Laminar Morphology Development Using Hybrid EVOH–Nylon Blends

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ABSTRACT: Properties of blends having two types of hybrid dispersed phases as laminar morphology were investigated. The hybrid dispersed phases were prepared by preblending nylon and ethylene–vinyl alcohol (EVOH) in solid state (E + N) and in melt state (E/N). Oxygen and toluene barrier properties through the hybrid-dispersed phases in low-density polyethylene (LDPE) matrix were analyzed considering the morphological changes (number and size of layers). Oxygen barrier properties of the blends of LDPE–E + N hybrid dispersed phase having separate domains of nylon and EVOH were found to be linearly dependent on EVOH composition in the blend, but toluene barrier properties of the blends exhibited negative deviation. The other hybrid dispersed phase (E/N) in LDPE matrix, having comingled dispersed phase of nylon and EVOH, exhibited positive deviations in both oxygen and toluene barrier properties. Tensile properties also showed positive deviation. Basic studies on the melt blend (E/N) of EVOH and nylon 6 showed some miscibility, which was revealed from melting point depression, and positive deviation in complex viscosity and tensile properties of the blend. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 2001–2014, 1998

Key words: hybrid dispersed phases; laminar morphology; oxygen and toluene barrier properties; tensile properties

INTRODUCTION

Ethylene–vinyl alcohol copolymer (EVOH) is recognized as the oxygen-barrier material in packaging applications for food and other products that require protection from oxygen due to its superior gas barrier property, excellent transparency, and high oil resistance.[1–3] However, EVOH also has a number of drawbacks. In particular, EVOH is relatively brittle, expensive, and absorbs moisture. On the other hand, it is also well recognized that nylon has good barrier properties against hydrocarbon solvent and exhibits outstanding levels of toughness while, at the same time, it offers good adhesion to a variety of resinous substrates or coatings. EVOH having 55 to 75 mol % of vinyl alcohol shows compatibility with nylon 6.[4–8] The industrial application of EVOH–nylon 6 blends has appeared in several patents.[4,5] However, detailed studies on their properties are sparse.[6–8]

In recent years, plastic containers having high barrier properties have been produced with a multilayer structure using coextrusion technology. One alternative to the multilayer extrusion is based on the use of a polymer blend system having dispersed lamellae of impermeable polymers. Many workers[9–15] have studied laminar morphology and barrier properties of blends, where EVOH or nylon has been chosen as the barrier layer. However, most studies on the laminar morphology have been focused on the use of single barrier polymer as a dispersed phase.

In this study, blends having two different barrier polymers, such as EVOH and nylon 6, as the dispersed phase in LDPE matrix were prepared, where the dispersed phase had two forms, dry

blend and melt blend of EVOH–nylon 6. We shall call these blends hybrid-dispersed phases. Morphology, oxygen, and toluene barrier properties and tensile properties of the blends having different hybrid dispersed phases, were investigated and compared to each other. It is also intended to compare them with the blends having exclusively one barrier polymer (EVOH or nylon 6) as the dispersed phase.

EXPERIMENTAL

Materials

As the matrix phase, LDPE (M.I.(g/10 min, 190°C, 2160 g) = 0.3) was obtained from LG Chemical Ltd., Korea. For dispersed phases, EVOH and nylon 6, which are known to have excellent barrier polymers, were used. EVOH [ethylene content (mol %) = 32] was obtained from Kuraray Co., Japan. Two commercial grades of nylon 6 having different melt viscosities were obtained from Tongyang Nylon Company, Korea: nylon 6 (L, low viscosity; Toplamid 1011; number-average molecular weight equal to 17,000) and nylon 6 (H, high viscosity; Toplamid 1031; number-average molecular weight equal to 23,000). Maleic anhydride-grafted LLDPE (LLD-*g*-MAH, wt % of MAH = 0.1) was used as the compatibilizer and was obtained from Mitsui Petrochemical Industries, Ltd., Japan.

Hybrid Dispersed Phase

E + N and E/N Preparation

Hybrid dispersed phases were prepared in two different methods. Dry blends of EVOH and nylon 6 (designated as E + N) were prepared by mixing dried pellets at room temperature. Melt blends of EVOH and nylon 6 (designated as E/N) were prepared by melt-mixing in a twin screw extruder (Brabender compounder DSK 42/7) operating at a constant rotating speed of 40 rpm and a temperature profile of 220, 230, 240, and 240°C. The weight ratio of the EVOH–nylon 6 blend is 75/25, 50/50, and 25/75. Before blending, EVOH and nylon 6 were respectively dried overnight in a vacuum oven at 60 and 100°C. The hybrid dispersed phases used in this study are summarized in Table I.

Analysis of E/N Blends

Properties of the melt-blended EVOH–nylon 6 (E/N) were investigated. Morphology of the

blends was observed with scanning electron microscope (SEM; Phillips 535M). The specimens were prepared by cryogenically fracturing a sample and covering with a thin layer of gold. Melting peak tmperatures of the blends were recorded using DuPont Thermal Analyzer 2000 model DSC at a heating rate of 10°C/min. Rheological properties of the blends were measured with a rotational rheometer (Physica Rheo-Lab MC120) using a cone and plate arrangement with a plate radius of 25 mm and a cone angle of 1°. In all cases, the sample gap was 50 μm, and the strain was maintained at 15%. The tests were carried out isothermally at 240°C. All tests were conducted in nitrogen atmosphere to prevent any oxidation effects. Tensile properties of the blends were measured with a tensile tester (Instron Model 4202) at room temperature following the procedure described in ASTM D638. For measurement of oxygen and toluene permeability of the blends, thin films were prepared by compression molding of the extruded pellets at 230°C for 2 min using Carver Lab Press Model C. Oxygen permeability of the blends was measured using a high-vacuum time lag technique described by Zhang et al.[16] The details of the procedure are summarized in Lee and Kim.[14] All tests were conducted at 30°C. Toluene permeability of the blends was determined by measuring the loss of weight in the permeation cell[13] with time. All tests were carried out at 30°C.

Film Extrusion of LDPE–(E + N, E/N)–LLD-g-MAH Blends

Blends having hybrid dispersed phases in the form of laminar morphology were prepared using C. W. Brabender Plasticorder ($\frac{3}{4}$ inch single screw extruder L/D = 20) fitted with annular blown film die. Biaxial stretching, such as drawing and blowing, was carried out to obtain elongated morphology. Draw-down and blow-up ratios were 3 in all cases. Processing temperature was in the range of 180–240°C, and the screw rotation speed was 60 rpm. Since the aim of this study was to achieve a layered dispersed phase structure with a small amount of the hybrid dispersed phase, the weight ratio of the LDPE–(E + N, E/N)–LLD-*g*-MAH was fixed at 74.1/18.5/7.4 wt %. Under a constant concentration of the hybrid dispersed phase (18.5 wt %), the relative weight ratios between EVOH and nylon 6 were changed from 75 : 25 to 25 : 75, as mentioned previously.

Characterization of LDPE–(E + N, E/N)–LLD-g-MAH Blends

Morphology of the blends was examined with the SEM described earlier. The specimens were pre-

Table I   Identification of Hybrid Dispersed Phases Used in This Study

EVOH : Nylon-6 (wt % : wt %)	Dry-Blended Phase (E + N)		Melt-Blended Phase (E/N)	
	E + NL[a]	E + NH[b]	E/NL	E/NH
75 : 25	E75 + NL25			
50 : 50	E50 + NL50	E50 + NH50	E50/NL50	E50/NH50
25 : 75	E25 + NL75			

[a] Low-viscosity nylon-6.
[b] High-viscosity nylon-6.

pared by cryogenically fracturing a sample and covering with a thin layer of gold. For the blends having E + N hybrid dispersed phase, SEM analysis was carried out on the fractured surface, which was previously treated for 24 h with a boiling dioxane–water mixture. Such mixture is a strong solvent for EVOH, while it is ineffective on nylon 6.[17] Therefore, it is possible that EVOH phase is selectively etched by the mixture. Oxygen and toluene permeability of the blends were measured with the same methods mentioned earlier. Tensile properties of the blends were also measured with the same method mentioned before.

