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Barrier Property by Controlled Laminar Morphology of LLDPE/EVOH Blends

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Abstract–Using the extrusion blown film process, we obtained linear low density polyethylene (LLDPE)/ethylene-vinyl alcohol copolymer (EVOH) blends with an improved barrier property by generating a laminar structure of the dispersed phase in the matrix phase. This laminar morphology induced by drawing and blowing was found to result in a significant decrease in toluene permeability with only 10 wt% EVOH. Effects of compatibilizer content and processing parameters such as blending sequence, screw configuration, and stretch ratio on the toluene permeability and morphology of the blends were investigated. It was revealed that the optimum amount of compatibilizer, maleic anhydride grafted LLDPE, should be used to improve the barrier property of the LLDPE/EVOH blends with a well developed laminar structure. The blending sequence had a significant influence on the permeability of the blends. The blend films exhibited a more pronounced laminar structure when all blend components were simultaneously melt blended in a single screw extruder. In addition, the screw configuration designed to impart a low shear stress and the balanced stretching in the machine and transverse directions were more favorable processing conditions in obtaining high barrier blends.

Key words : LLDPE/EVOH Blends, Barrier Property, Laminar Morphology, Toluene Permeability

INTRODUCTION

Plastic materials with good oxygen and solvent barrier properties have many advantages in comparison to metal and glass for use in packaging and solvent containers. These advantages include light weight, flexibility, strength, transparency, and ease of processing [Lohfink and Kamal, 1993; Faisant et al., 1998; Samios and Kalfoglou, 1998]. However, most single polymeric materials have high permeability of gases and organic solvents.

Polyolefins such as polyethylene and polypropylene are the most widely used resins in the application of films for packaging. These exhibit excellent moisture barrier properties but poor barrier properties for solvents and oxygen. On the other hand, ethylene-vinyl alcohol copolymer (EVOH) has high resistance to permeation of oxygen and hydrocarbons [Finch, 1993]. However, its permeation resistance is seriously reduced in the presence of moisture because water acts as a plasticizer, weakening the strong interchain forces. Thus, plastic films with high barrier properties are usually produced with a multi-layer structure using coextrusion or lamination process. During film processing, a layer of EVOH is sandwiched between layers of polyolefin resin having high water barrier properties [Finlayson, 1989]. These processing techniques require multiple extruders and dies, appropriate adhesives, and multi-step operations. Although multi-layer products attain a high degree of impermeability for packaging applications, they still require high capital investment and complex process control, and have a limitation of recyclability.

Currently, an alternative approach to overcome these shortcomings has been proposed by blending a small quantity of a barrier material with a lower cost polyolefin resin. In this polymer blend system, the improvement in barrier properties is accomplished through the formation of a laminar morphology of the dispersed phase, resulting in an increase of the tortuous path [Kamal et al., 1984; Subramanian, 1985; Subramanian and Mehra, 1987; Kamal et al., 1995; Holsti-Meittinen et al., 1995; Lee and Kim, 1997]. The barrier properties of a polymer blend depend not only on the intrinsic barrier property of each component but also on the final blend morphology. Droplet or fibrill-type morphology gives only modest permeability decrease with low content of barrier polymer, whereas a dramatic increase in barrier properties is achieved by generating a laminar morphology within the polymer blend during extrusion processing. The blend morphology is generally determined by many factors, such as rheological property of the components, interfacial tension, composition, stress level, mixing history, and procedure of blend preparation. Experimental studies have shown that high shear rate, viscosity ratio close to unity, and low interfacial tension are favorable for increasing the level of deformation and breakup of the dispersed phase droplets [Min et al., 1984; Wu, 1987; Gonzalez-Nunez et al., 1993]. It has been also confirmed that extensional flow is more efficient than shear flow in deformation of the dispersed phase during melt blending.

