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Phase Behavior of Poly(ethylene-*co*-vinyl alcohol)/Nylon 6—12 Blends

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ABSTRACT: Phase behavior of blends of poly(ethylene-*co*-vinyl alcohol) containing 59 mol% of ethylene units (EVOH59) with nylon 6—12 (PA6—12) containing 60 mol% of nylon 6 units was investigated by cloud point measurements and dynamic mechanical measurements. From the results, lower critical solution temperature (LCST) type phase behavior was found in EVOH59/PA6—12 blends above apparent melting points. To account for this, melting point depression was applied to EVOH59/PA6—12 blends to estimate the interaction parameter, χ, between EVOH59 and PA6—12. The estimated value of χ was -0.58.

KEY WORDS Blends / LCST Phase Behavior / Poly(ethylene-*co*-vinyl alcohol) / Nylon 6—12 / Melting Temperature Depression / χ Parameter /

In the last decades, advanced investigations of polymer blends have reported that induced synergistic properties of polymer blends are attributed to miscibility and phase separated structure.[1-4] Phase separated structures of polymer blends can be controlled by using phase diagram. Therefore, investigation of miscibility and phase behavior in polymer blends have great importance for polymer technology. To interpret miscibility and phase behavior in polymer blends, Flory–Huggins interaction parameter, χ, has great importance because of negligible small value of combinatorial entropy of mixing arisen from high value of degree of polymerization in each polymer components.

Several methods for direct determination of χ parameter have been proposed such as melting temperature depression,[5] small angle neutron scattering,[6] gas-liquid chromatography,[7] vapor sorption[8] and ellipsometory.[9] Among these, melting temperature depression is readily adaptable to a binary polymer mixtures containing crystalline polymer as one of its components. Melting temperature depression method for determination of χ parameter was applied to polymer blends by Nishi and Wang and several studies concerned with this method have been published[10] to determine χ parameter.

In this study, phase behavior of blends of poly(ethylene-*co*-vinyl alcohol) containing 59 mol% of ethylene units (EVOH59) with copolyamide constructed by nylon 6 and nylon 12 units containing 60 mol% of nylon 6 units (PA6—12) was investigated by cloud point measurements and dynamic mechanical measurements. χ for EVOH59/PA6—12 blends was determined by melting temperature depression method. Although both EVOH59 and PA6—12 were crystalline polymers, this method may be applied to this system using a temperature region where either EVOH59 or PA6—12 is crystallized.

Since poly(ethylene-*co*-vinyl alcohol) (EVOH) has excellent gas barrier properties, they have been applied to packages.[11,12] Especially, blends or composites of EVOH and nylon are used for tubes because the materials constructed from these polymers are strong enough to

withstand deformation.[11] Therefore, studies of EVOH/nylon blends or composites such as on miscibility are important. However, studies on EVOH have been mainly concerned with crystalline structure[13-16] and study on miscibility in blends including EVOH has not been reported. Therefore, study on miscibility of EVOH/nylon blends should indicate fundamental properties for technology of wrapping.

EXPERIMENTS

Samples

Poly(ethylene-*co*-vinyl alcohol) containing 59 mol% of ethylene units (EVOH59) was supplied by Kuraray Co., Ltd. Nylon 6—12 containing 60 mol% of nylon 6 units (PA6—12) was purchased from EMS Japan Co., Ltd. Properties of each polymers are listed in Table I. In this table, the values of thermal expansivity of EVOH59 and PA6—12 in melt state were determined by the density gradient method and dilatometer.

Preparation of Blend Samples

For cloud point measurements and differential scanning calorimetry (DSC), blend samples were prepared by solution mixing. In solution mixing, each polymers were dissolved in hexafluoroisopropanol at about 5 wt% of polymer concentration and stirred overnight. Solution were cast on glass plates and then placed at room temperature for a day. As-cast films, after placed at room temperature, were seasoned under vacuum at 80°C for a week.

For dynamic mechanical measurements, polymers were mixed mechanically using a roller mixer (Nitto Hannoki Seisakusho Co., Ltd.) at 180°C and then molded by hot-press at 180°C to prepare the test pieces.

Before measurements, all samples were annealed above melting temperature for 2 h to remove any internal strain of the samples.