RESULTS AND DISCUSSION

Melt Blends of EVOH and Nylon 6 (L) (E/NL)

Morphology

SEM electron micrographs of melt-blended EVOH–nylon 6 (L) are shown in Figure 1. Clear phase separation is not observed throughout the blend compositions tested. Such fine dispersion of EVOH–nylon 6 blends has been reported by other workers.[4–8] Following Venkatesh et al.[6] and Lee and Park,[7] it is reported that from Fourier transform infrared (FTIR) results, there are specific interactions between the hydroxyl group of EVOH and the amide group of nylon 6, where the intermolecular interactions increase with increasing concentration of nylon 6. These specific interactions could be responsible for the partial miscibility observed in the SEM results. The SEM results will also be discussed together with the other results from melting temperatures, rheological properties, and tensile properties in the next section.

Thermal Properties

Figure 2 shows DSC thermograms and variation of melting peak temperatures of the E/NL blends.

The melting peak temperatures for EVOH and nylon 6 (L) phases of the E/NL blends appear separately, and the melting peak temperature of one component decreases as the content of the other component increases. It is also seen that the melting peak temperature of EVOH is not clear in the nylon-rich composition. Melting point depression in polymer blends can be expressed by the following equation when both components are of high molecular weight[18,19]:

$$\Delta T_m = T_{m2}^0 - T_{m2} = -\frac{V_{2\mu}}{\Delta H_{2\mu}} B \phi_1^2 T_{m2}^0 \quad (1)$$

In this equation, component 2 is the crystallizable component, T_{m2}^0 is its equilibrium melting peak temperature, $\Delta H_{2\mu}/V_{2\mu}$ is its heat of fusion per unit volume of the repeat unit for 100 percent crystallinity, and ϕ_1 is the volume fraction of the other component in the amorphous phase. In a miscible blend, the interaction parameter B is related to the heat of mixing per unit volume (ΔH_{mix}) through

$$\Delta H_{\mathrm{mix}} = B \phi_1 \phi_2 \quad (2)$$

Therefore, with increasing miscibility, a smaller B and a larger effective ϕ_1 result, and this gives a larger ΔT_m. It is mentioned that the melting point depression of the blends confirms the fine (or no) phase separation observed by SEM.

Rheological Properties

Complex viscosities of the melt blended E/NL are given in Figure 3. In Figure 3, it is observed that nylon 6 (L) has lower viscosity than EVOH and that melt viscosities of the E/NL blends decrease with increasing concentration of nylon 6 (L). From Figure 3(b), we can find that the blends show positive deviation in complex viscosities over entire frequencies. It is known that the posi-
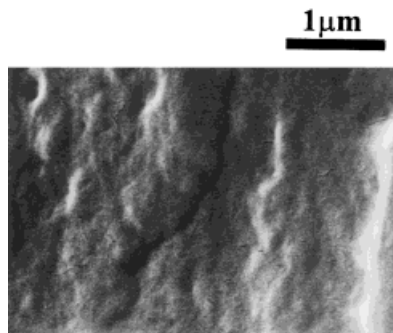
(a) E75/NL25


(b) E50/NL50

(c) E25/NL75

Figure 1 SEM electron micrographs of melt-blended EVOH–nylon 6 (L): (a) E75–NL25, (b) E50–NL50, and (c) E25–NL75.

tive deviation in viscosity generally occurs when strong interactions exist among components at low shear rate, or when the blend has an interlocked morphology.[20] In this system, it is difficult to distinguish the dispersed phase from the continuous phase. In addition to that, it is known that strong intermolecular interaction was attested by FTIR measurement.[6,7] These miscibility and strong intermolecular interaction may be responsible for

the positive deviation in complex viscosity. A typical modified Cole–Cole plot of the E/NL blends is shown in Figure 4. A modified Cole–Cole plot is useful in determining rheological compatibility of blends.[21–23] Rheological behaviors of immiscible polymer blends having dispersed minor phases are different from those of homogeneous polymer
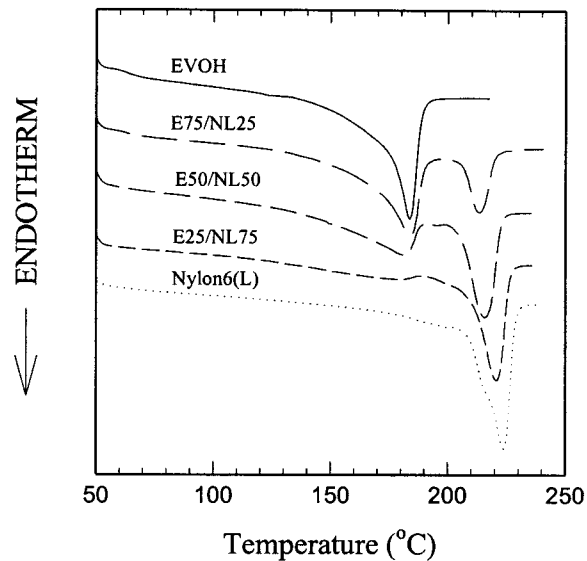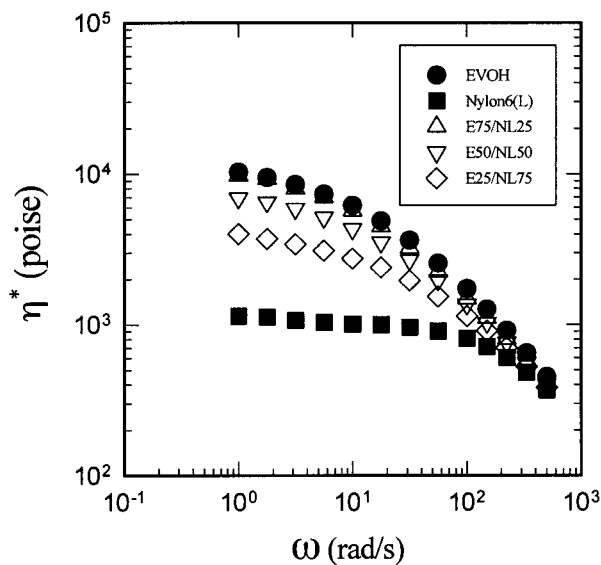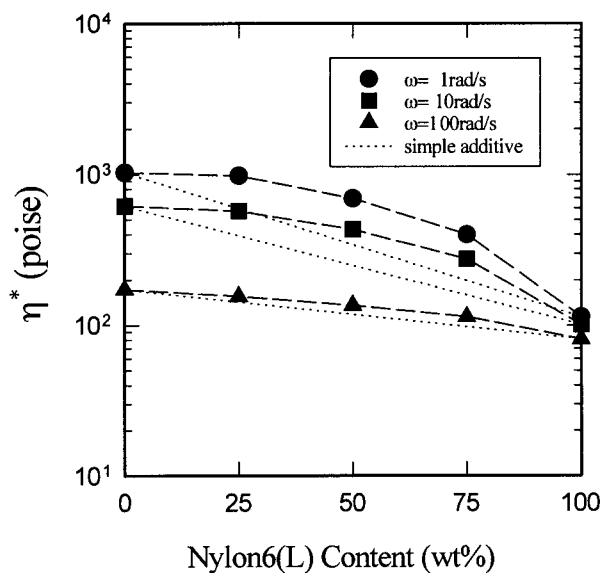