The first successful attempt in producing 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. Kamal et al. [1995] were also able to develop laminar morphology in PP/EVOH blends by incorporat-

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ing a specially designed slit die into the extrusion casting film process. Holsti-Miettinen et al. [1995] have studied the effects of composition, compatibilization, and blending procedure on oxygen barrier properties of injection-molded PP/PA6 blends having laminar morphology induced by shear and elongational flow.

The objectives of this study were : (i) to evaluate the feasibility of obtaining laminar morphology in the LLDPE/EVOH blend films using extrusion blown film process ; (ii) to study the effects of compatibilizer composition and processing parameters such as screw configuration, blending procedure, and stretch ratio on the barrier properties to solvents ; (iii) to investigate the relationship between the observed morphology and barrier properties of the LLDPE/EVOH blends.

EXPERIMENTAL

1. Materials

For the continuous phase, linear low density polyethylene (LLDPE, LLD6220F) supplied by Samsung General Chemicals was chosen. It is a blown film grade with density 0.92 g/cc, and melt flow index 0.9 g/min (190 °C, 2.16 kg). An ethylene vinyl alcohol copolymer (EVOH, EP-F101A) obtained from Kuraray Co. was used for the dispersed phase. This EVOH is a high barrier resin containing 32 % moles of ethylene with good optical clarity. It is a blow molding grade having density of 1.19 g/cc and melt flow index of 1.3 g/10 min. Since LLDPE and EVOH are incompatible, the compatibilizer as the interfacial agent was used to improve the interfacial adhesion between continuous and dispersed phase. This is an LLDPE resin with 0.1 wt %grafted maleic anhydride (LLDPE-g-MAH, Admer-NF510) manufactured by Mitsui Petrochemical Industries, Ltd. All three resins are commercially available, and are currently used in the extrusion process.

2. Preparation of Blend Films

Ternary blends of LLDPE/EVOH/LLDPE-g-MAH were prepared using an extrusion blown film machine (Placo LM-50B) with a screw diameter of 50 mm and L/D ratio of 29. Spiral mandrel die with a inner diameter of 100 mm and gap thickness of 2.4 mm was used. The temperature profiles for the three heating sections of the extruder barrel and die were set at 160, 180, 200, and 220 °C. Bubble cooling was carried out by air emerging from a cooling ring mounted directly on the die outlet. The blend films were stretched biaxially by drawing and blowing operation, which could result in the elongated morphology of the dispersed phase. In order to obtain the diverse patterns of morphology of the films, draw-down ratio (DDR), representing the degree of stretching in the machine direction (MD), was varied from 4.8, 9.6, 16.0, to 32.0, while bubble-up ratio (BUR), the degree of stretching in the transverse direction (TD), was fixed at 2.5. Generally, BUR and DDR are defined as the ratio of final film-tube diameter to die diameter, and the ratio of film velocity at the nip roll to average melt velocity in the die, respectively. Unstretched blend films having spherical morphology of the dispersed phase were prepared by hot pressing blend resins taken at the end of single-extruder from which the die was detached. Blends were processed in one or two steps to evaluate the effect of blending procedure on the barrier properties and the morphology of the blends. In the one-stage process, all blend components in pellet form were dry mixed mechanically, and then melt blended using a single screw extruder. The two-stage process consists in melt blending the compatibilizer and EVOH resin in twin screw extruder prior to dry blending with LLDPE. In addition to the energy transfer (ET) screw, a standard screw was also used to study the effect of screw configuration on the laminar morphology of the blends. An ET screw without mixing head is currently used for processing film-grade LLDPE in blown film applications. The standard screw, with a maddock mixing head placed at the end of the metering zone, has been generally applied in the polyolefin extrusion process. The length ratio of each section (feed/compression/metering) for ET and standard screw was 6 : 14 : 4 and 12 : 9 : 8, respectively. Before processing, EVOH was predried for 12 h at 70 °C in a dehumidifying dryer because of the hydroscopic behavior of EVOH. The standard conditions for compatibilizer composition and processing, which are summarized in Table 1, were used in all experiments except the variable to be investigated.

