Miscibility Studies of Polymer Blends by Viscometry Methods

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SYNOPSIS

The intrinsic viscosities of blends of poly(vinyl chloride)/poly(ethylene-co-vinyl acetate) (PVC/EVA), poly(vinyl chloride)/poly(styrene-co-acrylonitrile) (PVC/SAN), and poly(ethylene-co-vinyl acetate)/poly(styrene-co-acrylonitrile) (EVA/SAN) have been studied in cyclohexanone as a function of blend composition. In order to predict the compatibility of polymer pairs in solution, the interaction parameter term, Δb, obtained from the modified Krigbaum and Wall theory, and the difference in the intrinsic viscosities of the polymer mixtures and the weight average intrinsic viscosities of the two polymer solutions taken separately are used. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Blending has become the least expensive and the most versatile way of achieving materials with new desirable properties. However, the manifestation of superior properties depends upon miscibility of the homopolymers at the molecular level.

Many experimental and theoretical methods have been used to investigate polymer compatibility.[1] Heat of mixing, viscometry, glass-transition temperature measurements, morphology by optical and electron microscopy, light scattering, infrared spectroscopy, nuclear magnetic resonance spectroscopy, neutron scattering, fluorescence spectroscopy, and dynamic mechanical response are some of the methods extensively reported in the literature.[1-3]

Because of simplicity, viscometry becomes an attractive method for studying the compatibility of polymers in solution.[4-9] The basis for using dilute solution viscosity as a parameter for compatibility determination of polymer blends lies in the fact that while in solution the repulsive interaction may cause shrinkage of the polymer coils resulting in a viscosity of the polymer mixture that is lower than the value calculated from viscosities of the pure components

on the assumption of the additivity law. On the other hand, attractive interaction increases the viscosity of the system.

Kulshreshtha et al.[10] applied the viscosity method to the poly(vinyl chloride)/poly(acrylonitrile-co-butadiene-co-styrene) (PVC/ABS) poly blend system to study the compatibility. They found that the plot of absolute viscosity versus composition deviates from linearity according to the degree of compatibility. Chee[11] also proved viscometry as a simple and reliable tool for identifying the compatibility of poly(vinyl chloride)/poly(methyl methacrylate) (PVC/PMMA), poly(methyl methacrylate)/poly(isobutyl methacrylate) (PMMA/PiBMA), and PVC/PiBMA systems. The estimation of compatibility of different pairs of polymers based on viscosity data for ternary polymer/polymer/solvent systems has been attempted by several authors.[12-14]

Recently, the compatibility of solutions of polycarbonate (PC) and poly(hexamethylene sebacate) (PHMS) blends having different molecular weight has been characterized by a viscometry technique using the Krigbaum and Wall parameter, Δb, by Shih and Beatty.[15] The values of Δb for PC/PHMS mixtures were negative and therefore they concluded that these blends were not thermodynamically compatible under equilibrium conditions. Using T_g of the blend as a measure of bulk solid-state compatibility, a correlation was obtained with the Krigbaum and Wall parameter,[17] Δb.

Basically the dilute solution viscometry hinges on the classical Huggins equation[16] that expresses the specific viscosity (η_{sp}) of the polymer as a function of the concentration C, when one of the components is alone in the solution.

$$\frac{\eta_{sp}}{C} = [\eta] + K[\eta]^2 C \tag{1}$$

where $[\eta]$ is the intrinsic viscosity. If we put $K[\eta]^2 = b$, the Huggins equation becomes,

$$\frac{\eta_{sp}}{C} = [\eta] + bC \tag{2}$$

where b is the interaction term.

The theoretical consideration starts from the derivation by Krigbaum and Wall.[17] The specific viscosity, $\eta_{sp,m}$, of a mixed polymer solution can be expressed as follows.

$$\eta_{sp,m} = [\eta_1]C_1 + [\eta_2]C_2 + b_{11}C_1^2$$
$$+ b_{22}C_2^2 + 2b_{12}C_1C_2 \tag{3}$$

where $[\eta_1]$ is the intrinsic viscosity of component 1 alone in solution and $[\eta_2]$ is the intrinsic viscosity of component 2 in solution. C_1 and C_2 are the concentrations of component 1 and 2 in mixed polymer solutions, respectively, and b_{12} is the interaction coefficient for the mixture of components 1 and 2.

