

Miscibility Studies of Poly(ethylene oxide)–Poly(vinyl acetate) Blends by Viscometry Methods

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SYNOPSIS

The intrinsic viscosities of poly(ethylene oxide)–poly(vinyl acetate) blends (PEO–PVA) have been measured in chloroform as a function of molecular weights of blend components and compositions. The interaction parameters Δb obtained from the modified Krigbaum and Wall theory and the differences between the intrinsic viscosities of polymer mixtures and the weight-average intrinsic viscosities of the two blend components were both used to characterize the extent of miscibility of the blend mixtures. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Poly(ethylene oxide) (PEO) can act as a proton acceptor and form miscible blends with many proton-donating polymers,¹ since it has a partial negative charge on the oxygen atom.² There is a partial positive charge on the carbonyl carbon atom of poly(vinyl acetate) (PVA). Therefore, one can expect that PVA may interact favorably with PEO and form a miscible couple.

In fact, in the last decade, several research groups have investigated the miscibility of PEO and PVA.^{3–7} However, different and opposing conclusions about their miscibility have been obtained. Yin et al.⁸ reported a direct proof by measuring the enthalpy of mixing, ΔH_m , to verify whether this couple is miscible or not. The conclusion was that their miscibility strongly depends on the molecular weight of PVP. The main purpose of this work was to continue to investigate the effect of molecular weights of both blending components and the effect of blend compositions on their miscibility and the extent of miscibility. Due to its simplicity, the viscometry method has been adopted.

The viscometry method was built on the assumption that repulsive interaction may cause

shrinkage of the polymer coil, resulting in a lower value of the viscosity of the polymer blend than the value calculated from viscosities of both pure blend components on the assumption of the law of the additivity. On the other hand, if there is attractive interaction, an increase of the viscosity will be expected for the blend.

The theory of dilute solution viscometry originated from the classical Huggins equation⁹ that expresses the specific viscosity (η_{sp}) of a polymer as a function of the concentration C :

$$\frac{\eta_{sp}}{C} = [\eta] + K[\eta]^2 \times C \quad (1)$$

where $[\eta]$ is the intrinsic viscosity. If $K[\eta]^2$ is denoted as b , eq. (1) can be rewritten as

$$\frac{\eta_{sp}}{C} = [\eta] + bC \quad (2)$$

Krigbaum and Wall¹⁰ modified eq. (2) and derived an expression of the viscosity $\eta(C_1, C_2)$ of a dilute solution containing two polymers (1, 2) at concentrations (C_1, C_2):

$$\frac{\eta(C_1, C_2)}{\eta_0} - 1 = C_1[\eta_1] + C_2[\eta_2] + C_1^2 b_1 + C_2^2 b_2 + 2C_1 C_2 b_{12} + \dots \quad (3)$$

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where $[\eta_i]$ is the intrinsic viscosity of polymer i in pure solvent; η_0 , the solvent viscosity; and b_{12} , the interaction coefficient between the two polymers. The specific viscosity, $\eta_{sp,m}$, of a mixed polymer solution can be expressed as follows if b_1 , b_2 are replaced by b_{11} , b_{22} and the other terms are omitted except for the first five terms:

$$\eta_{sp,m} = [\eta_1]C_1 + [\eta_2]C_2 + b_{11}C_1^2 + b_{22}C_2^2 + 2b_{12}C_1C_2 \quad (4)$$

According to Williamson and Wright,¹¹ the interaction coefficient can be expressed as

$$b_{12} = (b_{11} + b_{22})/2 \quad (5)$$

The value of b_{12} can be obtained from eq. (4) by determining the specific viscosity of the mixture, $\eta_{sp,m}$, the intrinsic viscosity of the pure components $[\eta_i]$, and the values of b_{11} and b_{22} [measured from eq. (2)]. Also, parameter b_{12} can be theoretically calculated from eq. (5). Usually, b_{12} computed from eq. (5) is defined as b_{12}^* . Krigbaum and Wall¹⁰ suggested that information about the interaction between two polymers should be obtained from the difference of experimental b_{12} and theoretical b_{12}^* . The difference was defined as Δb and expressed as

$$\Delta b = b_{12} - b_{12}^* \quad (6)$$

Positive values of Δb refer to the attractive interaction and miscible mixtures. The larger the value of Δb , the higher the extent of miscibility. Negative values of Δb refer to repulsive interaction and incompatible mixes.