Table 1. Standard conditions for compatibilizer content and processing of LLDPE/EVOH blend films

Compatibilizer content	Screw type	Screw rpm	Stretch ratio	Blending sequence
4.0 wt%	ET	50	3.8	1-stage

3. Rheological Measurements

Using a Rosand capillary rheometer (model RH7-1C), we measured the shear viscosities of the molten LLDPE and EVOH in the range of shear rate between 4×10^1 and 2×10^3 sec^{-1}. The Bagley and Rabinowitch corrections were applied to the capillary rheometer data. The measurements were made at 210 °C and 230 °C, considering the actual temperature conditions in the extrusion die.

4. Morphological Analysis

The morphology of the blends was examined by a scanning electron microscope (SEM). In order to observe the structure of the dispersed phase after deformation by blown film extrusion, samples parallel to the machine direction were used. The blend samples were prepared by freeze-fracture in liquid nitrogen, and the fracture surfaces were coated with a thin layer of gold.

5. Permeability Measurements

The permeability of the LLDPE/EVOH blend was measured based on ASTM D2684-89. The sample with a diameter of 7.8 cm was inserted into the duralumin permeation cell separated by O-ring for sealing. Pure toluene was introduced in the cell and the solvent was allowed to penetrate under 40 °C in an air-circulating oven. The permeabilities were determined by measuring the average rate of loss weight.

RESULTS AND DISCUSSION

1. Rheological Properties

In the binary blend system, the viscosity ratio of the dispersed phase to the continuous phase ($\lambda=\eta_d/\eta_m$) is an important factor in controlling the blend morphology [Favis and Chalifoux, 1987]. A viscosity ratio close to unity induces easier deformation and breakup of the minor phase domains because of effective stress transfer from the continuous phase to the dispersed phase. Whereas, the extent of deformation is diminished as the deviation of the viscosity ratio from unity increases [Kamal et al., 1995]. Lee et al. [1997] also indicated that in the LDPE/EVOH blend, laminar structure was formed easily for a viscosity ratio close to one, but large fibrill structure was formed for the viscosity ratio of 2.41, resulting in poor barrier properties of the blends. To examine the range of viscosity ratio for pure component selected in this study, the melt shear viscosities as a function of shear rate were measured at 210 °C and 230 °C as shown in Fig. 1. The viscosity ratio of the EVOH dispersed phase to the LLDPE matrix could be obtained from the viscosity data. It can be seen that because of the shear sensitivity of viscosity of LLDPE, the viscosity ratio increases gradually with increase of shear rate, falling into the range between 0.65 and 1.05. The apparent shear rate in the annular die used for blown film processing can be expressed as follows [Lee and Kim, 1997],

$$\dot{\gamma}=\frac{32Q}{\pi D^3}\,\frac{[1-(1-\beta^2)/2\ln(1/\beta)]}{[(1-\beta^4)-(1-\beta^2)^2/\ln(1/\beta)]}$$

where Q is the volumetric flow rate (cc/s) ; D is the annular die diameter (10.0 cm) ; β is the ratio of inner die diameter divided by outer die diameter. In this blown film processing, shear rate in the die was estimated to be 80-100 sec^{-1} with melt temperature 230 °C and screw rpm 50. At both 210 °C and 230 °C the viscosity ratio corresponding to estimated shear rate is about 0.80, close to unity, which may provide the feasibility of producing laminar structure of the LLDPE/EVOH blends.

