

Miscibility studies of polyvinyl pyrrolidone / polyether sulfone blends by viscosity, ultrasonic velocity and polarized optical microscopic methods

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Abstract

The solutions of polyvinyl pyrrolidone and polyether sulfone blends of different compositions were prepared in a common solvent. The miscibility of these blends was probed viscosity, ultrasonic velocity and polarized optical microscopic techniques. The interaction parameters of these blends of different compositions were computed with the relevant equations. The immiscible nature of these blends was confirmed by the ultrasonic velocity and polarized optical microscopic methods. The immiscible nature of these blends suggests that these two polymers are favourable for preparing polymer alloys using a suitable compatibiliser.

Keywords: Polymer blends, Polyvinyl Pyrrolidone, Polyether sulfone, Miscibility, Ultrasonic velocity, Viscosity, Optical microscopy

INTRODUCTION

In order to obtain tailor made properties, blending of polymers is often carried out [1]. The gain in improved properties depends on the degree of compatibility or miscibility of the constituent polymers in a blend at molecular level. Often the blending of polymers leads to immiscible systems. However, immiscible blend systems often find applications as polymer alloys. Many techniques are available for probing the miscibility of polymer blends [2]. Unfortunately, some of these techniques are complicated, costly and time consuming. Hence, it is desirable to identify simple, low cost and rapid techniques to study the miscibility of the polymer blends. Chee [3] and Sun et al. [4] employed viscometry for the study of polymer – polymer miscibility. Hourston et al. [5] and Kuleznev et al. [6] suggested the use of ultrasonic and viscosity measurements for miscibility studies. Singh and Singh [7, 8] and Singh et al. [9] pointed out that ultrasonic velocity and viscosity measurements can be used to determine polymer – polymer miscibility.

Varada Rajulu et al. [10-16] extensively employed viscosity, ultrasonic velocity, density, refractive index, and polarized optical microscopic techniques to probe the polymer – polymer miscibility in several blend systems. In the present investigation, the authors carried out the miscibility studies of the poly blends of Poly vinyl pyrrolidone (PVP)/ Polyether sulfone (PES) by viscosity, ultrasonic velocity, and polarizing optical microscopic techniques. The authors selected PVP as it is biocompatible in nature. Similarly, PES is widely used as

the membranes. It is expected that by blending PES with other polymers, its properties can be improved.

EXPERIMENTAL DETAILS

The blends of PVP/PES of different compositions were prepared by mixing solutions of the polymers in dimethyl formamide (DMF). PVP (M/s. S.D. Fine chemicals, India, $\overline{Mn} = 40000$) and PES (M/s Aldrich, $\overline{Mn} = 100000$) were used in the present study. The total weight of the two components of particular blend in solution was always maintained at 2g/dl. The ultrasonic velocities of the blend solutions were measured by ultrasonic interferometric technique. The temperature was maintained at 35 °C by circulating water from the thermostat with a thermal stability of +0.05 °C through the double wall jacket of the ultrasonic experimental cell. The relative viscosities of blend solutions were measured at 35 °C using an Ubbelohde suspended level viscometer. The polarizing micrograms of the blend films cast for all compositions were recorded using a microprocessor controlled Carl Zeiss Polarising Microscope.

RESULTS AND DISCUSSION

The measured values of reduced viscosity for PVP, PES and PVP/ PES blend (in with weight fractions of both PVP and PES were 0.5:0.5) in DMF at 35 °C are presented in Table 1.

Table 1: Reduced viscosities of PVP, PES and PVP/PES blend (0.5: 0:5 composition) in DMF at 35 °C

Concentration (g/dl)	Reduced Viscosity (η_{sp} / C) (dl / g)		
	PVP	PES	PVP/PES
1.43	0.2181	0.4340	0.3762
1.54	0.2222	0.4807	0.3580
1.67	0.2696	0.4661	0.3513
1.82	0.3158	0.5770	0.3639
2.00	0.3388	0.5683	0.3635

In Figure 1, the Huggin's plot for the blend of PVP/ PES in which the weight fraction of both the components was maintained at 0.5 is presented.

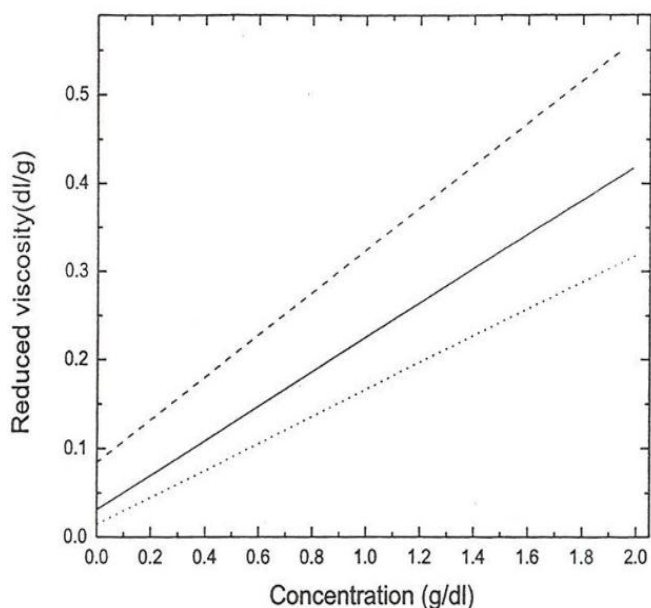


Fig. 1 Reduced Viscosity vs Concentration of PVP, PES and PVP (0.5)/ PES (0.5) blend ---- PES; --- PVP/PES Blend and ... PVP

In the same graph, the Huggin's plots for the homopolymers PVP and PES are also presented.

