend film with the laminar structure of dispersed phase, the compatibilizer content has a significant effect on the variation of frontal area; on the other hand, in the case of this PP/PA blend film with the ellipsoidal structure, the amount of compatibilizer has a minor effect on the variation of area of ellipsoid. Therefore, it can be deduced that the barrier property of blend

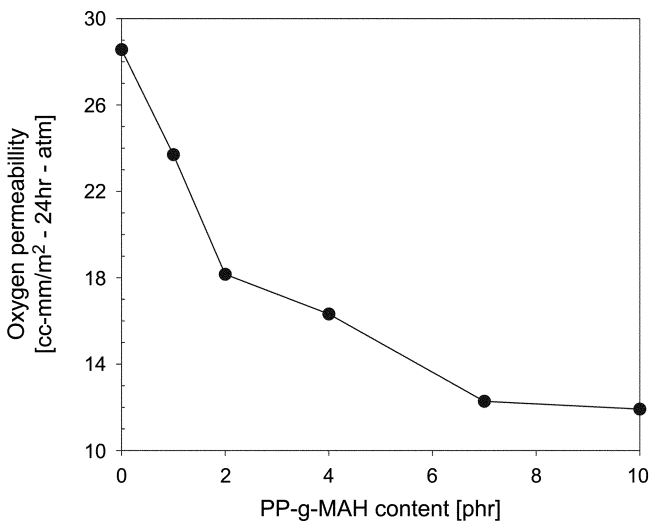

Fig. 5. Oxygen permeability of PP/PA (80/20) blend films as a function of compatibilizer content.

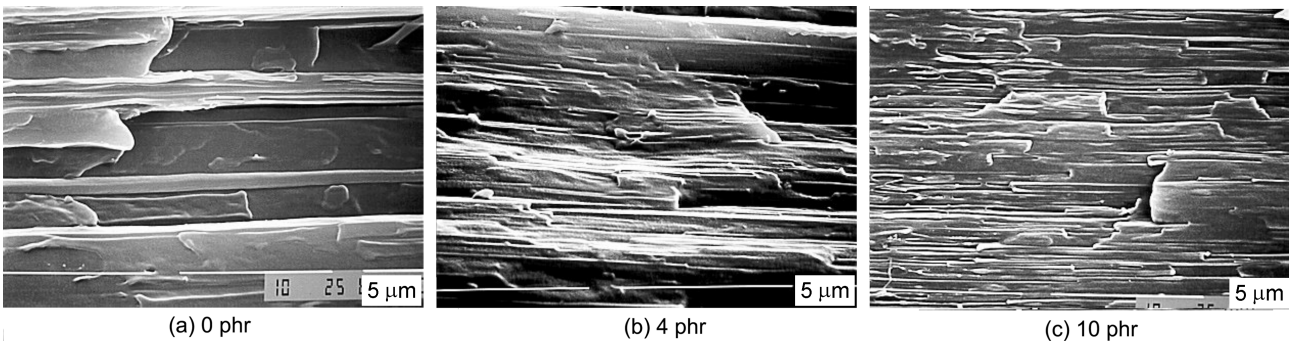

Fig. 6. SEM micrographs of PP/PA (80/20) blend films in machine direction with various compatibilizer content.

system with ellipsoidal shape of dispersed phase depends largely on the degree of interfacial adhesion between phases and on the homogeneous distribution of the dispersed phase.

Fig. 6 presents photomicrographs of the cross sections in the machine directions of PP/PA blend films produced at various compatibilizer contents. In this case, ellipsoidal morphology of the dispersed phase due to the dominant uniaxial extension in the machine direction could be achieved, exhibiting the distributed PA domains as large thin layers. These PA ellipsoids act as barriers to the permeant molecule by providing a long tortuous path. For the blend without compatibilizer, no morphological evidence of good interfacial adhesion between the dispersed and continuous phase could be observed, resulting in poor barrier property (permeability 28.6 cm^3-mm/m^2-24 hr-atm) because of diffusion of oxygen molecules through the microvoids formed at the interface during uniaxial orientation process.

4. Effect of Material and Process Parameter

The viscosity ratio playing an important role in morphology development depends on the viscosity of each component in the blends as well as the processing parameters such as shear rate and temperature. In this study, therefore, considering the factors affecting the viscosity ratio, the variations of oxygen permeability of blend film with various kinds of PP having different viscosities and screw rpm were investigated.