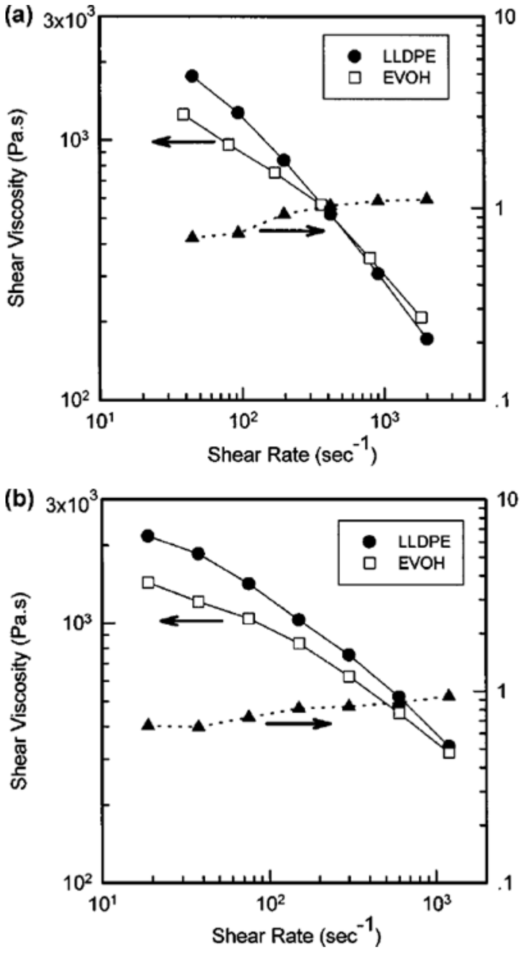

Fig. 1. Shear viscosity and viscosity ratio as a function of shear rate at (a) 210 °C and (b) 230 °C.

2. Effect of Dispersed Phase Morphology

Fig. 2 presents photomicrographs of LLDPE/EVOH blends fabricated under different processing conditions. Spherical dispersion was obtained by taking melted blends emerging from the end of a single-extruder prior to drawing and blowing. Fig. 2(b), (c) shows the photomicrographs of the cross sections in the machine and transverse directions of a LLDPE/EVOH film prepared by stretching the melted blends through the drawing and

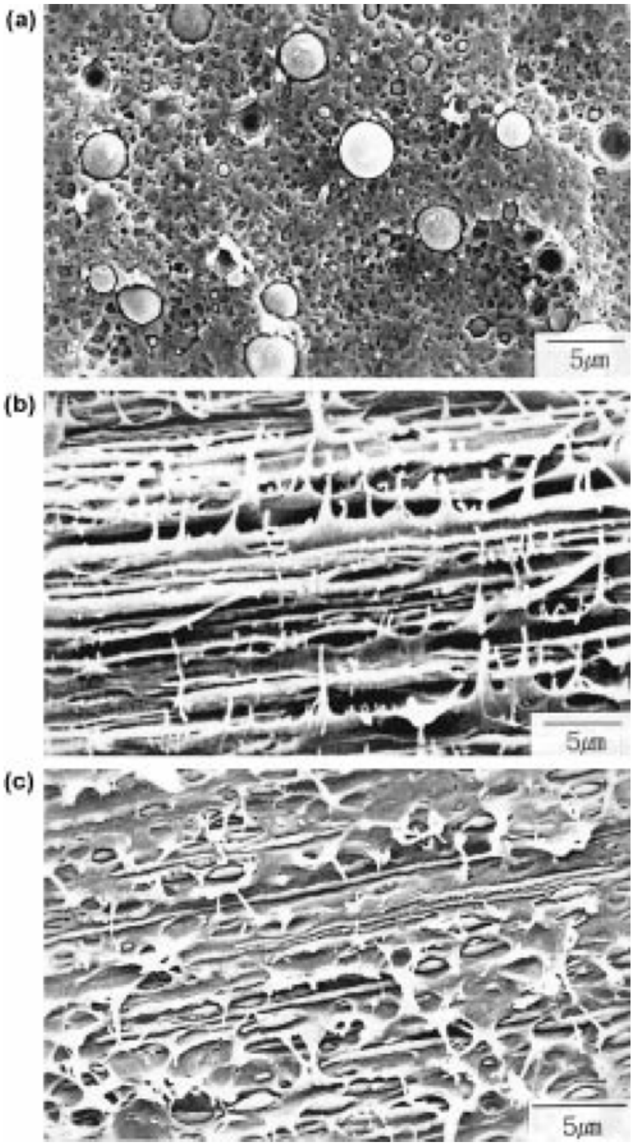

Fig. 2. SEM micrographs of LLDPE/EVOH (90/10) blends (a) before stretching, (b) after stretching (MD), (c) after stretching (TD).