(a)
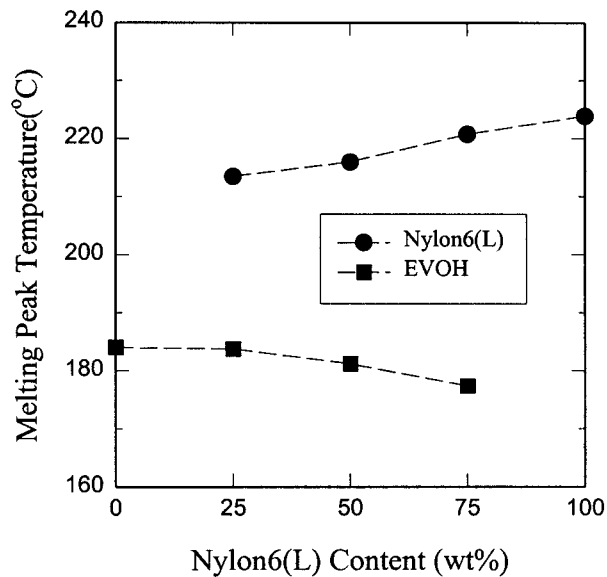
(b)

Figure 2 DSC heating thermograms and melting peak temperature (T_m) of melt blended EVOH–nylon 6 (L) (heating rate equals 10°C/min): (a) DSC heating thermograms; (b) melting peak temperature (T_m) versus nylon 6 (L) content.

systems owing to the contributions of the separated minor phase and of the interface between the two component phases. Figure 4 shows that, for a given G'', G' in the EVOH-rich composition is higher than those of other compositions, which implies the increase of the extent of phase separation in the EVOH-rich composition. It is known that the enhancement of elastic property G' at low frequency is due solely to the elastic interfacial
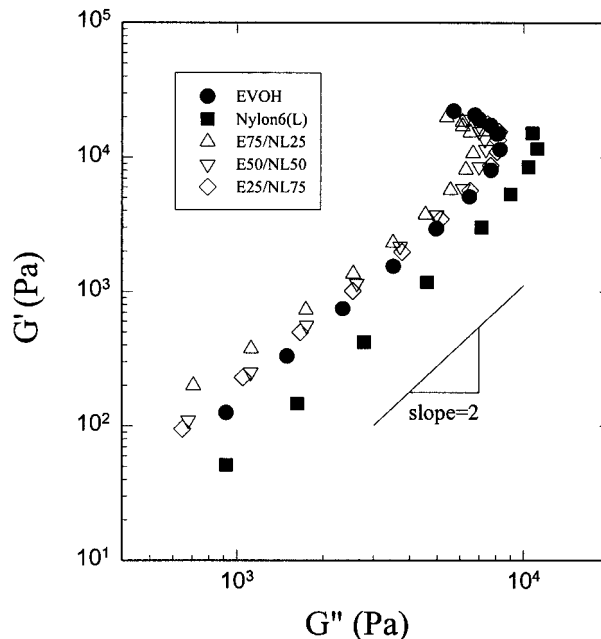

Figure 4 Modified Cole–Cole plots of melt-blended EVOH–nylon 6 (L).

energy associated with a separated minor phase.[24] In addition to the results of FTIR describing the larger intermolecular interaction in the nylon 6-rich composition,[6,7] the modified Cole–Cole plot again confirms the phase morphologies mentioned earlier, indicating a much finer phase separation in the nylon 6-rich composition than that of the EVOH-rich composition.

Tensile Properties

Tensile properties of the E/NL blends are shown in Figure 5. It is seen that tensile strength, tensile modulus, and elongation of the blends show a positive deviation from simple additive rule. The significant positive deviation in the elongation is especially worth noting. Similar to the results observed in the complex viscosity, the positive deviation in the tensile properties is probably related to the miscibility and strong intermolecular interaction between EVOH and nylon 6 (L).

Oxygen and Toluene Permeability

Oxygen and toluene permeability of the blends were investigated. The results are summarized in Table II. It is known that EVOH shows lower oxygen and toluene permeability than nylon 6,[3–5] and the oxygen barrier property difference between EVOH and nylon 6 is noticeably large. Table II shows that both the oxygen and toluene permeability of the blends decrease with increas-
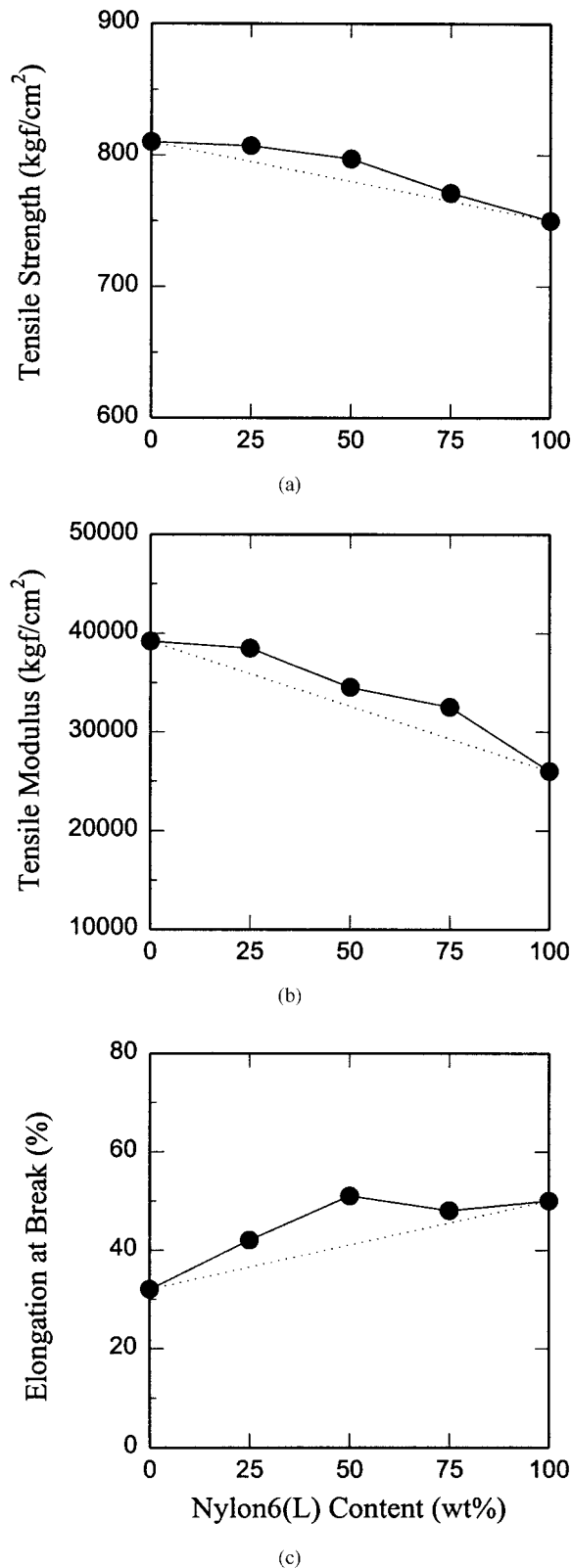

Figure 3 Complex viscosity (η^*) of melt-blended EVOH–nylon 6 (L): (a) complex viscosity (η^*) versus frequency (ω); (b) complex viscosity (η^* at $\omega = 1, 10, 100$ rad/s) versus nylon 6 (L) content.