For mathematical convenience Krigbaum and Wall[17] defined the interspecific interaction coefficient b_{12} as

$$b_{12} = \sqrt{b_{11}b_{22}}. \tag{4}$$

The values of b_{11} and b_{22} are obtained from comparison of eqs. (1) and (2),

$$K[\eta_1]^2 = b_{11} \tag{5}$$

$$K[\eta_2]^2 = b_{22}. \tag{6}$$

But the definition of b_{12} according to eq. (4) is not valid for systems that have negative values for b_{11} or b_{22}. Therefore the modification by Williamson and Wright[18] is used to evaluate b_{12}, which can be expressed as

$$b_{12} = \frac{[b_{11} + b_{22}]}{2}. \tag{7}$$

The value of b_{12} can be theoretically calculated from eq. (7) and can also be obtained from eq. (3).

According to Krigbaum and Wall,[17] information on the interaction between polymer molecule 1 and 2 should be obtainable from comparison of experimental b_{12} and theoretical b_{12} values. Here the compatibility of polymer mixture is characterized by a parameter Δb, can be expressed as

$$\Delta b = b_{12} - b_{12}^* \tag{8}$$

where b_{12}^* is calculated from eq. (7).

Negative values of Δb are found for solutions of incompatible polymer systems while positive values of Δb refer to attractive interaction. We can reduce eq. (3) to the following form when the total concentration of the mixture (C) approaches zero.

$$[\eta_{sp,m}/C] = [\eta_1](C_1/C) + [\eta_2](C_2/C). \tag{9}$$
$$C \to 0 \qquad C \to 0 \qquad C \to 0$$

For compatible systems the observed intrinsic viscosities are reported to be higher than the calculated values.

The present article discusses in detail our investigations of compatibility in solution of poly(vinyl chloride)/poly(ethylene-co-vinyl acetate) (PVC/EVA), poly(vinyl chloride)/poly(styrene-co-acrylonitrile) (PVC/SAN), and poly(ethylene-co-vinyl acetate)/poly(styrene-co-acrylonitrile) (EVA/SAN) blends. More specifically eq. (9) along with eq. (8) are used to characterize the compatibility of PVC/EVA, PVC/SAN, and EVA/SAN blends. Attempts have been made to correlate the compatibility in the solution state to that of the solid state.

EXPERIMENTAL

Table I shows the characterization data of materials used in this study. Cyclohexanone (Merck) was used as the solvent. This was dried over calcium chloride and distilled before use. The relative viscosities of the polymer solutions and their mixtures were determined by an Ubbelohde-type viscometer (Schott Gerate AVS 400 Viscometer).

The measurements were carried out at constant temperature of $28.9 \pm 0.01°C$ and was achieved in a waterbath with a thermostat (Schott Gerate CT 1450/2 thermostat).

Polymer solutions were prepared by dissolving accurately weighed samples in calculated amounts of solvents with a maximum concentration of 0.5 g/dL. Polymer mixtures with the desired proportion

Table I Characterization Data of Polymers Used

Abbreviation	Structure	T_g (°C)	Other Characteristics	Source
PVC	$+CH_2-CHCl+_n$	81	K value, 65	Plastics & Chemicals Ltd. Madras, India
EVA	$+CH_2-CH_2-CH_2-CH+_n$ $\|$ O $\|$ C=O $\|$ CH_3	-16	VA content, 45%	Exxon Chemical Co., Texas, USA
SAN	CN $\|$ $+CH_2-CH-CH_2-CH+_n$ ⬡	106	Acrylonitrile content, 28%	Adrich Chemical Co.

PVC, poly(vinyl chloride); EVA, poly(ethylene-co-vinyl acetate); SAN, poly(styrene-co-acrylonitrile).

of polymers were prepared by mixing measured volumes of individual polymer solutions.

The solid-state miscibility was studied by cloud point measurements. The lower critical solution temperature (LCST) was observed by using a procedure previously reported.[19] Samples with thickness of 0.05 mm, cut from solvent cast films were used for LCST measurements. A heating rate of 10°C/min was employed and cloud point temperatures were taken as the mean value for three runs. Infrared spectra were recorded with a Shimadzu 470 infrared spectrometer.