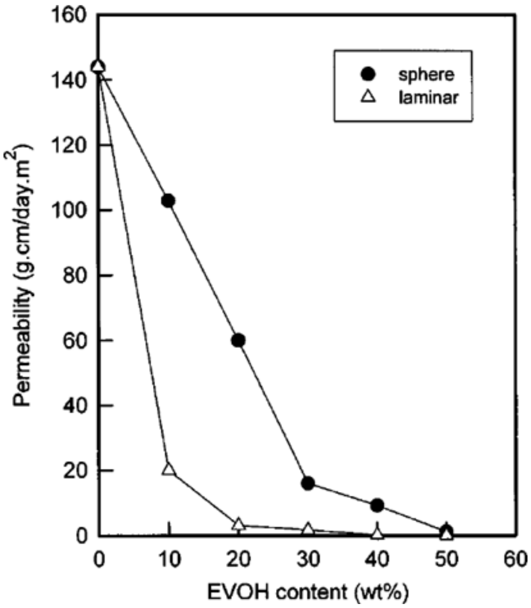

Fig. 3. Permeability of LLDPE/EVOH blends having different dispersed phase morphologies as a function of EVOH content.

blowing process. In this case, laminar morphology due to the biaxial extension could be achieved, showing the distributed EVOH domains as large thin sheets. These EVOH platelets act as barriers to the permeant molecule by providing a long tortuous path.

Permeability through a blend may be affected by factors such as phase separation, size distribution of the dispersed phase, and variations in shapes of the dispersed phase [Kamal et al., 1984]. Fig. 3 shows the permeability of LLDPE/EVOH blends for the different morphological shapes of the dispersed phase as a function of EVOH content. As expected, the results show that incorporation of EVOH reduces the toluene permeability. As the EVOH content increases, the permeability of the blend with spherical dispersion decreases modestly. However, the films with laminar dispersion offer significantly improved barrier properties at more than 10 wt% of EVOH. It is interesting to point out that irrespective of morphological shape, the permeabilities of the blends with 50 wt% of EVOH are almost identical, which may be attributed to the phase inversion that EVOH becomes the continuous phase.

3. Effect of Compatibilizer Content

In this study, the compatibilizer (LLD-g-MAH) was used to enhance the interfacial adhesion between dispersed and continuous phase and to obtain stable morphology in immiscible binary blends of LLDPE and EVOH. Compatibilization reaction between alcohol group of EVOH and maleic anhydride groups has been reported to give a finer and more homogeneous dispersion than in noncompatibilized blends [Botros, 1996; Hope et al., 1996]. In order to examine the compatibilization effect, the weight ratio of LLDPE/EVOH blend was fixed at 90/10, while the amount of compatibilizer was varied from 0 to 8 % of the weight of the blend. As shown in Fig. 4 permeability is initially reduced with increasing of compatibilizer content because of a larger number of thinner EVOH layers. However, poor barrier properties were obtained at high level of compatibilizer content. It appears that exceeding an optimum amount of compatibilizer content (4 wt% in this study) tends to extremely reduce the size of predeformed EVOH domains, and consequently diminish the length of EVOH layers. From this result, it is confirmed that there exists an optimum level of the maleic anhydride content for obtaining improved barrier properties with a well developed laminar structure.

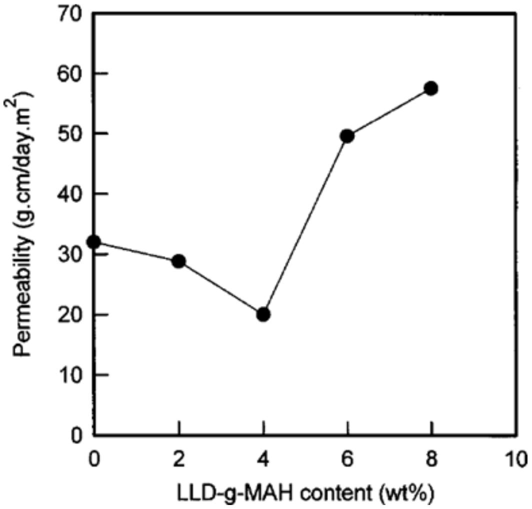

Fig. 4. Permeability of LLDPE/EVOH (90/10) blends as a function of compatibilizer content.