Dynamic Mechanical Measurements

Dynamic mechanical measurements were carried out in a tension mode at 0.01 Hz of frequency and 1 deg min^{-1} of heating rate by using Seiko Instruments Inc. Rheol. Station SDM 5600H system equipped with DMS-200. Before measurements, samples were annealed at 150 or 170°C for 2 h and then quenched in liquid N_2.

Cloud Point Measurements

Cloud points were measured using a hand made thermo-photometer[17-19] equipped with CHINO KP-1131 temperature controller in heating process with various heating rate. A He–Ne gas laser (Spectra Physics Model 105-1) of wave length 632.8 nm was used as the light source. A laser beam was applied vertically to the film samples and transmitted light intensity was detected by photo diode.

Melting Point Measurements

Samples, after annealed at 170°C for 2 h, were quenched to desired crystallization temperature (T_c) and kept at T_c for several hours. Melting temperature (T_m) was measured by a Du Pont 990 thermal analyzer equipped with 910 DSC. Since heating rate dependence of T_m was not observed in EVOH59, measurements for the other samples

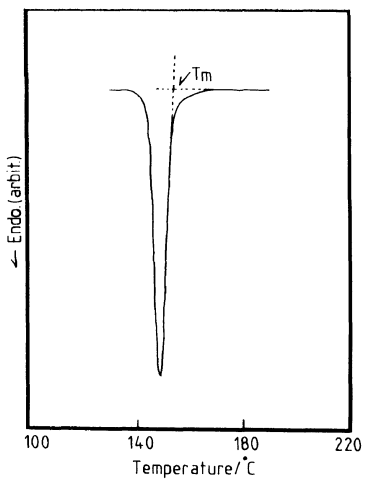

Figure 1. DSC thermogram of EVOH59/PA6—12 90/10 blends around the melting temperature of EVOH59.

were carried at 10 deg min^{-1} of heating rate. T_m's of all the samples were determined as shown in Figure 1.

RESULTS AND DISCUSSION

Miscibility and Lower Critical Solution Temperature (LCST) Behavior

In Figure 2, plots of tan δ spectra corresponding to glass transition region for EVOH59/PA6-12 blends annealed at 150°C are shown. As shown in Figure 2, a single peak indicating miscibility appeared in EVOH59/PA6—12 blends throughout the entire composition range. This suggest that EVOH59/PA6—12 blends are miscible at 150°C. Similar spectra for EVOH59/PA6—12 50/50, 60/40, and 70/30 blends annealed at 170°C are shown in Figure 3. As shown in Figure 3, double peaks which indicate that phase separation occurred in these blends are observed. Resultant T_{Dmax}, the temperature giving the maximum tan δ peak in Figure 2, are plotted against blend composition in Figure 4. In this figure, filled circles symbolize T_{Dmax}'s obtained from Figure 2 and solid line, the composition dependence of T_{Dmax} predicted by following Fox equation,[20]

$$1/T_{Dmax} = W_1/T_{Dmax1} + W_2/T_{Dmax2} \qquad (1)$$

where W_1 and W_2 represent weight fraction and T_{Dmax1} and T_{Dmax2} represent T_{Dmax} of components 1 and 2, respectively. T_{Dmax}'s change along the solid line in Figure 4. In general, eq 1 is used for prediction of T_g variation of random copolymers against copolymer composition. Therefore, it is concluded that EVOH59/PA6—12 blends are miscible in the molten state in overall blend composition at 150°C. Therefore, it was suggested that EVOH59/PA6—12 blends show LCST type phase behavior. Therefore, EVOH-59/PA6—12 50/50 blend has LCST around

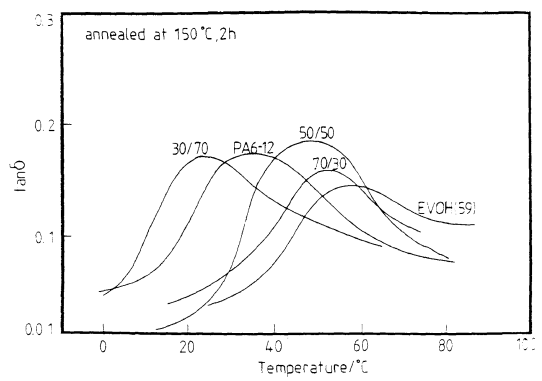

Figure 2. Plots of tan δ against temperature for EVOH-59/PA6—12 blends annealed at 150°C for 2 h.

