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# Interfacial tension of poly (ethylene-*co*-vinyl alcohol)/ polyamide blends

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## Summary

Interfacial tensions ( $\gamma$ ) between poly(ethylene-co-vinyl alcohol) (EVOH) and polyamide6-co-12 (PA6-12) were measured by pendant drop method. In the measurements for PA6-12 and EVOH of high ethylene contents, $\gamma$ 's were decreasing with elevating temperature. On the other hand, in the measurements for PA6-12 and EVOH of low ethylene contents, $\gamma$'s were increasing with elevating temperature. On the basis of these results, interaction parameters, $\chi$, were estimated. Resulting temperature dependence of $\chi$ parameters predicted a LCST phase behavior for the blends of PA6-12 and EVOH of low ethylene contents corresponding to our previous study.

## Introduction

In prediction of phase behavior and phase structure of polymer blends, the properties of interfaces, such as interfacial tension ( $\gamma$) and interfacial thickness ( $\lambda$ ), provide valuable information (1-8). Hence, many experimental and theoretical studies have been performed on the relation ship between $\gamma$ or $\lambda$ and phase behavior in polymer blends (1-8). Especially, $\lambda$ has enabled prediction of phase behavior in immiscible polymer blends (2, 3). Recently, Nose and co-workers reported the temperature dependence of $\gamma$ in the mixture of polystyrene (PS) and polydimethylsiloxane (PDMS) which showed LCST phase behavior (5, 6). In their results, it was found that $\gamma$ was increasing with elevating temperature corresponding to LCST phase behavior of PS/PDMS blends. The results pointed out the possibility of the predictions of phase behavior in polymer blends by $\gamma$.

In our previous study (9, 10), we found LCST phase behavior in blends of poly (ethylene-co-vinyl alcohol) containing 59 mol% ethylene units (EVOH59) and polyamide6-co-12 containing 60 mol% polyamide-6 units (PA6-12). In addition, it was also found that the blends of EVOH with another ethylene contents and PA6-12 were immiscible in measurable temperature and entire composition range. However, detail relationship between phase behavior and copolymer composition of EVOH in EVOH/PA6-12 blend was not revealed. Hence, it was interested for the interpretation of phase behavior in EVOH/PA6-12 blends to investigate temperature and copolymer composition dependence of $\gamma$ for the blends of EVOH with various ethylene contents and PA6-12. Then, in the present paper, temperature and copolymer composition dependencies were investigated for the blends of EVOH with various ethylene contents and PA6-12.

## Experiments

Polymers used in this study were poly (ethylene-co-vinyl alcohol) (EVOH) supplied from Kuraray Co., Ltd. and polyamide6-co-12 containing 60 mol% polyamide-6 units (PA6-12) purchased from EMS Japan Co., Ltd. Molecular characteristics of each polymer were listed in Table I.

Interfacial tensions ( $\gamma$ ) were measured by pendant drop method according to the method of Andreas et. al.(11). For the system of EVOH59 and PA6-12, $\gamma$ was measured between the two mixtures prepared on the basis of the phase diagram of EVOH59/PA6-12 blends as shown in Figure 1. For another systems, $\gamma$'s were measured between EVOH's and PA6-12 because these blends were immiscible in most composition.

**Table** I Molecular characteristics of EVOH and PA6-12.

| Code | Ethylene Content/ mol% | DP | $T_m$/℃ | $T_g$/℃ | $V_0$/$m^3$/unit |
|---|---|---|---|---|---|
| PE | 100 | 800 | 104 | …… | $9.50\times10^{-32}T+4.61\times10^{-29}$* |
| EVOH72 | 72 | 780 | 110 | …… | $5.17\times10^{-32}T+5.42\times10^{-29}$** |
| EVOH59 | 59 | 680 | 159 | 31 | $3.67\times10^{-32}T+5.74\times10^{-29}$** |
| EVOH44 | 44 | 950 | 170 | 46 | $1.83\times10^{-32}T+6.12\times10^{-29}$** |
| EVOH32 | 32 | 1120 | 190 | 58 | $8.33\times10^{-33}T+6.59\times10^{-29}$** |
| PA6-12 | …… | 1200 | 146 | 29 | $1.67\times10^{-31}T+2.24\times10^{-29}$** |