Figure 5 Tensile properties of melt-blended EVOH–nylon 6 (L): (a) tensile strength, (b) tensile modulus, and (c) elongation at break.

ing concentration of EVOH. We find that the dependence of the permeabilities on the composition of the blends exhibits typical characteristics expected from partially miscible or even miscible blends. Partial miscibility of these blends has been previously cited in terms of morphology, thermal, rheological, and tensile properties. The decrease in the permeabilities of the blends seems to be a nonlinear function. The improvement in the barrier property is much greater than the increase in EVOH concentration would predict. It is also noticeable that the permeabilities in the EVOH-rich composition are comparable to those of 100% EVOH. Compared to the toluene barrier properties, it is remarkable that the oxygen barrier properties of the blends are highly improved by the addition of EVOH, which is possibly due to the difference in the oxygen and toluene barrier properties of EVOH itself, as mentioned previously.

LDPE–(E + N or E/N)–LLD-g-MAH Blends

Morphology

Effects of the blending type of the hybrid dispersed phase and the composition of EVOH and nylon 6 (L) in the hybrid dispersed phase on the laminar morphology of LDPE–(E + NL or E/NL)–LLD-g-MAH blends are shown in Figure 6.

We shall first consider the morphology of the dry-blended LDPE–(E + NL)–LLD-g-MAH blends. In these blends, a selective solvent of dioxane–water mixture for the EVOH phase was used to etch the dispersed EVOH phase. It is seen that EVOH and nylon 6 (L) separately exist as two independent dispersed phases. Although melt blending of EVOH and nylon 6 (L) may occur during film extrusion, the amount of the melt blend may be very small compared to EVOH and nylon 6 (L) phases existing separately in the LDPE ma-

Table II Oxygen and Toluene Permeability of Melt-Blended EVOH–Nylon 6 (L) (Measured at 30°C)

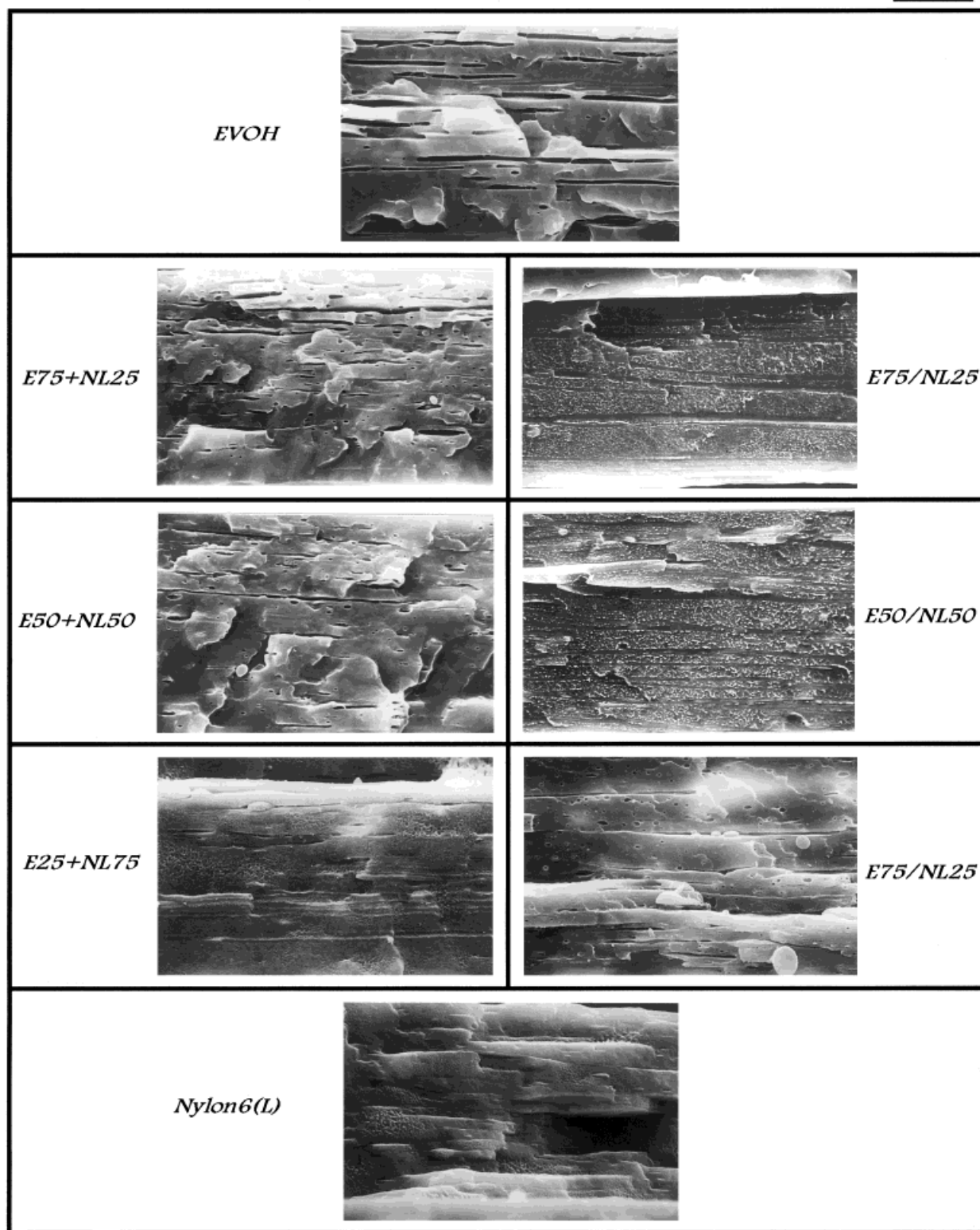| E/NL	P (oxygen) $\times 10^{13}$ (cm^3 cm s^{-1} cm^{-2} cmHg^{-1})	P (toluene) (g mm m^{-2} 24 h^{-1})
EVOH	0.31	0.08
E75/NL25	0.57	0.10
E50/NL50	1.63	0.14
E25/NL75	4.87	0.23
Nylon 6 (L)	13.79	0.29

Figure 6 SEM electron micrographs of LDPE–(E + NL or E/NL)–LLD-*g*-MAH (74.1/18.5/7.4 wt %) blends with different composition of EVOH and nylon 6.

trix. The morphology of the blends seems to be dependent mainly on the composition of EVOH and nylon 6 (L) in the E + NL hybrid dispersed phase. Many studies on the laminar morphology[9-15] have reported that the number and size of layers are largely dependent on the concentration of dispersed phase. Under the constant concentration of the hybrid dispersed phase (18.5 wt %), a larger portion of one component (EVOH or nylon 6 (L)) in the E + NL hybrid dispersed phase results in an increasing number of stacked pronounced layers of the component and a small number of short layers of the other component. Therefore, it is likely that the E + NL hybrid dispersed phase of the blends is composed of a simple sum of EVOH and nylon 6 (L) existing separately in the LDPE matrix. It is also noticed that the number and size of each dispersed phase comprising the E + NL hybrid dispersed phase are dependent on the relative composition of EVOH and nylon 6 (L).