Equation (4) can be reduced to a simple form when the total concentration of the mixture (C) approaches zero:

$$\left[\frac{\eta_{sp,m}}{C} \right]_{C \rightarrow 0} = \left[\frac{[\eta_1]C_1}{C} \right]_{C \rightarrow 0} + \left[\frac{[\eta_2]C_2}{C} \right]_{C \rightarrow 0} \quad (7)$$

This means that the intrinsic viscosity of a mixture of two polymers can be expressed as the weight-average of the intrinsic viscosities of the two polymers. Williamson and Wright¹¹ used eq. (7) as a criterion for ideal solution behavior.

During the last two decades, viscometry methods have been successfully used to investigate and characterize miscibilities of some polymer couples by Shih and Beatty,¹² Lizymol and Thoms,¹³ and other research groups.¹⁴⁻¹⁶

EXPERIMENTAL

Materials

PEO with molecular weights of 2300 and 76,100 was purchased from Fluka AG. PVA was obtained from Aldrich-Chemie. Their molecular weights are characterized by viscometry methods and are shown in Table I. PVA was purified by dissolving it in acetone, filtering the solution with a G2 sintered glass funnel, and precipitating by adding an excess of petroleum ether. Chloroform, acetone, petroleum ether, and tetrahydrofuran solvents used in this work are all of analytical purity.

Fractionating of PVA

To obtain PVA samples with different molecular weights, a step precipitation method was used to fractionate the PVA. Acetone was used as the solvent, and petroleum, as the nonsolvent. All fractions were washed with petroleum ether and dried in a vacuum oven for at least 24 h at 333 K. The molecular characteristics of the fractions were determined by viscometry and are reported in Table I.

Viscosity Determination

The specific viscosity and the intrinsic viscosity of PEO, PVA, and their mixtures were determined by a Ubbelohde-type viscometer. Chloroform was used as the solvent. The measurements were performed at a constant temperature of $25 \pm 0.01^\circ\text{C}$. A water bath with a thermoregulator was used to keep temperature constant.

Polymer solutions were prepared by dissolving accurately weighed samples in calculated amounts of solvents with a maximum concentration of 3 g/100 mL. Dilute solutions of polymer mixtures, with the desired proportion of PEO and PVA, were prepared as follows: According to the compositions of mixtures of PEO and PVA, concentrations, and vol-

Table I Molecular Characterization of PEO and PVA

Material	$M_n \times 10^{-4}$	$[\eta]$ (mL/g)	b	r
PEO-1	7.61	56.8	1049.8	.998
PEO-2	0.23	9.8	65.1	.999
PVA-1	18.21	125.0	5959.4	.997
PVA-2	7.63	65.8	1592.9	.998
PVA-3	1.51	19.2	170.0	.996

umes of solutions, the desired amounts of PEO and PVA were determined and dissolved in fixed volumes of the solvent.

RESULTS AND DISCUSSION

Effect of Molecular Weights of Blend Components on Δb

Δb values of PEO/PVA blends of varying molecular weights of both blend components as a function of concentration, C , are shown in Figures 1-3. As shown in Figure 1, when the ratio of PEO/PVA is 75/25, Δb values of PEO-2/PVA-1 and PEO-1/PVA-1 are negative, and the Δb values of PEO-2/PVA-3, PEO-1/PVA-3, PEO-1/PVA-2, and PEO-2/PVA-2 are positive or zero. The above results reveal that the first two blends are not miscible in the solid state and that the other four blends are miscible. As listed in Table I, PVA-1 has the highest molecular weight ($M_n = 18.21 \times 10^4$) among the three PVA samples. Two blends with PVA-1 as the blend component are not miscible. This fact indicates that the miscibility of PEO and PVA is strongly dependent upon the molecular weight of PVA. It also can be seen from Figure 1 that there is a different influence