RESULTS AND DISCUSSION

The plot of η_{sp}/c versus C for PVC, EVA, and SAN are given in Figure 1. The graphs are linear and the points are fitted to the straight line very well. The intercept of this line with the Y axis gives the intrinsic viscosities, $[\eta]$, of the corresponding polymer solutions. The intrinsic viscosity values of the homopolymers are given in Table II. The γ^2 values are correction factors in linear regression analysis. The values are almost equal to unity, which shows perfect fit.

PVC/EVA Blends

The experimental and calculated intrinsic viscosity values of the blends are given in Table II. All the

compositions show a slight positive deviation from ideal behavior. This shows that the PVC/EVA system is compatible in solution at low concentrations. The values of Δb according to eq. (8) for different total concentrations of PVC/EVA mixtures are given in Fig. 2. It is seen that Δb values of PVC/EVA 70/30 and 30/70 compositions are positive at all concentrations indicating attractive interactions.[17] The Δb values of 50/50 PVC/EVA blends are very close to zero. Now let us try to relate these findings with the solid-state miscibility studies. We have examined the phase separation behavior of these blends by LCST measurements (Fig. 3). The
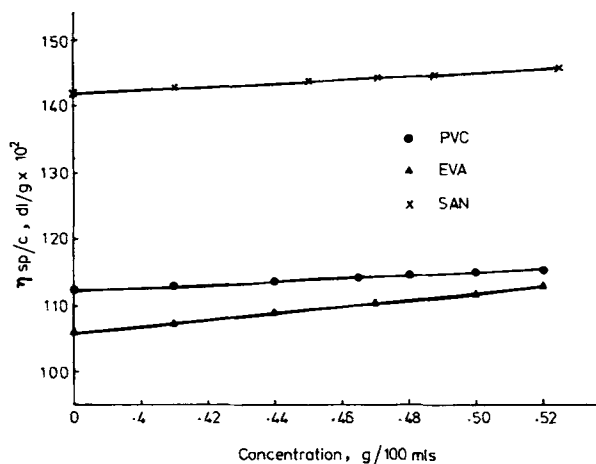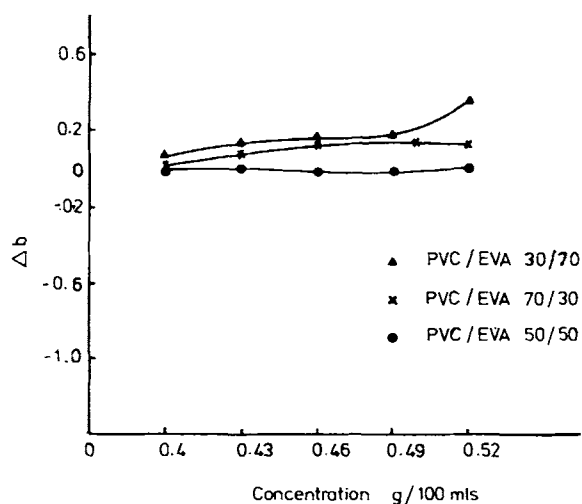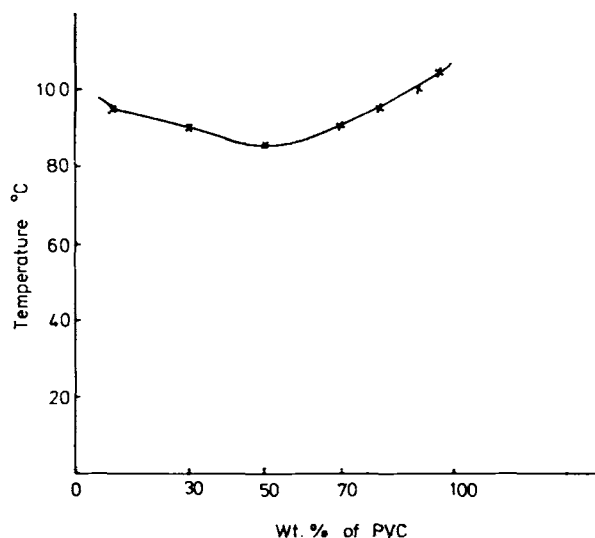
Figure 1 η_{sp}/c versus C for PVC, EVA, and SAN.