Morphology of the melt-blended LDPE–(E/NL)–LLD-g-MAH blends is also investigated in Figure 6. Compared to the E + NL hybrid dispersed phase, the E/NL hybrid dispersed phase of these blends seems to form one dispersed phase, which is probably due to the partially miscible nature of EVOH and nylon 6 (L), as mentioned earlier. It is seen that as the relative portion of nylon 6 (L) in the E/NL hybrid dispersed phase increases, the thickness of layers becomes thinner, and the number of layers increases. It has been previously observed that nylon 6 (L) has the lower melt viscosity than EVOH and melt viscosities of the E/NL hybrid dispersed phases themselves show a tendency to decrease with increasing concentration of nylon 6 (L), which can influence the viscosity ratio between the E/NL hybrid dispersed phase and LDPE matrix. Figure 7 shows the viscosity ratio (η_d/η_m, where d is the dispersed phase and m is the matrix) of (E/NL)–LDPE as a function of frequency at 240°C. In Figure 7(a), it is seen that the viscosity ratio decreases over all frequencies with increasing nylon 6 (L) composition in the E/NL hybrid dispersed phase, which seems to be attributable to the decreased viscosities of the E/NL hybrid dispersed phases themselves. The effect of the viscosity ratio on the formation of elongated morphology has been studied by various investigators.[10-15,25-28] They observed various morphologies, depending on the viscosity ratio, and reported that lower viscosity ratio is more favorable for the deformation of domains. It is possible that, in the case of the E/NL hybrid dispersed phase, the decreased viscosity ratio favors the formation of well-developed laminar
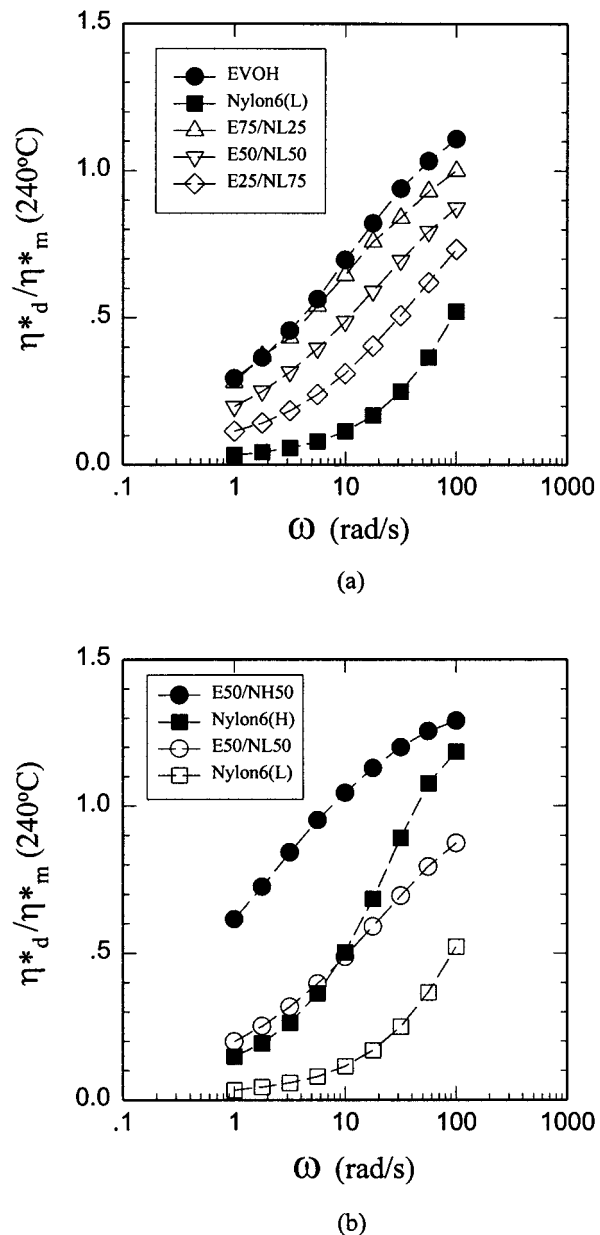

(a)

(b)

Figure 7 Viscosity ratio (η_d/η_m) of (E/N hybrid dispersed phase)–LDPE versus frequency (ω) at 240°C: (a) $\eta_{d(E/NL)}/\eta_{m(LDPE)}$ versus frequency (ω); (b) comparison of E/NL and E/NH.

structure. In these blends, it is likely that the E/NL hybrid dispersed phase seems to act as a new dispersed phase having different properties from EVOH and nylon 6 (L) themselves.

Morphology of LDPE–(E50 + NH50 or E50/NH50)–LLD-g-MAH blends is presented in Figure 8. Different from the E + NL and E/NL hybrid dispersed phases using nylon 6 (L), nylon 6 (H) was used in this case. Figure 8 shows that, compared to the hybrid dispersed phase of E50
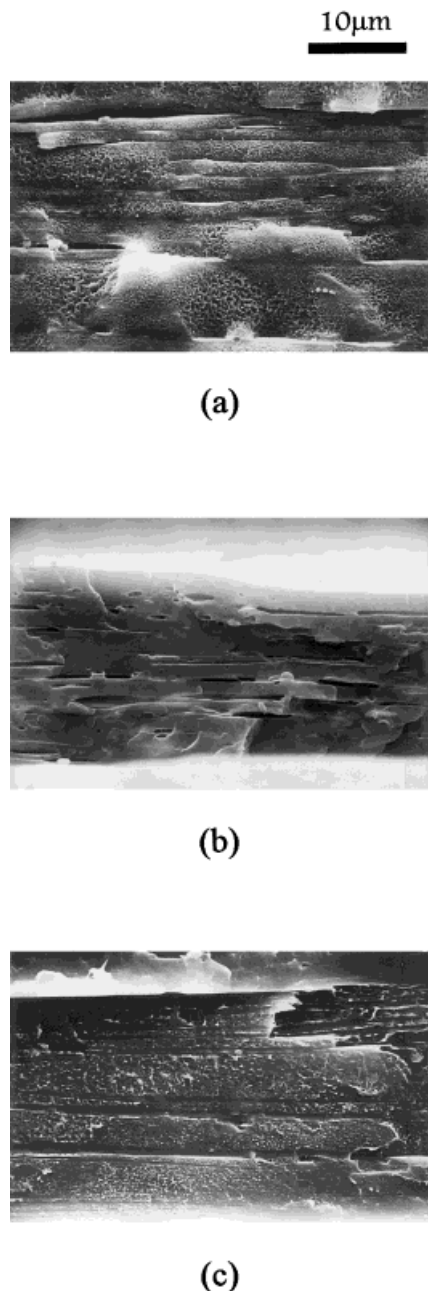
(a)

(b)

(c)

Figure 8 SEM electron micrographs of LDPE–(E50 + NH50 or E50–NH50)–LLD-*g*-MAH blends (74.1/ 18.5/7.4 wt %): (a) LDPE–nylon 6 (H)–LLD-*g*-MAH; (b) LDPE–(E50 + NH50)–LLD-*g*-MAH; (c) LDPE–(E50/NH50)–LLD-*g*-MAH.

+ NL50 or E50/NL50, these blends exhibit a small number of thicker layers, which may result from the higher viscosity ratio between the hybrid dispersed phase and LDPE matrix. In Figure 7(b), it is observed that when nylon 6 (H) is used, the viscosity ratio between the nylon 6 (H) (or E50/ NH50) and LDPE becomes higher than when the nylon 6 (L) is used. As mentioned previously, it is

believed that higher viscosity ratio in immiscible blends is not a favorable condition for the deformation of domains. Thus, it can be concluded that viscosity of nylon 6, as well as the relative portion of EVOH and nylon 6 in the hybrid dispersed phase, has an influence on the melt viscosity ratio of the blends, resulting in a significant effect on the laminar morphology formation.

Oxygen and Toluene Barrier Properties

Two different hybrid dispersed phases (E + N and E/N) are compared to each other in terms of oxygen and toluene barrier properties (Fig. 9) at a constant concentration of the hybrid dispersed phase (18.5 wt %). In Figure 9, barrier properties are presented as the barrier factor (P_{LDPE}/P_{Blend}).[13–15]

Let us first consider oxygen barrier properties of the blends. In Figure 9(a), it is seen that blend having an exclusively EVOH dispersed phase exhibits much better oxygen barrier properties than the blend having an exclusively nylon 6 (L) dispersed phase, which is probably due to the oxygen permeability difference of EVOH and nylon 6 themselves, as mentioned earlier. From Figure 9(a), we find that oxygen barrier factors of the blends having the E + NL hybrid dispersed phases become higher with an increasing relative EVOH portion in the E + NL hybrid dispersed phases, which seems to follow an approximately simple additive rule. Compared to the blends having the E + NL hybrid dispersed phases, it is observed that the oxygen barrier properties of the blends having the E/NL hybrid dispersed phases are superior and show positive deviation, which is a similar tendency observed in the E/NL hybrid dispersed phases themselves, which also exhibit disproportionately improved barrier properties (Table II).