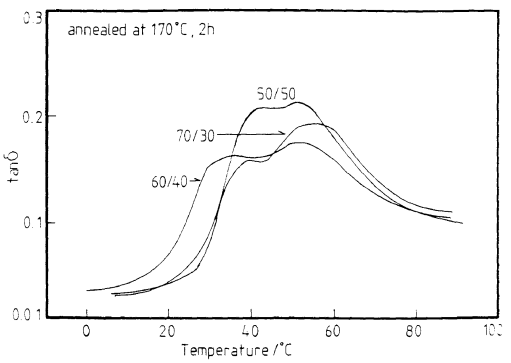

Figure 3. Plots of tan δ against temperature for EVOH-59/PA6—12 blends annealed at 170°C for 2 h.

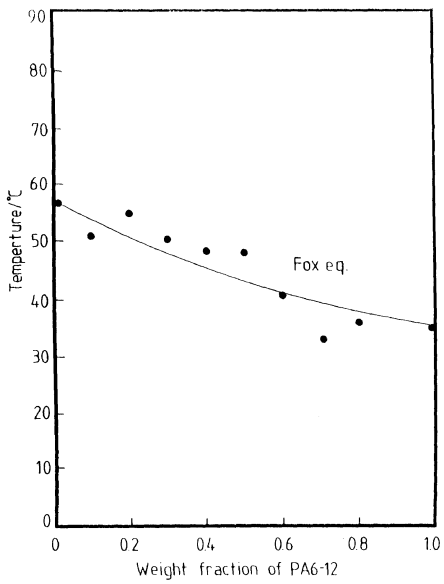

Figure 4. Composition dependence of Tg of EVOH59/PA6-12 blends annealed at 150°C for 2 h. Composition dependence of T_g follows the Fox equation.

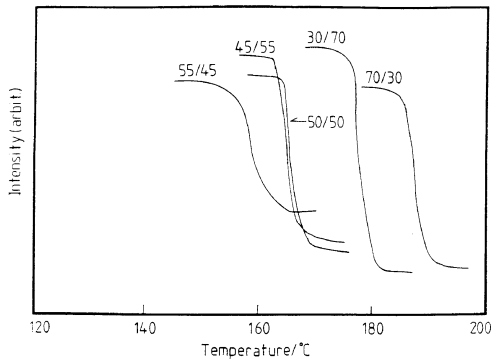

Figure 5. Plots of transparent light intensity against temperature for EVOH59/PA6—12 blends.

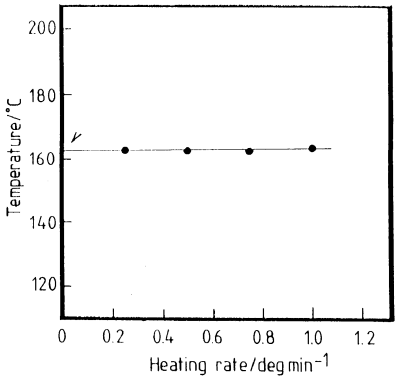

Figure 6. Heating rate dependence of cloud points in EVOH59/PA6—12 50/50 blends. Solid line is least square straight line between cloud points and heating rate.

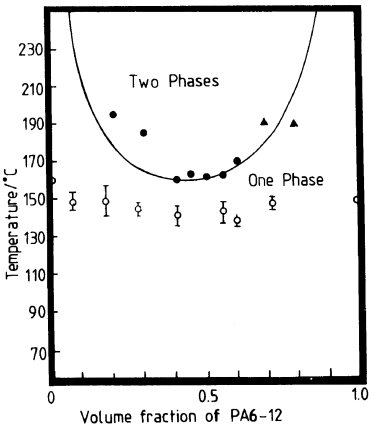

Figure 7. LCST phase diagram of EVOH59/PA6—12 blends. Closed circles are cloud points and open circles, apparent melting temperature.

160°C. Cloud point measurements were made using a handmade thermo-photometer.