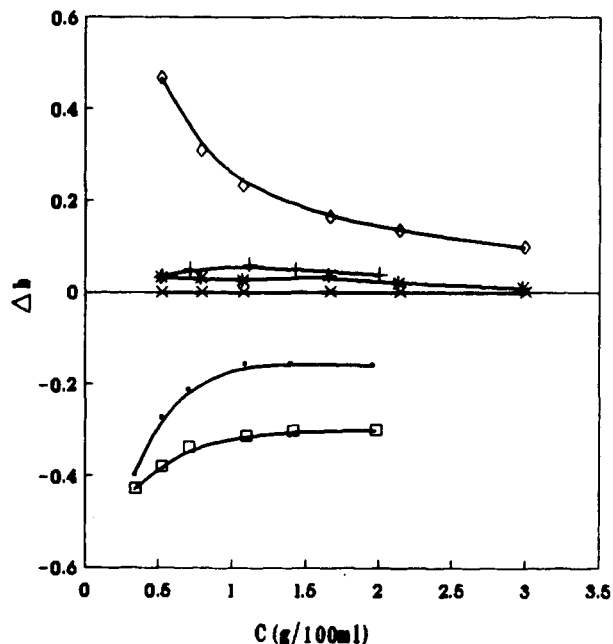


Figure 1 Δb values of PEO/PVA (75/25) blends of varying molecular weight of both components as a function of concentration C : (\diamond) PEO-2/PVA-3; (+) PEO-1/PVA-2; (*) PEO-1/PVA-3; (X) PEO-2/PVA-2; (\bullet) PEO-1/PVA-1; (\square) PEO-2/PVA-1.

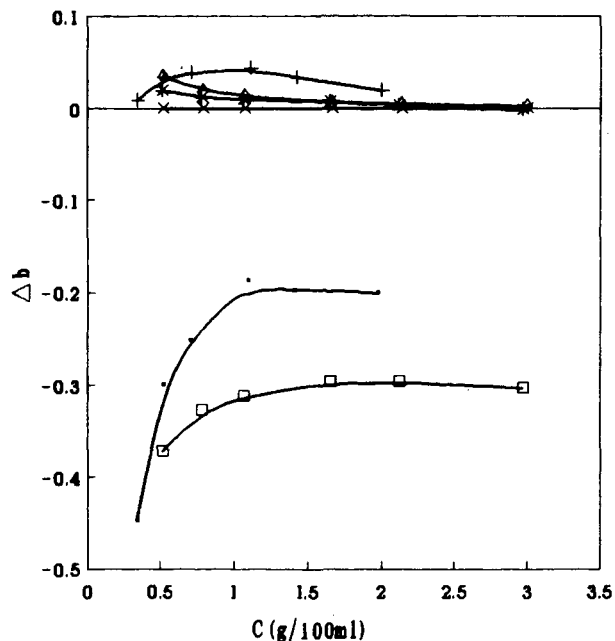


Figure 2 Δb values of PEO/PVA (50/50) blends of varying molecular weight of both components as a function of concentration C : (+) PEO-1/PVA-2; (\diamond) PEO-2/PVA-3; (*) PEO-1/PVA-3; (X) PEO-2/PVA-2; (\bullet) PEO-1/PVA-1; (\square) PEO-2/PVA-1.

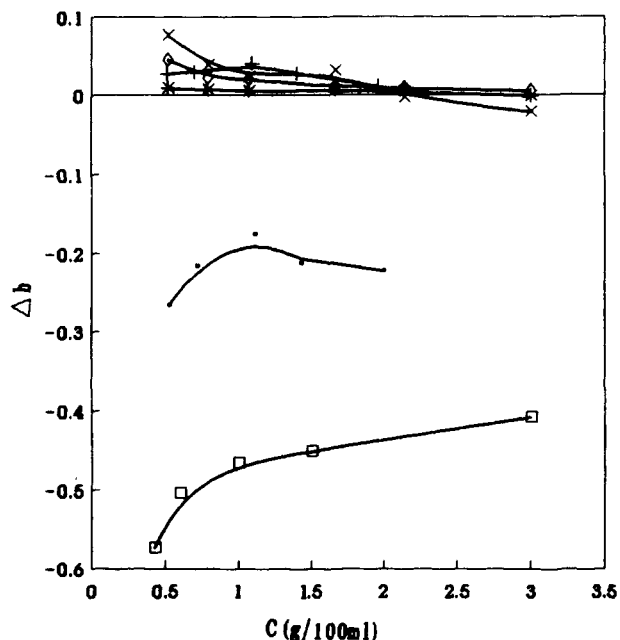


Figure 3 Δb values of PEO/PVA (25/75) blends of varying molecular weight of both components as a function of concentration C : (+) PEO-1/PVA-2; (\diamond) PEO-2/PVA-3; (*) PEO-1/PVA-3; (X) PEO-2/PVA-2; (\bullet) PEO-1/PVA-1; (\square) PEO-2/PVA-1.