The influence of the viscosity of PP matrix and screw rpm on the oxygen permeability of the blend film is described in Fig. 7 and Fig. 8, respectively. The values of viscosity ratio corresponding to M.I. of PP and shear rate calculated by Eq. (1) were determined from the data shown in Fig. 2. As shown in the figures, the permeability of the blend film decreases as the viscosity ratio is reduced. It is believed that a lower viscosity ratio of less than unity induces easier deformation of dispersed phase, and thus generates the formation of well-extended ellipsoidal morphology with an enlarged aspect ratio (L/W), ultimately resulting in higher barrier property by increasing the tortuous path through blends. Therefore, matrix resin and rotation speed of screw to impart a lower viscosity ratio are found to be more favorable material and process parameters for producing blend films with high barrier property.

5. Effect of Moisture Absorption

Among the high barrier polymers, hygroscopic polymers such as PA and EVOH show serious reduction of permeation resistance in the presence of moisture, because water acts as a plasticizer, weakening the strong intermolecular forces. Thus, tracing the variation of the barrier property of blend film with contents of absorbed water is very essential for the application of packing material that is used in the atmosphere containing moisture.

Fig. 9 shows the absorbed moisture contents of blend films as a function of dispersed PA contents. Absorbed moisture increases

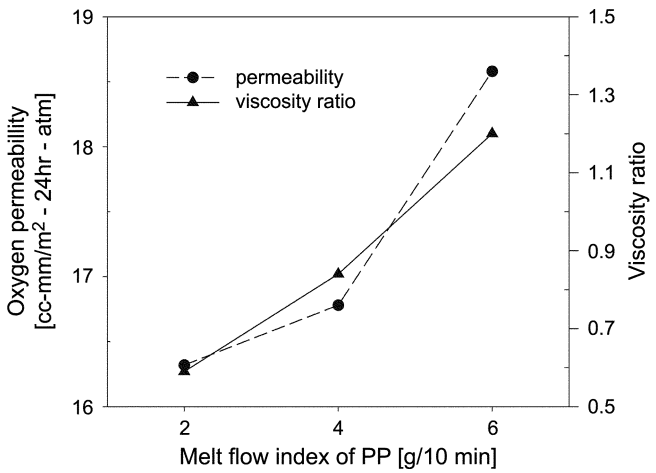

Fig. 7. The effect of rheological properties of PP matrix on the permeability of PP/PA blend film.

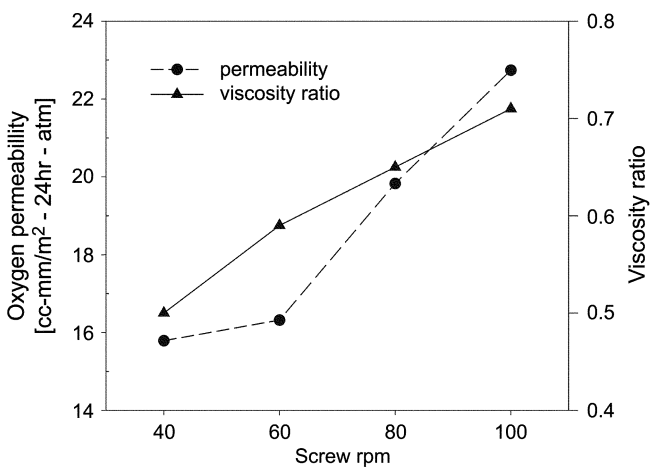

Fig. 8. Oxygen permeability and viscosity ratio of PP/PA blends as a function of screw rpm.

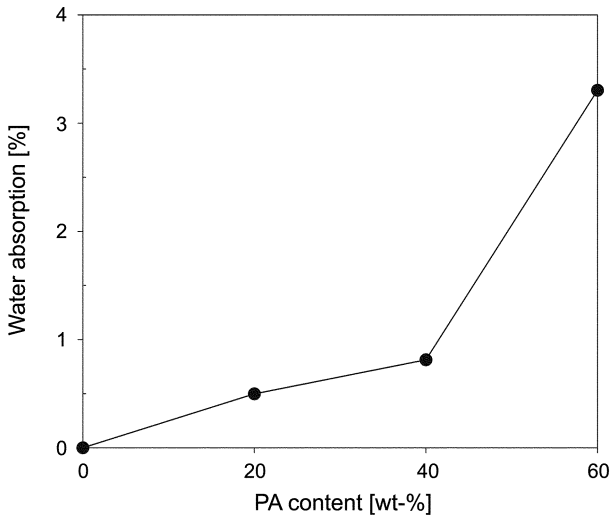

Fig. 9. Water absorption of PP/PA blends as a function of PA content.