In general, transmitted light intensity dramatically changes around liquid–liquid phase transition temperature since light is scattered by samples at two phase region of phase diagram.[19] Some plots of transmitted light intensity *versus* temperature are shown in Figure 5. It can be seen in Figure 5 that transmitted light intensity decreases with temperature. The temperature at which transmitted light intensity decreased is close to the temperature where heterogeneous phase structure appeared in morphological observation. Therefore, decrease of transmitted light intensity with increasing temperature comes from LCST phase behavior. Cloud points were determined following the previous study.[17-19] In general, cloud points obtained in heating process depend on heating rate because phase separation is a time-dependent process.[22] In Figure 6, heating rate dependency of cloud points in EVOH59/PA6—12 55/45 blends are shown. It can be seen that heating rate dependency of cloud points in this system is negligible. This means that liquid–liquid phase transition in this system is fast. However, since resultant cloud points showed weak dependency on heating rate, real cloud points were determined as points of extrapolation of least square straight line between cloud points and heating rate to 0 deg min^{-1}. Resultant cloud points are plotted against blend composition in Figure 7. In this figure, filled circles represent cloud points and open circles, apparent melting points of the blends obtained by DSC. The cloud point curve was typical of the LCST type phase diagram. The miscible region of EVOH59/PA6—12 blends was narrow above the apparent melting temperature. The blends of EVOH containing 0, 32, 44, 72, and 100 mol% of ethylene units with PA6—12 were also investigated.[23] It was found that these systems were immiscible from apparent melting tem-

perature to thermal degradation temperature and liquid–liquid phase transition behavior of these systems has never appeared except in EVOH59/PA6—12 blends. EVOH/PA6—12 blends may thus be immiscible in melt state because melting temperature in EVOH of lower ethylene unit contents is too high and intermolecular interactions between EVOH with higher ethylene unit contents and PA6—12 are too weak to show miscibility in the region between the apparent melting temperature and thermal degradation temperature of these systems.

Melting Temperature Depression

Since LCST type phase behavior was observed in EVOH59/PA6—12 blends as mentioned above, intermolecular interactions between these polymers may be strong. Therefore, Flory–Huggins interaction parameter, χ, should play an important role.

For estimation of χ in EVOH59/PA6—12 blends, analysis of melting temperature depression was made for EVOH59/PA6—12 blends. In general, this analysis has been made for the blends which include crystalline polymer as one of its components. Since EVOH59 and PA6—12 are crystalline polymers, melting temperature depression can be made for the blends to estimate χ.

According to Hoffman and Weeks' analysis,[24,25] apparent melting temperature is expected to follow a linear relationship with isothermal crystallization temperature such as;

$$T_m^0 - T_m = \psi(T_m^0 - T_c) \qquad (2)$$

where T_m is the resultant apparent melting temperature after isothermal crystallization at T_c, ψ is a stability parameter which has dependency on the thickness of crystal. T_m^0 is the equilibrium melting temperature estimated by extrapolation of straight line following eq 2 to $T_m = T_c$ in plots of T_m *versus* T_c. In Figure 8, some Hoffman–Weeks plots for EVOH59/PA6—12 blends are shown. In this figure, filled circles are resultant T_m after annealing at T_c and solid lines are least square straight lines for experimental data. The error bars are experimental error. Following eq 2, equilibrium melting temperature was determined by extrapolation of such straight line to $T_m = T_c$. Resultant equilibrium melting temperature, T_m^0, and stability parameter, ψ, for EVOH59/PA6—12 blends are listed in Table II. In Table II, T_m^0's are decreasing with increasing content of PA6—12 in EVOH59/PA6—12 blends. In addition, ψ's of EVOH59/PA6—12 blends are close to each other as

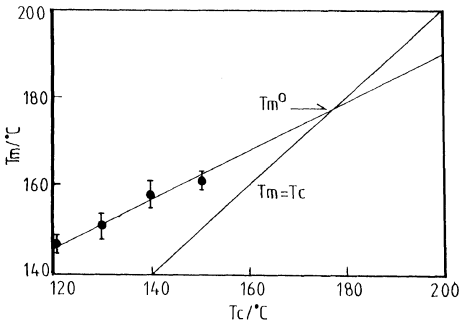

Figure 8. Hoffman–Weeks plots of EVOH59/PA6—12 9/1 blends.

Table I. Table 1 Properties of EVOH59 and PA6—12

Samples	DP[a]	T_g/°C[b]	T_m/°C[b]	Thermal expansivity (in melt state)
EVOH59	680	31.0	159.0	6.264×10^{-4}
PA6—12	1200	29.0	146.0	6.993×10^{-4}

[a] DP represents degree of polymerization.
[b] Values were obtained from DSC measurements.