Table II   Observed and Calculated Intrinsic Viscosities of Polymer Systems

Polymer System	γ^2	$[\eta]$ (dL/g)	
		Observed	Calculated
PVC	1.0	1.12	
EVA	0.9955	1.06	
SAN	1.0	1.42	
PVC/EVA			
70/30	1	1.110	1.102
50/50	0.9997	1.095	1.090
30/70	0.9989	1.084	1.078
PVC/SAN			
70/30	0.9946	1.215	1.215
50/50	0.9845	1.255	1.271
30/70	0.9996	1.300	1.331
EVA/SAN			
70/30	0.9994	1.125	1.168
50/50	1.0	1.225	1.241
30/70	0.9893	1.300	1.311

Figure 3   LCST of PVC/EVA blends.

results show that blends with higher concentrations of the functional group have higher phase separation temperature. This indicates that blends containing a higher proportion of functional group are more compatible. Several studies have already been reported on the miscibility of EVA with chlorinated polymers in the solid state. Walsh et al.[20] reported that in the case of EVA/chlorinated polyethylene blends, compositions with a higher concentration of functional groups, chlorine, or acetate show higher LCST and hence are more compatible. Coleman et

al.[21] postulated that a blend of PVC and EVA with vinylacetate (VAc) content of 45% should exhibit similar phase behavior to chlorinated polyethylene/EVA blends as the chlorine contents of PVC are similar. They have shown that the miscibility of PVC/EVA is due to a hydrogen bonding type of interaction. Studies of Feldman and Rusu[22] on a PVC/EVA system with VAc content of 45% indicated that the tangent of dielectric loss had only a single and new absorption maximum at 46°C. Diagrams representing the variation of physico-mechanical index with temperature of PVC/EVA blends showed a single inflection point. All these studies indicate the molecular level miscibility of PVC/EVA blends.[23] Therefore, it can be concluded that compatibility studies by viscometry are in agreement with the solid-state miscibility analysis.

Figure 2 Δb versus C for PVC/EVA blends: 70/30, 50/50, and 30/70.
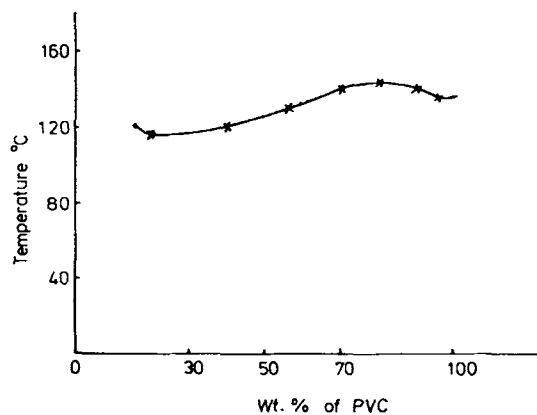
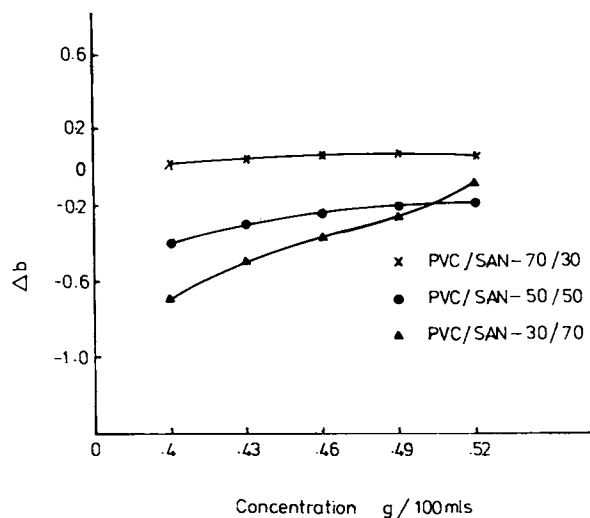**Figure 4**   LCST of PVC/SAN blends.

Figure 5 Δb versus C for PVC/SAN blends: 70/30, 50/50, and 30/70.