of the total concentration of the mixture on Δb values. For blends with PVA-1 as the blend component, values of Δb increase with the concentrations of mixtures when the total concentration is lower than 1.5 g/100 mL. As the concentration is further enhanced, Δb values remain constant. The value of Δb of PEO-2/PVA-3 decreases as the concentration of the mixture increases. Nearly constant Δb values appear in the investigated range of the total concentrations of mixtures for the other four blends.

Similar experimental results are observed when the ratio of PEO/PVA is 50/50 or 25/75 (shown in Figs. 2 and 3, respectively). Blends with PVA-1 as the blend component are still negative. These results verify the previous conclusion that there is a decisive effect of the molecular weight of PVA on the miscibility of PEO and PVA mixtures on their solid states.

Effect of Blend Compositions on Δb

Δb values of blends with different compositions as a function of the total concentrations of mixtures are shown in Figures 4 and 5. As shown in Figure 4, all blends can be divided into three groups ac-

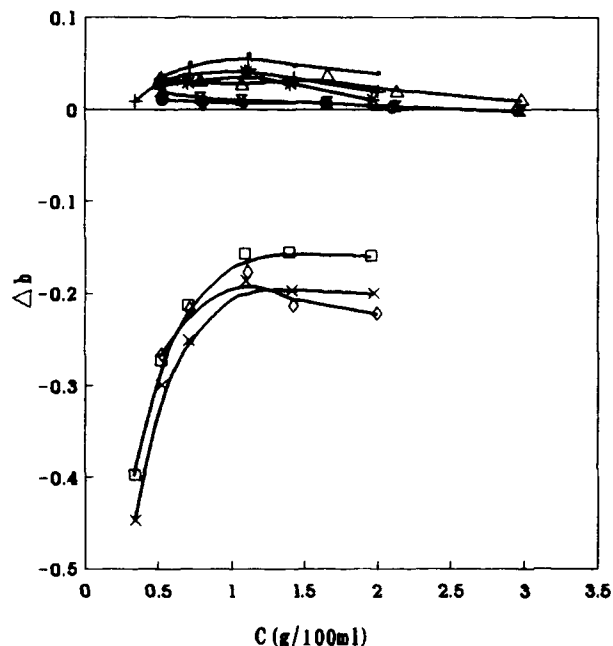


Figure 4 Δb values of PEO-1/PVA blends of varying compositions as a function of concentration C : (●) PEO-1/PVA-2 = 75/25; (+) PEO-1/PVA-2 = 50/50; (*) PEO-1/PVA-2 = 25/75; (Δ) PEO-1/PVA-3 = 75/25; (\bar{X}) PEO-1/PVA-3 = 50/50; (○) PEO-1/PVA-3 = 25/75; (□) PEO-1/PVA-1 = 75/25; (X) PEO-1/PVA-1 = 50/50; (\diamond) PEO-1/PVA-1 = 25/75.