Table II. Equilibrium melting temperature and stability parameter, ψ, of EVOH59/PA6—12 blends

Volume fraction of PA6—12	T_m^0	ψ
0	181.8	0.566
0.047	179.4	0.485
0.095	177.0	0.550
0.143	173.6	0.517
0.191	170.4	0.414

shown in Table II. Hence, melting temperature depression in EVOH59/PA6—12 blends occurred without effect of crystal structure. Nishi and Wang derived a relationship between equilibrium melting temperature and blend composition for polymers of infinite molecular weight on the basis of Flory–Huggins theory as following equation,[5]

$$1/T^0_{\mathrm{m\,blend}} - 1/T_{\mathrm{m}}{}^0 = -RV_2/\Delta H_{2\mathrm{u}} V_1 \chi_{12} \phi_1{}^2 \quad (3)$$

where $T_m{}^0$ blend is the equilibrium melting temperature for blends, $T_{\mathrm{m}}{}^0$ is the value for a pure component, $\Delta H_{2\mathrm{u}}$ is the heat of fusion per mole of repeating units for crystalline component, V_1 and V_2 are molar volumes of the repeating units for amorphous and crystalline component, respectively, ϕ_1 is volume fraction of amorphous component, R is gas constant and χ_{12} is an interaction parameter. They applied eq 3 to poly(vinylidene fluoride)/polystyrene blends which show LCST type phase behavior. By eq 3, a plot of $1/T_{\mathrm{m}}{}^0{}_{\mathrm{blend}} - 1/T_{\mathrm{m}}{}^0$ against $\phi_1{}^2$ should give a straight line across the original point with a slope of χ_{12}. Plots of the left side in eq 3 *versus* $\phi_{\mathrm{PA6-12}}{}^2$ are shown in Figure 9. The error bars in Figure 9 are experimental error in T_{m}s. The following parameter values were used in our calculation: $\Delta H_{2\mathrm{u}} = 4.22\,\mathrm{kJmol^{-1}}$, $V_1 = 29.79\,\mathrm{cm^3 mol^{-1}}$, $V_2 = 37.80\,\mathrm{cm^3\,mol^{-1}}$. Using these values, the value of χ_{12} is estimated as -0.58. There thus may be comparatively strong intermolecular interactions between EVOH59 and PA6—12. However, since the straight line does not pass through the original point, χ_{12} is not reliable. This may be due to the contribution of composition dependence of χ_{12}[26,27] and/or morphological effects of crystalline structure to T_{m},[28,29] not taken into account in eq 3.

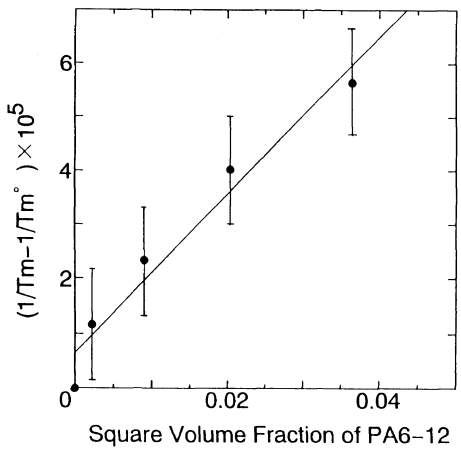

Figure 9. Plots of left hand side of eq 3 against volume fraction of PA6—12 in EVOH59/PA6—12 blends.

CONCLUSION

From the results of cloud point measurements, morphological observation and tan δ behavior in dynamic mechanical measurements, LCST type phase behavior of EVOH59/PA6—12 blends was found in a narrow temperature region between the apparent melting temperature and thermal degradation temperature of this system. Since composition dependence of T_{Dmax} for EVOH59/PA6—12 blends annealed at 150°C followed the Fox equation, the blends were shown to be miscible in the molten state in the overall blend composition range at 150°C.

Using the analysis of melting temperature depression, the Flory–Huggins interaction parameter, χ, for EVOH59/PA6—12 blends was estimated as -0.58 suggesting that there were comparatively strong intermolecular interactions between EVOH59 and PA6—12.

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