4. Effect of Blending Sequence

In compatibilized blends, the morphology of the dispersed phase has been found to strongly depend on the blending procedure [Holsti-Meittinen et al., 1995; Lee and Kim, 1997]. The effect of the blending sequence on the morphology and permeability was examined in LLDPE/EVOH blends compatibilized by LLD-g-MAH. The LLDPE/EVOH (95/5, 90/10, 85/15) blends were prepared by adding LLD-g-MAH compatibilizer with 2 %, 4 %, and 6 %, respectively. The influence of processing on

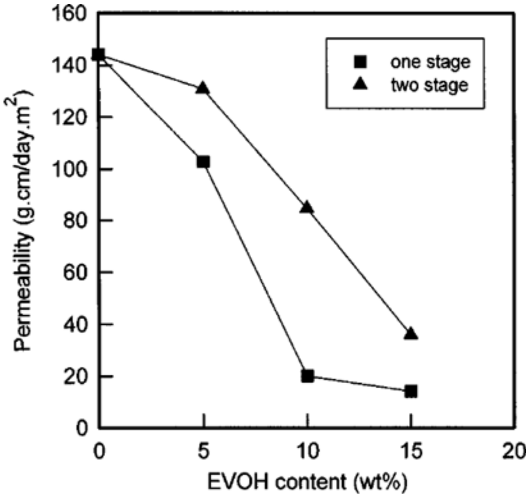

Fig. 5. Effects of blending sequence on the permeability of LLDPE/EVOH blends. The compatibilizer content was fixed at 4 % of the blend weight in all blends.

the permeability is depicted in Fig. 5. The permeability of the blends processed by two-stage method is higher than that of blends by one-stage method within the range of EVOH content up to 15 wt%. This result can be explained by morphological variation in the final blown film samples. In a two-stage process, preceding melt blending of EVOH with LLD-g-MAH enables the interfacial reaction between alcohol and anhydride to take place. The compatibilizer may be dispersed in the EVOH phase after melt blending. LLDPE-EVOH graft copolymer resulting from reaction between alcohol and anhydride seems to act as the effective compatibilizer. The copolymer may be preferentially located at the LLD-g-MAH/EVOH interface. When LLDPE is then melt blended with the blend of compatibilizer/EVOH, the improved compatibilization can be ensured by sufficient miscibility between the polyolefinic segments of the effective compatibilizer and LLDPE as well as additional reaction between unreacted MAH and alcohol group during extrusion blown film processing. Compared with 1-stage blending having insufficient compatibilization reaction, 2-stage blending method yields smaller predeformed domain size of the dispersed phase, which results in shorter EVOH platelets in elongated blown films. Fig. 6 shows the morphology of the compatibilized LLDPE/EVOH (90/10) blend films observed for the different blending methods. As shown in the figure, one-stage blending produced well-developed laminar morphology with a larger area of EVOH layers in comparison with two-step blending. Therefore, one-stage blending provides a longer path to travel through the blends and thus yields a lower toluene permeability.