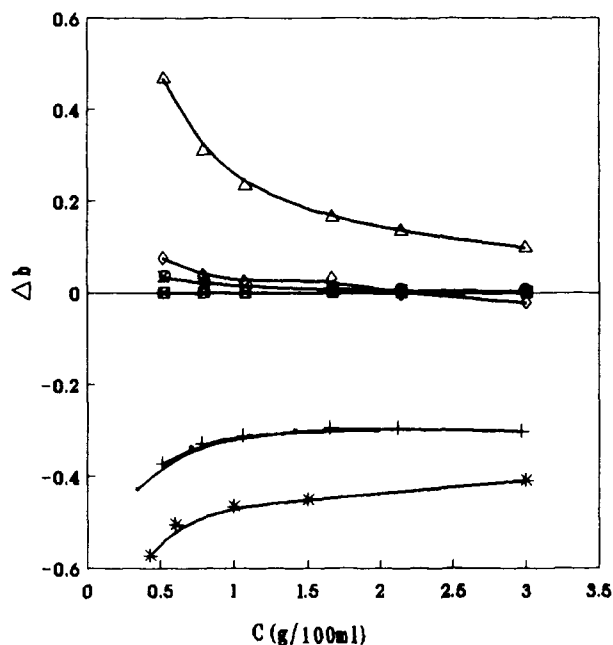


Figure 5 Δb values of PEO-2/PVA blends of varying compositions as a function of concentration C : (Δ) PEO-2/PVA-3 = 75/25; (\bar{X}) PEO-2/PVA-3 = 50/50; (○) PEO-2/PVA-3 = 25/75; (□) PEO-2/PVA-2 = 75/25; (X) PEO-2/PVA-2 = 50/50; (\diamond) PEO-2/PVA-2 = 25/75; (●) PEO-2/PVA-1 = 75/25; (+) PEO-2/PVA-1 = 50/50; (*) PEO-2/PVA-1 = 25/75.

cording to the molecular weight of PVA since the component PEO-1 is fixed. In each group, the order of Δb values is nearly the same as follows: PEO/PVA, 75/25 > 50/50 > 25/75. This trend reveals that the extent of compatibility of PEO and PVA is dependent upon the blend compositions. Generally, the compatibility extent of these two polymers increases with the content of PEO. The Δb values of the PEO-1/PVA-1 group increase with the total concentrations when the concentration is lower than 1 g/100 mL and then nearly remain constant with a further increase of concentration. However, all their Δb values are negative, which indicates that this group is not miscible. There are no obvious changes of Δb values with the total concentrations for the other two groups, for which all Δb values are positive or nearly zero. Miscible blend systems are formed for PEO-1/PVA-2 and PEO-1/PVA-3 blends.

In Figure 5, one can find similar features for the dependence of Δb values on blend compositions. Δb values of both PEO/PVA = 75/25 and 50/50 compositions are higher than the one for the composition PEO/PVA = 25/75 in PEO-2/PVA-3 and PEO-2/PVA-1 groups. This feature is not too obvious for the PEO-2/PVA-2 mixtures.

Intrinsic Viscosity and Miscibility

As expressed in eq. (7), for an ideal solution, the intrinsic viscosity of a mixture of two polymers can be considered as the weight-average of the intrinsic viscosities of the two polymers. Therefore, by comparing the determined intrinsic viscosity of a mixture with the calculated one from eq. (7), some information about the miscibility of a mixture can be obtained.

PEO-1/PVA-1 and PEO-2/PVA-1 Mixtures

The intrinsic viscosities of PEO-1/PVA-1 and PEO-2/PVA-2 mixtures are shown in Figure 6. The straight line represents the intrinsic viscosity of ideal solutions. All points of these two blend systems lie below the straight line. A negative deviation from ideal solution behavior is obtained. This feature suggests a repulsive interaction between the two blend components. It can be concluded that the two blend systems are not miscible in the solid state.

PEO-1/PVA-2 and PEO-2/PVA-2 Mixtures

Figure 7 shows a plot of intrinsic viscosity vs. blend composition for the PEO-1/PVA-2 and PEO-2/PVA-2 systems. PEO-1/PVA-2 mixtures have values slightly higher than that of an ideal solution,