PVC/SAN Blends

Table II shows the intrinsic viscosity for various concentrations of the PVC/SAN system. The blend with 30% SAN shows ideal behavior. Other compositions deviate from ideal behavior and show negative deviation indicating repulsive interaction. LCST results obtained from the solid films (Fig. 4) also show that PVC/SAN blends with higher concentrations of PVC are more compatible. Huarng et al.[24] reported that PVC/SAN blends are not totally

miscible. Compositions with SAN content above 30% had two distinct glass-transition temperatures. Kim et al.[25] have shown that the intramolecular repulsion between styrene and acrylonitrile units in SAN is the cause of miscibility of SAN/PVC blends.

The plot of Δb versus concentration of PVC/SAN blends is given in Fig. 5. It was found that the values of Δb decrease as the amount of SAN in the mixture increases when compared at the same concentration. These solution results suggest that the PVC/SAN blend system becomes more compatible as the SAN concentration in the mixture decreases. This is in full agreement with the reported solid-state miscibility studies of these blends.

EVA/SAN Blends

Table II shows the intrinsic viscosity of EVA/SAN blends of various compositions. The results indicate that all the compositions show negative deviation from ideal behavior. EVA/SAN mixtures in solution become turbid at moderate concentration and the dried films are opaque. Spectroscopic studies also do not give any information about interaction between EVA and SAN. Figures 6 and 7 show the infrared spectra of these samples. The carbonyl absorption frequencies of EVA in the blends remain unaffected.

The plot of Δb versus total concentration for the EVA/SAN system is given in Figure 8. Δb decreases as the total concentration decreases. This may be