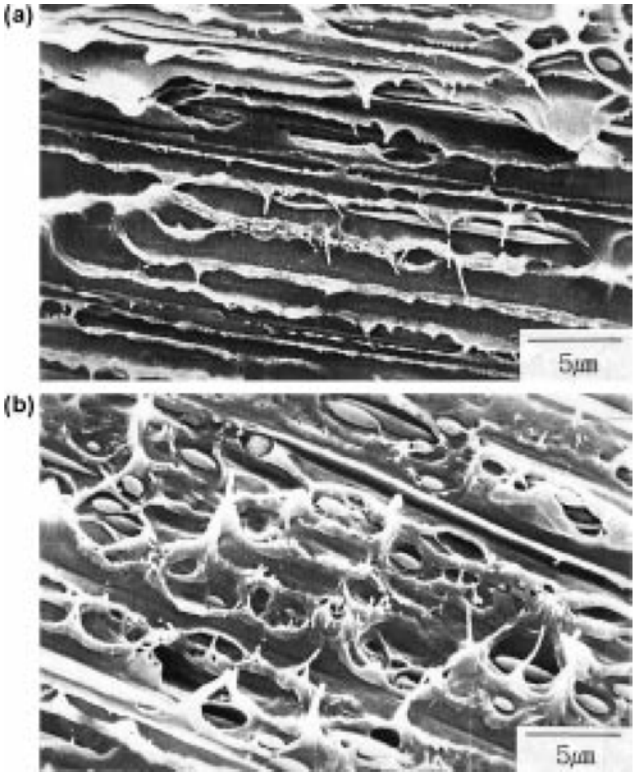

Fig. 6. SEM micrographs of LLDPE/EVOH (90/10) blends with different blending sequences; (a) one-stage blending, (b) two-stage blending.

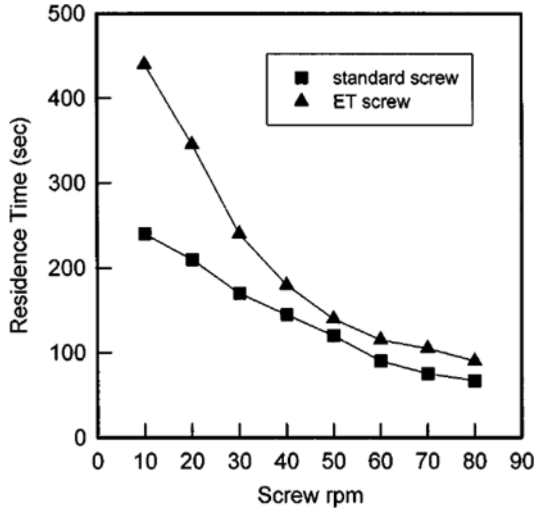

Fig. 7. Residence time vs. screw rpm for two different kinds of screw.

5. Effect of Screw Configuration

Two kinds of screws were used to study the effect of screw configurations on the permeability of the blends. As mentioned before, a standard screw with a maddock mixing head imparts a greater shear stress to the blend in the extruder barrel. The experimentally measured residence time as a function of screw rpm for two different kinds of screws is represented in Fig. 7. It reveals that the ET screw provides a longer residence time than a standard screw, and the difference is decreased initially and then becomes nearly constant at more than about 40 rpm.

The permeability of the compatibilized LLDPE/EVOH blend film processed at screw speed of 50 rpm was measured as a function of EVOH content as shown in Fig. 8. It reveals that the configuration of the ET screw is more effective to obtain high barrier blends through extrusion blown film processing. This result is somewhat different from that reported by Lee

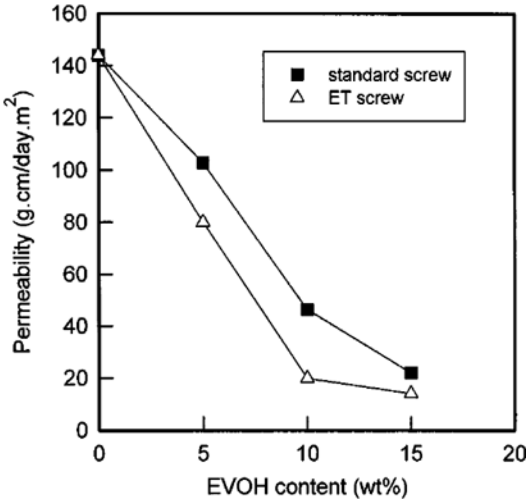

Fig. 8. Effects of screw configuration on the permeability of LLDPE/EVOH blends. The blends were processed at screw speed of 50 rpm.