*: obtained from ref. 10

**: obtained by dilatometory above melting temperature

*,**: T represents temperature/℃

## Results and Discussion

In Figure 2, $\gamma$ 's between EVOH's and PA6-12 were plotted as a function of temperature. In PE/PA6-12 and EVOH72/PA6-12 systems, $\gamma$ 's were decreasing with elevating temperature as same as general results (7). Therefore, in these systems, EVOH and PA6-12 became attractive with elevating temperature. On the contrary, in the systems of

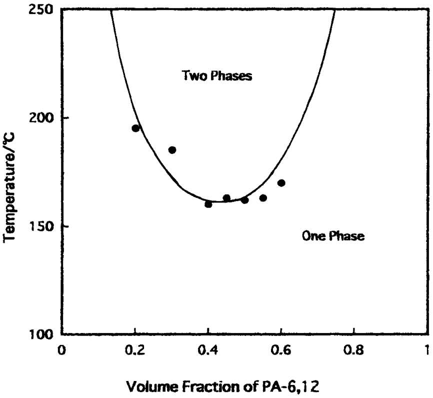

**Figure 1** LCST phase diagram of EVOH59/PA6-12 blend reproduced from ref. 9.

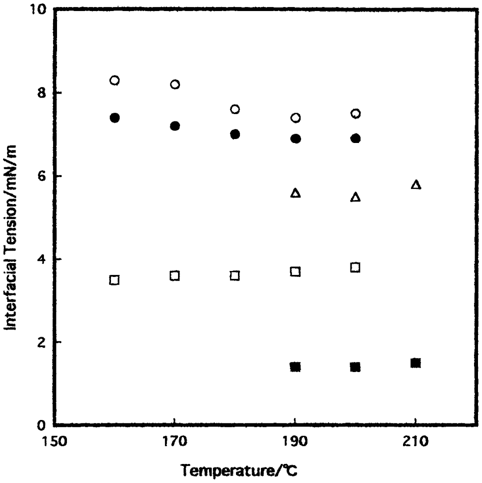

**Figure 2** Temperature dependence of $\gamma$ between EVOH and PA6-12; ○: PE, ●: EVOH72, □: EVOH59, ■: EVOH44, △: EVOH32.

EVOH59, EVOH44 and EVOH32 with PA6-12, $\gamma$ 's were increasing with elevating temperature. It meant that these systems were dewetting with elevating temperature. Hence, it was expected that blends of EVOH with high ethylene contents and PA6-12 became miscible with elevating temperature and the blends of EVOH with low ethylene contents and PA6-12 became immiscible with elevating temperature. It was well-known that $\gamma$ was closely relating with Flory-Huggins interaction parameter ( $\chi$ ). According to the theory derived by Broseta et. al. (8), the relationship between $\gamma$ and $\chi$ was expressed by following equation,

$$\gamma = \frac{kT\chi^{1/2}a}{\sqrt{6}v_0}\left[1-\frac{\pi^2}{12\chi}(N_1^{-1}+N_2^{-1})\right] \qquad (1)$$

where k, T, a, $v_0$ and $N_i$ represented Boltzman constant, absolute temperature, Kuhn-segment length, volume per unit and degree of polymerization of component i, respectively. According to equation (1), the tendency of temperature dependence of $\gamma$ for EVOH59/PA6-12 blend was corresponding to LCST phase behavior in this blend. Therefore, estimations of $\chi$ parameters for EVOH's/PA6-12 blends should have significant value for prediction of phase behavior of EVOH/PA6-12 blends.

In Figure 3, $\chi$ parameters for EVOH/PA6-12 blends calculated by equation (1) were plotted against reciprocal temperature. Each $\chi$ parameter was calculated by using the value of $v_0$ and a, where $v_0$ and a were determined as geometrical average of the values for EVOH's and PA6-12. In general $\chi$ parameter was proportional to reciprocal temperature (13). The straight lines in Figure3 were drawn by least square approximation. Resulting temperature dependence of $\chi$ parameter for each blend was listed in Table II. As shown in Figure 3 and Table II, $\chi$ parameters were monotonously decreasing with elevating temperature in PE/PA6-12 and EVOH72/PA6-12 blends. On the other hand, $\chi$ parameters were almost constant or slightly increasing with elevating temperature in the systems of EVOH with low ethylene contents and PA6-12. Hence, it was predicted that UCST phase behavior should appear in the blends using EVOH with high ethylene contents and LCST phase behavior in the blends using EVOH with low ethylene contents. In addition, $\chi$ parameter was decreasing with increasing vinyl alcohol (VOH) unit in the range between 100 and 44 mol% ethylene unit. Since $\chi$ parameter was decreasing with increasing VOH unit of EVOH in high ethylene contents, it was suggested that intermolecular associative force between -OH group of EVOH and amide group of PA6-12 enhanced miscible region of the blends. On the contrary, $\chi$ of EVOH32/PA6-12 blend is larger than that of