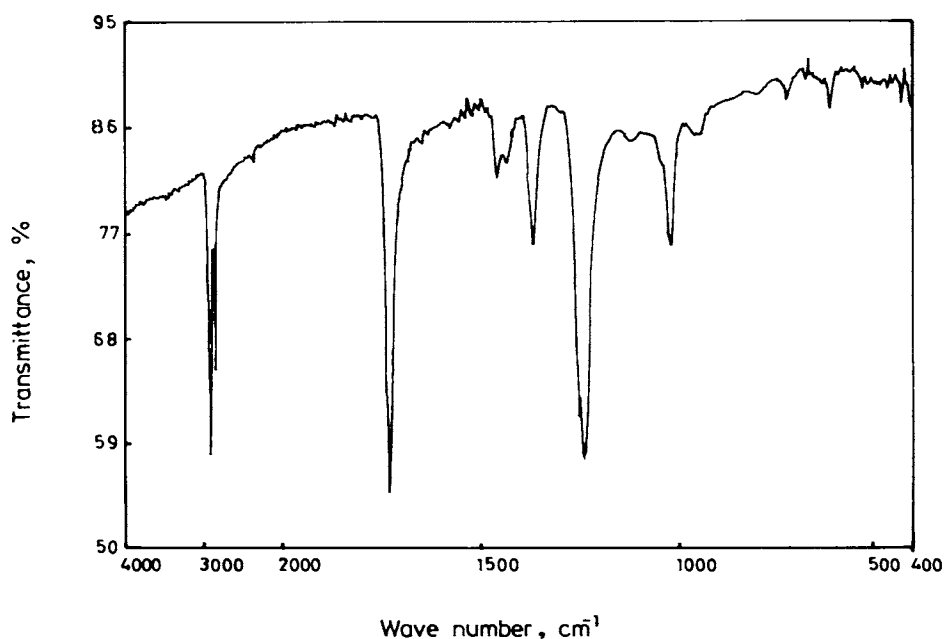

Wave number, cm^{-1}

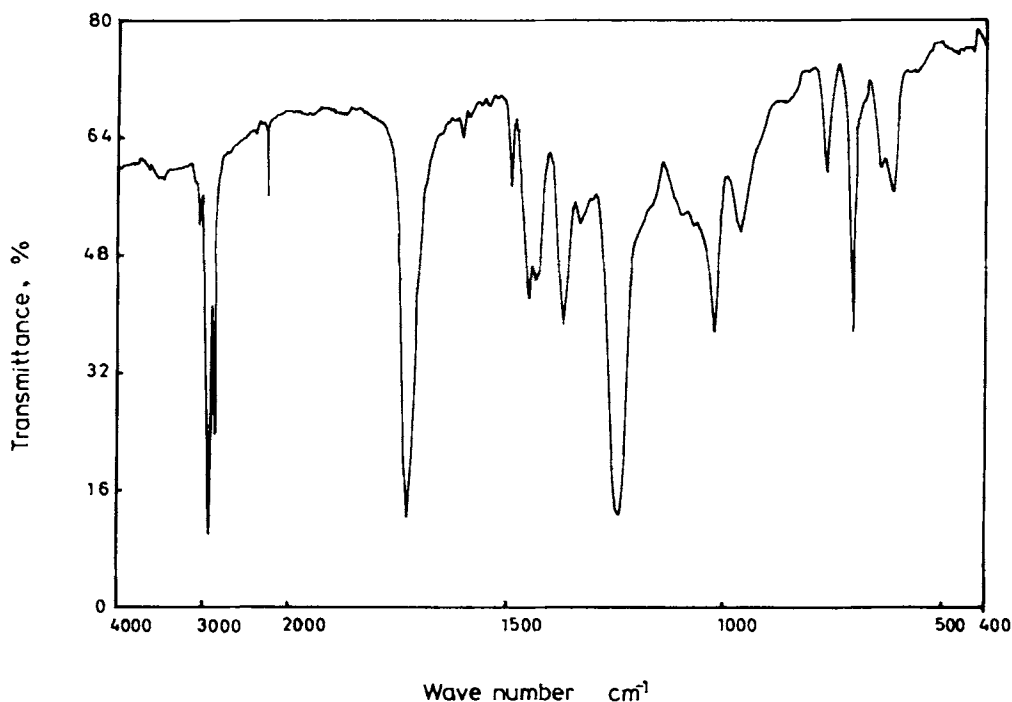**Figure 6** IR spectrum of pure EVA.

Figure 7 IR spectrum of EVA/SAN 50/50 blend.

due to the increase in polymer–solvent interaction with the increase in solvent concentration. In other words, the polymer–solvent interaction exceeds the polymer–polymer interaction at very high dilution. The values of Δb are negative at all concentrations and compositions indicating the repulsive interaction between EVA and SAN. This suggests that EVA/SAN blends are incompatible. Solid-state analysis by infrared spectroscopy and transparency also indicated incompatibility.

CONCLUSIONS

The value of Δb for PVC/EVA blends are positive, indicating attractive interaction between the component polymers. The Δb values of PVC/SAN blends are positive for 70/30 and negative for all other compositions showing that these blends are compatible at higher concentrations of PVC. For the EVA/SAN system, Δb values are negative for all compositions, which is an indication of repulsive interaction between component polymers.

The observed and calculated intrinsic viscosity values indicate that the PVC/EVA systems show positive deviation from ideal behavior. PVC/SAN systems show both ideal behavior (70/30 blend) and negative deviation (50/50 and 30/70 blends). The EVA/SAN blends show negative deviation for all

compositions. These results are in agreement with the solid-state miscibility of these blends reported.

Finally it is important to mention that both eq. (6) that is,

$$\Delta b = b_{12} - b_{12}^*$$

(modified form of Krigbaum and Wall[17]) and eq. (7),

$$(\eta_{sp,m}/C)_{C \to 0} = [\eta_1](C_1/C)_{C \to 0} + [\eta_2](C_2/C)_{C \to 0}$$
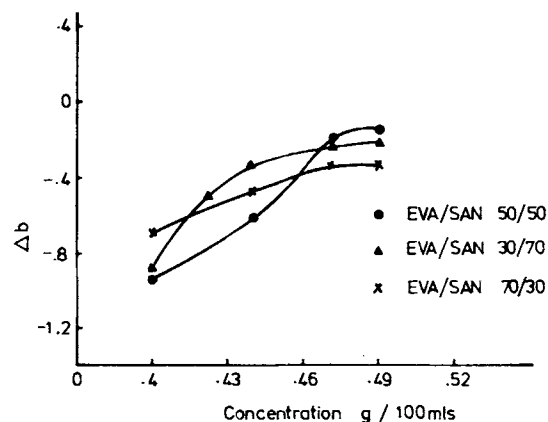

Figure 8 Δb versus C for EVA/SAN blends: 70/30, 50/50, and 30/70.

are highly useful to characterize the compatibility of binary polymer blends.

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