It is well known that barrier properties of blends are largely dependent on morphology and permeability of components themselves.[9–15] It is possible that the oxygen barrier properties of the blends having the E + NL hybrid dispersed phases depend mainly on the relative portion of EVOH and nylon 6 in the E + NL hybrid dispersed phases. This implies that the oxygen barrier properties of the blends increase proportionally to the EVOH composition in the E + NL hybrid dispersed phases because EVOH shows much better oxygen barrier properties than nylon 6 (L).

For the blends having the E/NL hybrid dispersed phases, it has been previously mentioned that the E/NL acts as a new dispersed phase different from EVOH and nylon 6 (L) themselves,
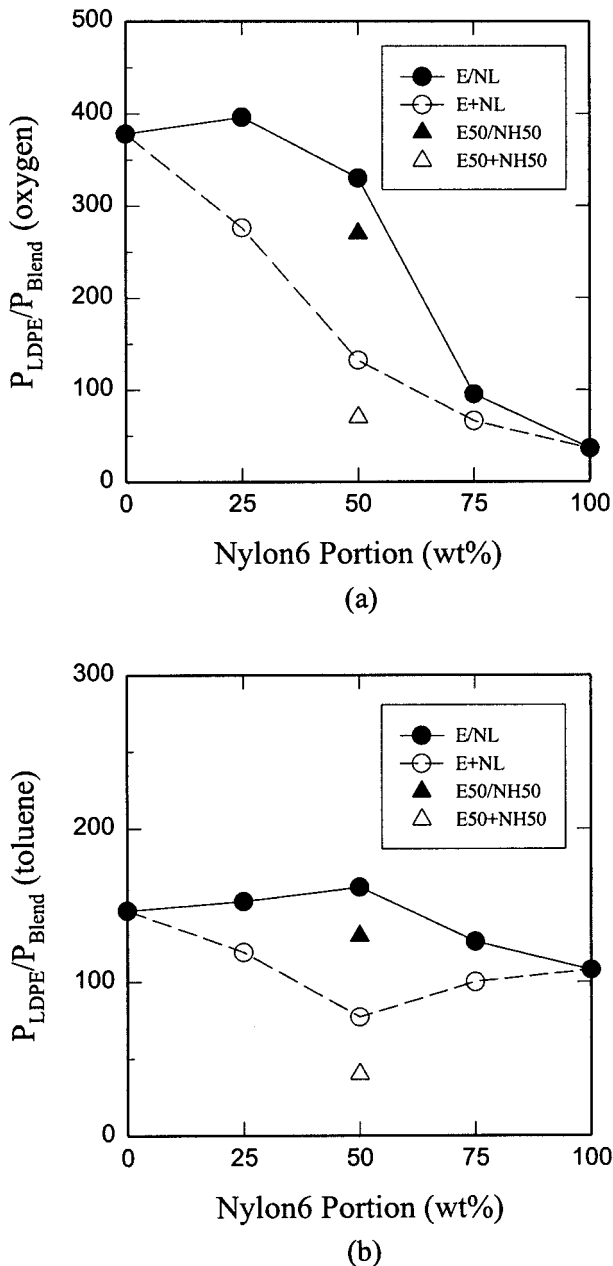
Figure 9 Oxygen and toluene barrier properties of LDPE−(E + N or E/N)−LLD-*g*-MAH blends: (a) oxygen barrier properties versus relative nylon 6 portion in the hybrid dispersed phase; (b) toluene barrier properties versus relative nylon 6 portion in the hybrid dispersed phase.

showing decreased oxygen barrier properties, as well as lower viscosity with increasing the relative nylon 6 (L) portion. Therefore, it is suggested that the oxygen barrier properties of the blends having the E/NL hybrid dispersed phases are influenced by both oxygen permeabilities of the E/NL hybrid dispersed phases themselves and morphological

changes of the blends due to the different viscosity ratio between the E/NL dispersed phase and LDPE matrix. For the blends having E75/NL25 and E50/NL50 as hybrid dispersed phases, the decrease in the oxygen barrier properties of the E/NL hybrid dispersed phases themselves is relatively small (Table II), and more and thinner layers are formed than the blend having exclusively EVOH dispersed phase, resulting in good oxygen barrier properties comparable to that of the blend having exclusively EVOH dispersed phase. Lee and Kim[14,15] reported that in LDPE−EVOH blends, thin and long EVOH layers in large numbers are more effective in improving oxygen barrier properties of the blends than thick and short layers. For the blends having E25/NL75 as a hybrid dispersed phase, the decrease in the oxygen barrier property of the E25/NL75 itself is severe, but it is still better than nylon 6 (L) itself, thus resulting in somewhat improved oxygen barrier properties than the blend having an exclusively nylon 6 (L) dispersed phase. Influence of the two different hybrid dispersed phases (E + NL, E/NL) on the oxygen barrier properties of the blends is schematically presented in Figure 10(a) in terms of the morphological changes and the oxygen barrier properties of the hybrid dispersed phases themselves, where brightness of color in the layer reflects oxygen barrier properties of the dispersed phases themselves; the darker the color, the better the oxygen barrier properties. It is seen that E + NL and E/NL form different shapes of dispersed phases, as previously discussed. In Figure 10(a), it is again confirmed that morphology and oxygen barrier properties of the blends are dependent on the relative portion of EVOH and nylon 6 (L) in the hybrid dispersed phase.