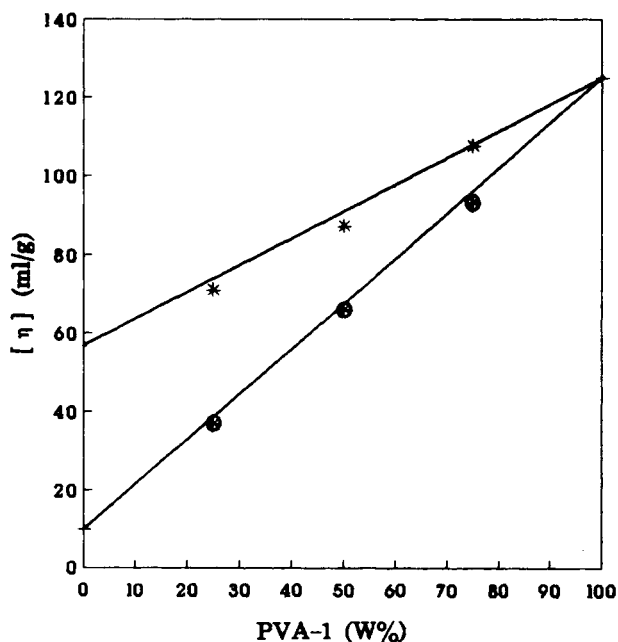


Figure 6 $[\eta]$ vs. blend compositions, W (wt % of PVA), for PEO-1/PVA-1 and PEO-2/PVA-1 blends: (*) PEO-1/PVA-1; (⊙) PEO-2/PVA-1.

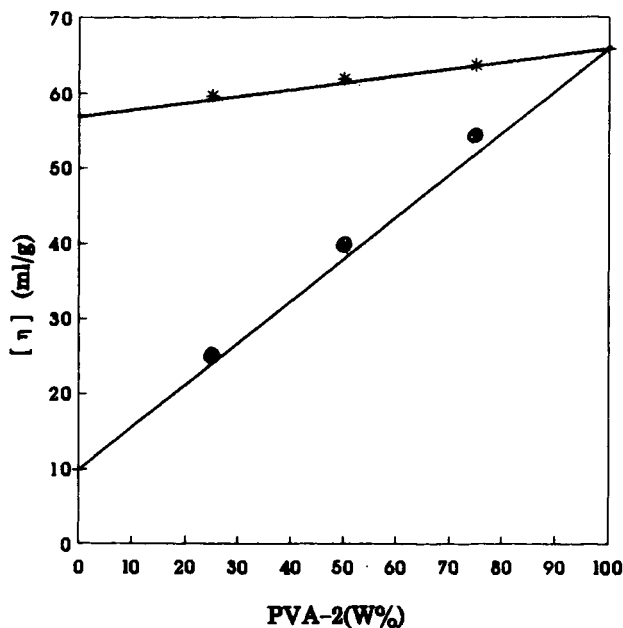


Figure 7 $[\eta]$ vs. blend compositions, W (wt % of PVA), for PEO-1/PVA-2 and PEO-2/PVA-2 blends: (*) PEO-1/PVA-2; (⊙) PEO-2/PVA-2.

while all data for PEO-2/PVA-2 mixtures lie on the ideal solution line. These results confirm again that PEO-1/PVA-2 and PEO-2/PVA-2 mixtures are miscible.

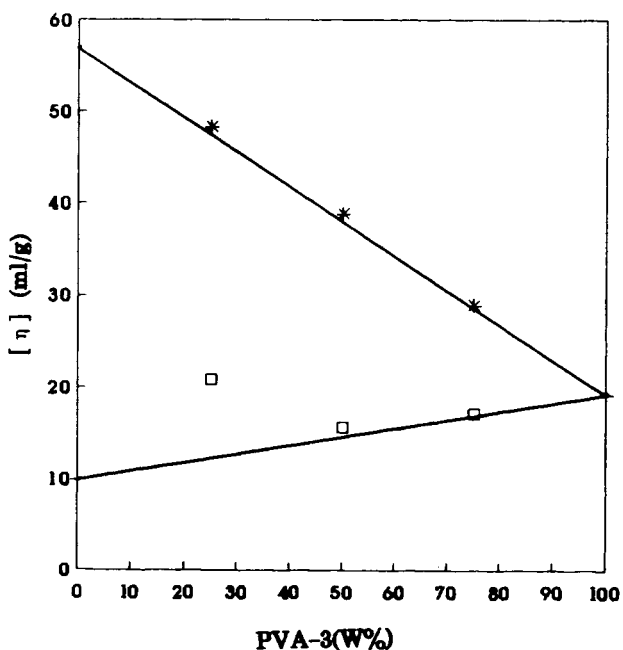


Figure 8 $[\eta]$ vs. blend compositions, W (wt % of PVA), for PEO-1/PVA-3 and PEO-2/PVA-3 blends: (*) PEO-1/PVA-3; (□) PEO-2/PVA-3.