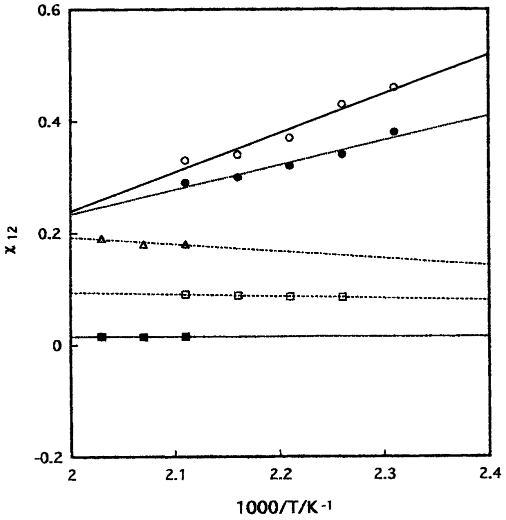

**Figure 3** Temperature dependence of $\chi$ parameters for EVOH/PA6-12 blends; ○: PE, ●: EVOH72, □: EVOH59, ■: EVOH44, △: EVOH32.

**Table II** Temperature dependence of $\chi$ parameters for EVOH/PA6-12 blends estimated from interfacial tension.

| Blends | $\chi$ (=a/T+b) |
|---|---|
| PE/PA6-12 | $7.0\times10^{2}/T-1.2$ |
| EVOH72/PA6-12 | $4.4\times10^{2}/T-6.5\times10^{-1}$ |
| EVOH59/PA6-12 | $-34/T+1.6\times10^{-1}$ |
| EVOH44/PA6-12 | $-1.5\times10^{-2}$ |
| EVOH32/PA6-12 | $-1.3\times10^{2}/T+4.4\times10^{-1}$ |

EVOH44/PA6-12 blend in spite of increase in VOH content of EVOH. It suggest that association between - OH groups became effective interaction. Hence, it was also suggested that intramolecular repulsive force between ethylene and VOH unit in EVOH extended miscible region in EVOH/PA6-12 blends because $\chi$ parameter was decreasing with increasing VOH unit in low VOH contents. However, on the basis of the results shown in Table II, EVOH44/PA6-12 blend was miscible in measurable temperature and entire composition because of constant and negative value of $\chi$ of EVOH44/PA6-12 blend. In addition, resulting critical solution temperature ($T_c$) of EVOH59/PA6-12 blend was equal to 216K and did not coincided with the phase diagram for this blend shown in Figure 1, where $T_c$ was the temperature at which $\chi = \chi_c$. and $\chi_c$ was expressed by following equation;

$$\chi_c = \frac{1}{2}\left(\frac{1}{\sqrt{N_1}} + \frac{1}{\sqrt{N_2}}\right)^2 \qquad (2)$$

It was thought that the uncertainty of the results were arisen from the value of a and $v_0$ values using estimation of $\chi$ parameter because of averaged values. Hence, quantitative discussions on phase behavior in EVOH/PA6-12 blends were unable. However, it was rare case for polymer blends that $\gamma$ was increasing with elevating temperature. Further, the tendency of the temperature dependence of $\chi$ parameter for EVOH59/PA6-12 blend was corresponding to phase behavior of the blend. Therefore, the results of this study indicated qualitative tendency of EVOH/PA6-12 blends.

## Conclusion

For EVOH with high ethylene contents, $\gamma$ 's were decreasing with elevating temperature. On the other hand, for EVOH's with low ethylene contents, $\gamma$ 's were increasing with elevating temperature. According to the theory of Broseta et. al., $\chi$ parameters were estimated. Resulting temperature dependence of $\chi$ 's predicted LCST phase behavior for the blends of EVOH's having small amount of ethylene unit with PA6-12 and UCST phase behavior for the blends using EVOH's with high ethylene contents. In addition, copolymer composition dependencies of $\chi$ parameters pointed out miscibility of EVOH/PA6-12 blends were strongly affected by intermolecular association force between -OH group and amide group and intramolecular repulsive force between ethylene unit and vinyl alcohol unit.

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