Toluene barrier properties of the blends having two different hybrid dispersed phases (E + NL and E/NL) are compared in Figure 9(b). It is seen that toluene permeability of the blends shows different results from oxygen permeability of the blends. Figure 9(b) shows that toluene barrier property of the blend having an exclusively EVOH dispersed phase is slightly better than that of the blend having an exclusively nylon 6 (L) dispersed phase. In Figure 9(b), blends having the E + NL hybrid dispersed phases show a negative deviation in toluene barrier properties, and a minimum value is observed at E50 + NL50 hybrid dispersed phase. Contrary to the blends having the E + NL hybrid dispersed phases, blends having the E/NL hybrid dispersed phases exhibit a positive deviation in toluene barrier properties, and a maximum
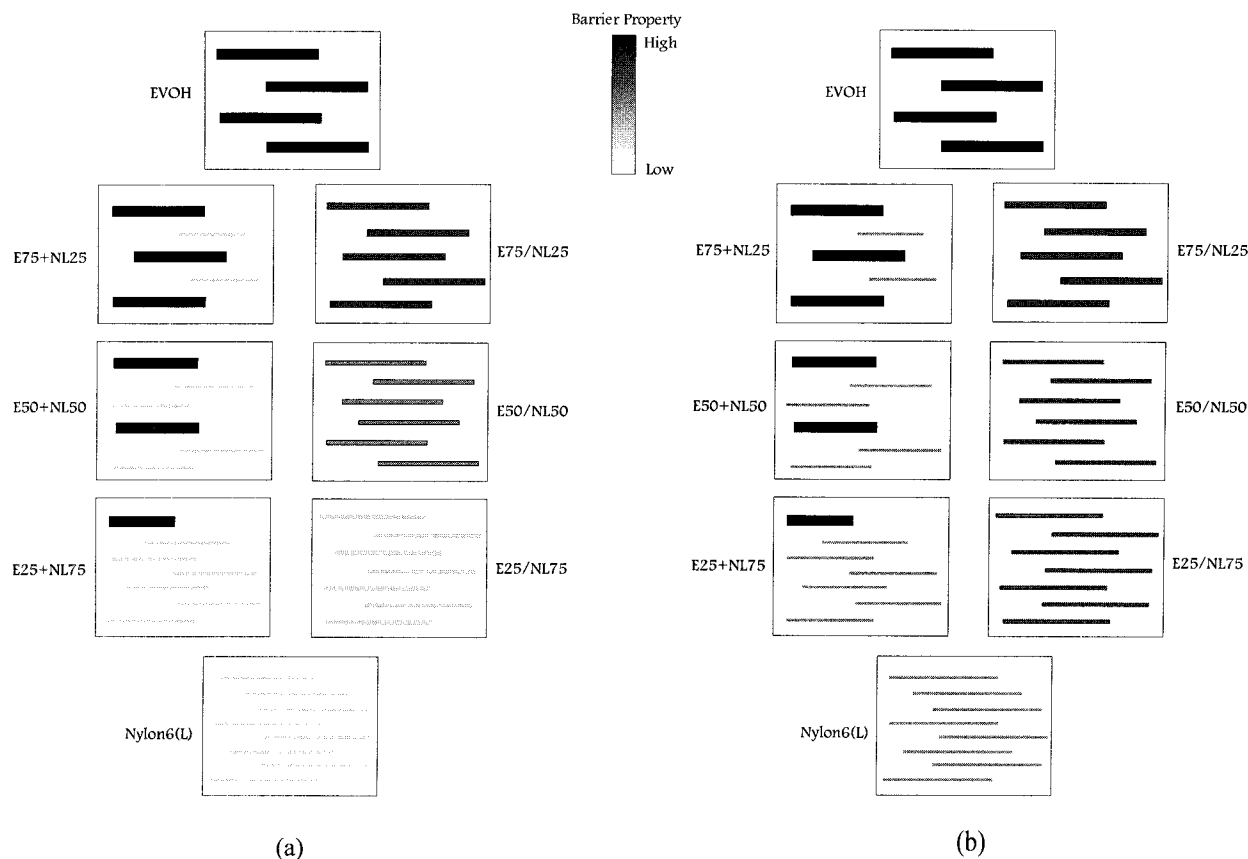
Figure 10 Schematic representation of the correlation between morphology and barrier properties of LDPE–(E + NL or E/NL)–LLD-*g*-MAH blends: (a) for oxygen barrier properties and (b) for toluene barrier properties.

value is observed at E50/NL50 hybrid dispersed phase.

Since the difference in toluene permeability between EVOH and nylon 6 (L) is small, it is possible that the toluene barrier properties of the blends having the E + NL hybrid dispersed phases are dependent mainly on the morphology of the dispersed phases, namely, the number and size of the dispersed phases, where a large number of long layers of the dispersed phases can be more useful in improving toluene barrier properties. As mentioned previously, the E + NL hybrid dispersed phase consists of simple sum of EVOH and nylon 6 (L) existing separately, whose number and size are, respectively, dependent on the relative portion of EVOH and nylon 6 (L). It indicates that in E75 + NL25 and E25 + NL75 hybrid dispersed phases, a large number of long layers of the major component and a small number of short layers of the minor component are formed; and in the E50 + NL50 hybrid dispersed phase, both components [EVOH and nylon 6 (L)] have an average number of medium-sized layers.

Therefore, the lower toluene barrier property of the blend having the E50 + NL50 hybrid dispersed phase results mainly from a relatively small number of short layers, compared to the other dispersed phases having a large number of long layers of at least one component.

For the blends having the E/NL hybrid dispersed phases, it is already mentioned that large number of thin layers are formed with increasing nylon 6 (L) portion in the E/NL hybrid dispersed phases. It has been mentioned already that, compared to the sharp decline of oxygen barrier properties of the E/NL hybrid dispersed phases themselves with increasing nylon 6 (L) portion, the decrease of toluene barrier properties of the E/NL hybrid dispersed phases themselves are small (Table II). It is believed that comparable toluene barrier properties of the E/NL hybrid dispersed phases themselves and favorable morphological changes may be responsible for the positive deviation in toluene barrier properties. For the blends having E75/NL25 and E50/NL50 hybrid dispersed phases, extensibility of the dispersed

phases is higher, owing to a lower viscosity ratio between the dispersed phase and LDPE matrix, where the contribution of morphological changes to the toluene barrier properties becomes more significant than a slight decrease of toluene barrier properties of the dispersed phases themselves, thus resulting in good toluene barrier properties. Similar to the oxygen barrier properties of the blends, the influence of two different hybrid dispersed phases (E + NL, E/NL) on the toluene barrier properties of the blends is schematically presented in Figure 10(b). It is seen that the difference in brightness of color between the dispersed phases is not severe, which is considered to be a main reason why the toluene barrier properties of the blends show different pattern from oxygen barrier properties under the same morphology for both cases. Figure 9 also shows that both oxygen and toluene barrier properties of the blends having E50 + NH50 or E50/NH50 hybrid dispersed phase are respectively lower than those of the blends having E50 + NL50 or E50/NL50. This is attributable to relatively small number of thick layers of the dispersed phases, which is due to the higher viscosity of nylon 6 (H) than that of nylon 6 (L). As discussed previously, the higher viscosity ratio between dispersed phase and matrix is not a favorable condition for the deformation of domains, thus yielding poor barrier properties of the blends. Considering above the oxygen and toluene barrier properties of the blends, it can be concluded that both morphological changes and difference in barrier properties of the dispersed phases themselves have influence on the barrier properties of the blends.

Tensile Properties

Tensile properties of the blends having two different types of the hybrid dispersed phases are compared in Figure 11. For the blends having the E + NL hybrid dispersed phases, tensile properties seem to be linearly dependent on the relative portion of EVOH and nylon 6 (L) in the E + NL hybrid dispersed phases, following the simple additive rule. As mentioned before, the E + NL hybrid dispersed phase is composed of a simple sum of EVOH and nylon 6 (L) existing separately in the LDPE matrix. Under this morphology of the blends, it is possible that the tensile properties of the blends are proportional to the relative portion of the components in the E + NL hybrid dispersed phases. Compared to the blends having E + NL hybrid dispersed phases, the blends having E/NL hybrid dispersed phases exhibit positive deviation

in tensile properties. It has been already mentioned that the E/NL dispersed phases themselves show positive deviation in tensile properties (Fig. 5), which may be responsible for the positive deviation of the blends. It is likely that both the morphological changes and the difference in tensile properties of the hybrid dispersed phases themselves have influence on the tensile properties of the blends.

CONCLUSIONS

In this study, blends having two different types of the hybrid dispersed phases (E + N and E/N) were compared in terms of morphology, oxygen and toluene barrier properties, and tensile properties. Basic properties of the E/NL hybrid dispersed phases themselves were also investigated. The results led to the following conclusions.

1. Fine phase separation, melting point depression, and positive deviation in complex viscosity and tensile properties were observed in the E/NL hybrid dispersed phases themselves, which were probably due to the miscible nature and increased intermolecular interaction between EVOH and nylon 6 (L). Intermolecular interaction between EVOH and nylon 6 (L) increased with increasing nylon 6 (L) content.