PEO-1/PVA-3 and PEO-2/PVA-3 Mixtures

The intrinsic viscosities of PEO-1/PVA-3 and PEO-2/PVA-3 blend systems are shown in Figure 8 as a function of blend composition. The mixture of PEO-2/PVA-3 shows a big positive deviation from ideal solution behavior when the content of PEO-2 is 75%. This kind of positive deviation decreases with increase of the content of PVA-3, suggesting that the PEO-2/PVA-3 solid-state blends are more miscible at high PEO-2 concentrations than at low PEO-2 concentrations. All points of PEO-1/PVA-3 mixtures lie slightly beyond the ideal solution behavior. This means that PEO-1/PVA-3 mixtures are miscible in the solid state within all composition ranges. All these results are completely consistent with the analyses using Δb values.

CONCLUSIONS

1. The values of Δb for PEO-1/PVA-1 and PEO-2/PVA-1 blends are negative. This suggests that these two blend systems are not thermodynamically miscible in the solid state. This is due to the blend component PVA-1 having the maximum molecular weight among the three PVA samples. Δb values are relevant to the blending compositions and the total concentrations of mixtures. The higher the content of PEO, the bigger the Δb value is. Usually, the values of Δb at high concentrations of mixtures are larger than at low concentrations.
2. The values of Δb for PEO-1/PVA-2, PEO-2/PVA-2, PEO-1/PVA-3, and PEO-2/PVA-3 are positive or zero. This suggests that the above four blend systems are thermodynamically miscible in their solid states, which indicates that in the investigated range of molecular weights of PVA and PEO (M_n of PVA $\leq 7.63 \times 10^4$ and M_n of PEO $\leq 7.61 \times 10^4$) a miscible PEO/PVA blend can be obtained. Similar to the above situation, high Δb values can be obtained at a high content of PEO in

a PEO/PVA blend. Concentrations of mixtures have no apparent effect on Δb values except for the PEO-2/PVA-3 blend.

3. Conclusions obtained from the analyses of intrinsic viscosities of the PEO/PVA mixture are consistent with the results in 1 and 2.

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REFERENCES

1. M. Robeson, W. F. Hale, and N. C. Merriam, *Macromolecules*, **14**, 1644 (1981).
2. G. Ramana Rao, C. Castiglioni, G. Zerbi, and E. Martuscelli, *Polymer*, **26**, 811 (1985).
3. C. Silvestre, F. E. Karasz, W. J. Macknight, and E. Martuscelli, *Eur. Polym. J.*, **23**, 745 (1987).
4. M. L. Addonizio, E. Martuscelli, and C. Silvestre, *J. Polym. Mater.*, **7**, 63 (1990).
5. N. K. Kalfoglou, *J. Polym. Sci. Polym. Phys. Ed.*, **20**, 1295 (1982).
6. N. K. Kalfoglou, D. D. Sotiropoulou, and A. G. Margarities, *Eur. Polym. J.*, **4**, 389 (1988).
7. E. Munoz, M. Calahorra, and A. Suatamaria, *Polym. Bull.*, **7**, 295 (1982).
8. J. Yin, G. C. Alfonso, A. Turturro, and E. Pedemonte, *Polymer*, **34**(7), 1465 (1993).
9. M. L. Huggins, *J. Am. Chem. Soc.*, **64**, 2716 (1942).
10. W. R. Krigbaum and F. J. Wall, *J. Polym. Sci.*, **5**, 505 (1950).
11. G. R. Williamson and B. Wright, *J. Polym. Sci. A*, **3**, 3885 (1965).
12. K. S. Shih and C. L. Beatty, *Br. Polym. J.*, **22**, 11 (1990).
13. P. P. Lizymol and S. Thoms, *J. Appl. Polym. Sci.*, **51**, 635 (1994).
14. A. K. Kunda, S. S. Ray, B. Adhikari, S. Maiti, *Eur. Polym. J.*, **22**, 369 (1986).
15. Y. R. Singh and R. P. Singh, *Eur. Polym. J.*, **19**, 535 (1983).
16. V. N. Kuleznev, O. L. Melnikova, and V. D. Klykova, *Eur. Polym. J.*, **14**, 455 (1978).

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