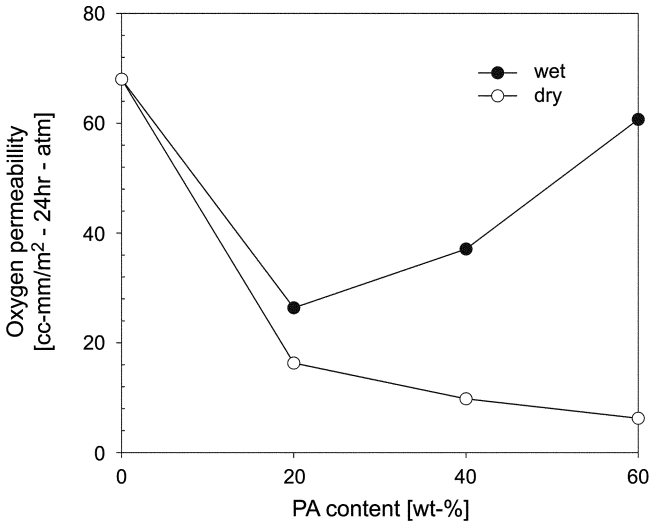

Fig. 10. Oxygen permeability of dried and wetted blend film as a function of PA content.

modestly up to 40 wt% of PA resin as PP with high moisture barrier property can suppress the moisture permeation into the blends, whereas, for the blend film containing 60 wt% of PA, dramatic increase in water absorption is observed due to phase inversion that the hygroscopic PA resin becomes the continuous phase.

The oxygen permeabilities of dried and wetted blend film are exhibited in Fig. 10. It is interesting to point out that the permeabilities of dried and wetted films decrease in a similar pattern up to 20 wt% of PA, but above this PA content, the permeability of wetted blend film increases in spite of increased PA content due to the effect of absorbed moisture. In addition, an increase of PA content contained in blend films resulted in an increase of discrepancy in permeabilities between two samples. These results imply that a blend film as a packaging material should be produced by incorporating small quantity of PA resin (below 20 wt% in this study) with PP matrix to be used in the humid atmosphere without loss of barrier property.

CONCLUSIONS

Using the extrusion casting film process, we obtained enhanced barrier PP/PA blend films having ellipsoidal structure of the dispersed phase. The effects of material, process parameters, and the absorbed moisture on the barrier property of the blends were investigated. In addition, the explanation on the variation of barrier property of blend film could be partially supported by morphological analysis and permeability modeling. The following conclusions have been made.

1. The predicted permeabilities of the blend film with ellipsoidal structure of the PA dispersed phase showed a good agreement with measured values by using Fricke's model expression, where the value of 19.6 for the aspect ratio (L/W) of the ellipsoid was determined from morphological observations.
2. The barrier property of the blend film was improved with an increase of added compatibilizer content, but above 7 phr, the amount of compatibilizer gave little effect on the barrier property, indicating that the barrier property of blend system with ellipsoidal structure depends largely on the interface between phases and on the homogeneity of the dispersed phase.
3. For the blend system with ellipsoidal structure of the dispersed phase, the control of material and process parameter to induce lower viscosity ratio less than unity was significant in obtaining high barrier blend films.
4. The moisture absorbed in the PP/PA blend film was found to be significant factor deteriorating the barrier property. It was revealed that blend film containing small quantity of PA resin (somewhat 20 wt%) was more favorable for packaging film to be used in the humid atmosphere without severe variation of barrier property.

NOMENCLATURE

B : width of die gap [cm]
H : height of the die gap [cm]
P : permeability [cc-mm/m^2-24 hr-atm]
Q : volumetric flow rate [cc/sec]

Greek Letters

$\dot{\gamma}$: shear rate [sec^{-1}]
η : viscosity [Pa·s]
λ : viscosity ratio
ϕ : volume fraction

Subscripts

d : dispersed phase
m : matrix phase

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