2. For the LDPE–(E + NL)–LLD-*g*-MAH blends, the E + NL hybrid dispersed phase was composed of simple sum of EVOH and nylon 6 (L) existing separately in the LDPE matrix. At a constant composition (LDPE–(E + NL)–LLD-*g*-MAH = 74.1/18.5/7.4 wt %), the number and size of the dispersed phases were respectively dependent on the relative portion of EVOH and nylon 6 (L). Properties of the blends were found to be linearly dependent on the relative portion of the components in the E + NL hybrid dispersed phases, which could affect morphology of the blends. Oxygen barrier properties of the blends were linearly dependent on the EVOH portion in the E + NL hybrid dispersed phases, and toluene barrier properties showed negative deviation under the same morphology for both cases, which possibly resulted from the difference in the oxygen and toluene permeability of EVOH and nylon 6 (L) themselves. Tensile properties of the blends were proportional to the relative por-
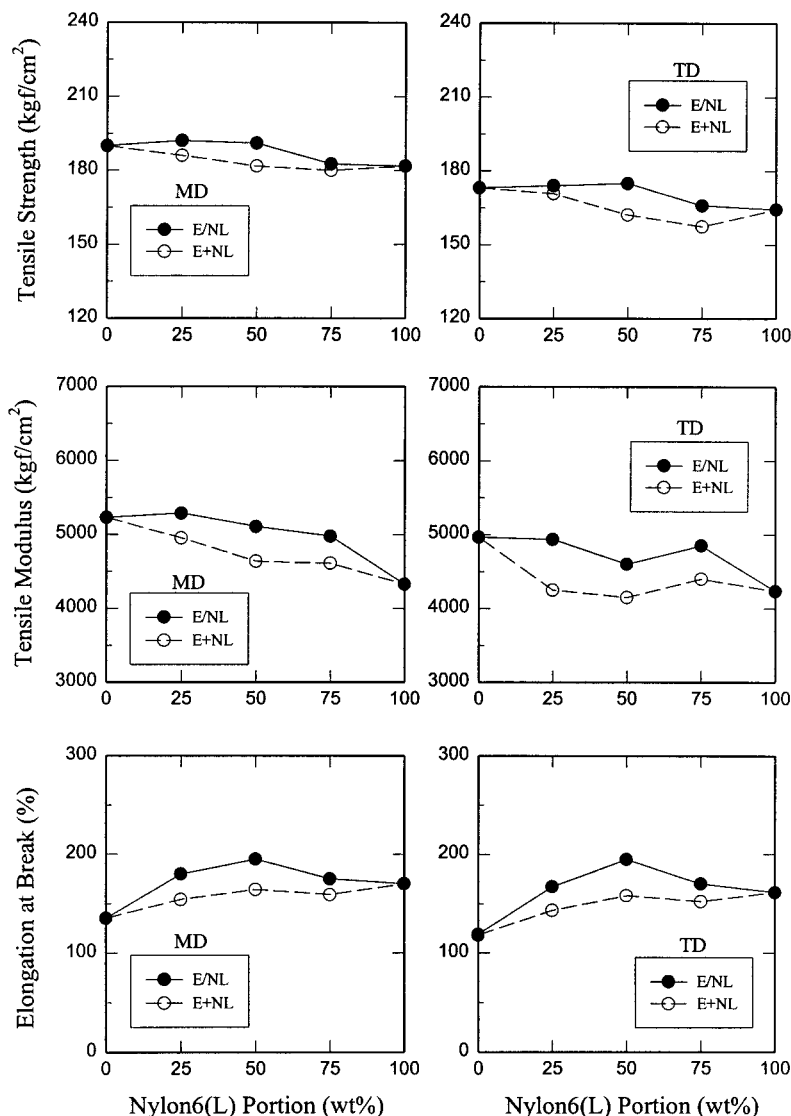
Figure 11 Tensile properties of LDPE–(E + NL or E/NL)–LLD-*g*-MAH blends versus the relative nylon 6 (L) portion in the hybrid dispersed phases.

tion of the components in the E + NL hybrid dispersed phases.

3. For the LDPE–(E/NL)–LLD-*g*-MAH blends, the E/NL hybrid dispersed phase seemed to act as a new dispersed phase having different properties from EVOH and nylon 6 (L) themselves. At a constant composition, a large number of thin layers were formed with increasing nylon 6 (L) portion, which was due to the decreased viscosity ratio between the dispersed phase and LDPE matrix. Positive deviation in both oxygen and toluene barrier properties of the blends was observed, which was probably resulted from comparable barrier properties of the E/NL hybrid dispersed phases themselves and favorable morphologi-

cal changes. Tensile properties of the blends also exhibited positive deviation, which seemed to be influenced by positive deviation in tensile properties of the E/NL hybrid dispersed phases themselves.

4. Compared to the blends having a E50 + NL50 (or E50/NL50) hybrid dispersed phase, blends having a E50 + NH50 (or E50/NH50) hybrid dispersed phase showed a small number of thick layers, which was believed to be due to the higher viscosity of nylon 6 (H) than that of nylon 6 (L). It was also responsible for relatively poor oxygen and toluene barrier properties of the blends.

REFERENCES

1. C. A. Finch, *Polyvinyl Alcohol,* John Wiley and Sons, New York, 1992.
2. W. J. Karos, *Barrier Polymers and Structures,* ACS Symposium Series 423, American Chemical Society, Washington, DC, 1989.
3. K. M. Finlayson, Plastic Film Technology: High Barrier Plastic Film for Packaging, Technomic Publishing Co., Lancaster, Pa. (1989).
4. U.S. Pat. 4,347,332 (1982).
5. U.S. Pat. 4,427,825 (1984).
6. G. M. Venkatesh, R. D. Gilbert, and R. E. Fornes, *Polymer,* **26,** 45 (1985).
7. J. W. Lee and O. O. Park, M. Eng. Thesis, KAIST, Taejon, Korea, 1996.
8. T. O. Ahn, C. K. Kim, B. K. Kim, H. M. Jeong, and J. D. Huh, *Polym. Eng. Sci.,* **30,** 341 (1990).
9. P. M. Subramanian and V. Mehra, *Polym. Eng. Sci.,* **27,** 663 (1987).
10. G. W. Lohfink and M. R. Kamal, *Polym. Eng. Sci.,* **33,** 1404 (1993).
11. M. R. Kamal, M. Garmabi, S. Hozhahr, and L. Arghyris, *Polym. Eng. Sci.,* **35,** 41 (1995).
12. R. Gopalakrishnan, J. M. Schultz, and R. M. Gohil, *J. Appl. Polym. Sci.,* **56,** 1749 (1995).
13. S. Y. Lee and S. C. Kim, *Korean J. Rheol.,* **5,** 125 (1993).
14. S. Y. Lee and S. C. Kim, *Int. Polym. Proc.,* **11,** 238 (1996).
15. S. Y. Lee and S. C. Kim, *Polym. Eng. Sci.,* **37,** 463 (1997).
16. W. Z. Zhang, M. Satoh, and J. Kamiyama, *J. Membr. Sci.,* **31,** 147 (1987).
17. P. Laurienzo and M. Malinconico, *Proceedings of the Twelfth Annual Meeting of The Polymer Processing Society,* Sorrento, Italy, 1996, p. 205.
18. T. Nishi and T. T. Wang, *Macromolecules,* **8,** 909 (1975).
19. A. C. Fernandes, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.,* **29,** 1971 (1984).
20. C. D. Han, *Multiphase Flow in Polymer Processing,* Academic Press, New York (1981).
21. C. D. Han and J. K. Kim, *Polymer,* **34,** 2533 (1993).
22. C. D. Han, D. M. Baek, and J. K. Kim, *Macromolecules,* **23,** 561 (1990).
23. S. S. Kim and C. D. Han, *Macromolecules,* **26,** 3176 (1993).
24. J. D. Lee and S. M. Yang, *Polym. Eng. Sci.,* **35,** 1821 (1995).
25. R. Gonzalez-Nunenz, B. D. Favis, and P. J. Carreau, *Polym. Eng. Sci.,* **35,** 851 (1993).
26. P. V. Gheluwe, B. D. Favis, and J. P. Chalifoux, *J. Mater. Sci.,* **28,** 3910 (1988).
27. K. Min and J. L. White, *Polym. Eng. Sci.,* **24,** 1327 (1984).
28. L. A. Utracki, *Polymer Alloys and Blends,* Oxford University Press, New York (1989).