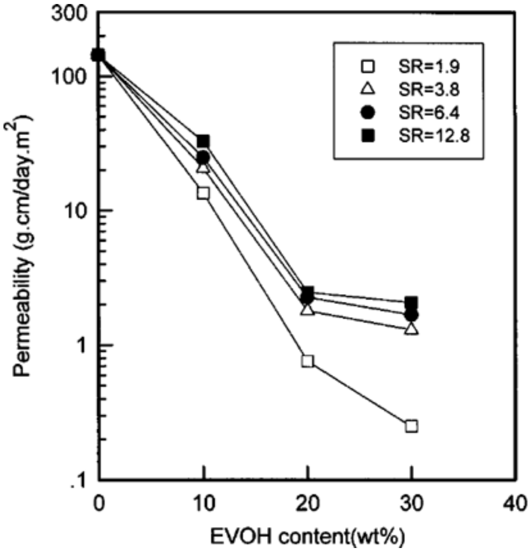

Fig. 9. Permeability of LLDPE/EVOH blends as a function of EVOH content for various stretch ratios.

and Kim [1997], who suggested that high screw rpm related to the short residence time yielded a larger predeformed domain due to insufficient melting of the dispersed phase, which resulted in more pronounced laminar structure in the LDPE/EVOH blend film. In this study, however, screw configuration rather than residence time was found to be the more significant processing parameter to control the morphological size of the dispersed phase, which depends on the mixing intensity. Subramanian [1985, 1987] also indicated that good mixing conditions with a high mixing intensity would not be suitable to produce laminar structure of the dispersed phase in the matrix phase.

6. Effect of Stretch Ratio

Stretch ratio (SR), defined as the ratio of DDR to BUR, is also an important processing variable in controlling the morphological structure of the dispersed phase. Fig. 9 shows the permeability of the blend film as a function of EVOH content for various values of SR. As shown in the figure, permeability was reduced with decreasing of SR at the same content of EVOH. A large value of SR implies that the degree of stretching in the machine direction is more dominant than that in the transverse direction, resulting in the fibrill morphology of the dispersed phase. On the other hand, a small value close to unity of SR means balanced stretching in both directions, which can ultimately produce laminar arrangements of the dispersed phase in the blown blend films. From these results, it is evident that balanced stretching is a more favorable processing condition for obtaining high barrier LLDPE/EVOH blend films.

CONCLUSIONS

Using the extrusion blown film process, it was possible to obtain laminar structure of the dispersed phase in LLDPE/EVOH blend films. The effects of morphological variation of the dispersed phase, compatibilizer content, blending sequence, screw configuration, and stretch ratio on toluene permeability of the blends were studied, and the results were partly explained by morphological analysis. The following conclusions were obtained.

1. A high increase in barrier properties of LLDPE/EVOH blends could be achieved by producing laminar structure within the blends through extrusion drawing and blowing process.
2. When LLD-g-MAH was used as a compatibilizer in this study, there existed an optimum level of compatibilizer content for obtaining improved barrier properties with a well developed laminar structure.
3. The blending sequence was found to have an influence on the permeability of the blends. For obtaining high barrier blend films with a larger number of thinner EVOH layers, the 1-stage blending method, in which all components were blended simultaneously in a single screw extruder, was more favorable than 2-stage blending accompanied by preblending of EVOH with LLD-g-MAH.
4. The screw configuration designed to generate a low shear stress was more effective in obtaining high barrier blends through extrusion blown film processing.
5. When stretch ratio (SR) close to unity was used in blown film processing, high barrier blends due to balanced stretching of the dispersed phase were obtained.

NOMENCLATURE

D : annular die diameter [cm]
Q : volumetric flow rate [cc/sec]

Greek Letters

β : ratio of inner die diameter to outer die diameter
$\dot{\gamma}$: shear rate [sec^{-1}]
η : viscosity [Pa · s]
λ : viscosity ratio

Subscripts

d : dispersed phase
m : matrix phase

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