Chee [3] gave the expression for the interaction parameter (ΔB) when the polymers are mixed in weight fractions W_1 and W_2 as:

$$\Delta B = (b - \bar{b}) / (2 W_1 W_2) \quad \dots (1)$$

Where $\bar{b} = W_1 b_{11} + W_2 b_{22}$,

Where b_{11} and b_{22} are the slopes of the viscosity curves for the components and b is related to Huggin's coefficient K_H as

$$b = K_H [\eta]^2 \quad \dots (2)$$

For ternary system, it is also given by

$$B = W_1^2 b_{11} + W_2^2 b_{22} + 2 W_1 W_2 b_{12} \quad \dots (3)$$

Where b_{12} is the slope for the curve of blend solution. Using these values, Chee3 defined a more effective parameter

$$\Delta B$$

$$\mu = \frac{\Delta B}{\left\{ [\eta]_2 - [\eta]_1 \right\}^2} \quad \dots (4)$$

Where $[\eta]_1$ and $[\eta]_2$ are intrinsic viscosities for pure component solutions.

The blend is miscible of $\mu \geq 0$ and immiscible when $\mu < 0$ [3]. Recently, Sun et al. [4] suggested a new equation for the determination of miscibility of polymers as:

$$\alpha = K_m \frac{K_1 [\eta]_1^2 W_1^2 + K_2 [\eta]_2^2 W_2^2 + 2(K_1 K_2)^{1/2} [\eta]_1 [\eta]_2 W_1 W_2}{\left\{ [\eta]_1 W_1 + [\eta]_2 W_2 \right\} \left\{ [\eta]_1 W_1 + [\eta]_2 W_2 \right\}} \quad \dots (5)$$

Where K_1, K_2 and K_m are the Huggin's constants for individual components 1, 2 and blend respectively. While deriving this equation [Eq. (5)], the long range hydrodynamic interactions are taken into account. Sun et al. [4] suggested that the blend would be miscible if $\alpha \geq 0$ and immiscible when $\alpha < 0$.

For the PVP/ PES blend, the μ and α values were calculated using Equations 4 and 5 respectively. These values for the blends of different compositions are presented in Table 2.

Table 2: Interaction parameters μ and α for PVP/ PES blends of different compositions in DMF at 35 °C

Weight fraction of PVP/ PES Blend	μ	α
0.2/0.8	-4.055	-130.25
0.4/0.6	-4.733	-140.88
0.5/0.5	-5.513	-170.58
0.6/0.4	-5.899	-148.76
0.8/0.2	-0.617	-005.90

From this table, it is clearly evident that μ and α for PVP/ PES blends of all compositions are negative. This clearly indicates that the blends under investigation are immiscible in nature. In order to further probe the miscibility of the polymer blends under study, the ultrasonic velocity of the polymer blend solutions were measured. The variation of ultrasonic velocity of PVP/ PES polymer blends with composition is depicted in Figure 2.

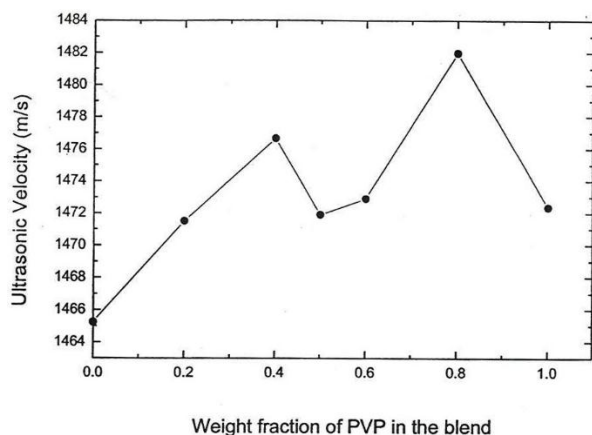


Fig. 2 Variation of ultrasonic velocity with weight fraction of PVP in PVP/ PES Blend in DMF at 35 °C

From this figure, it is clearly evident that the variation is non-linear for the system under study showing multiphase nature in the blend. Singh and Singh [7] have also attributed the non-linear variation of ultrasonic velocity with blend compositions to the immiscible nature of several blends.

In order to further probe the miscibility or otherwise of PVP/PES blend, the authors used the solid – state technique, viz., polarized optical microscopy. The optical micrograms of the PVP/PES blends of different compositions are presented in Figure 3.

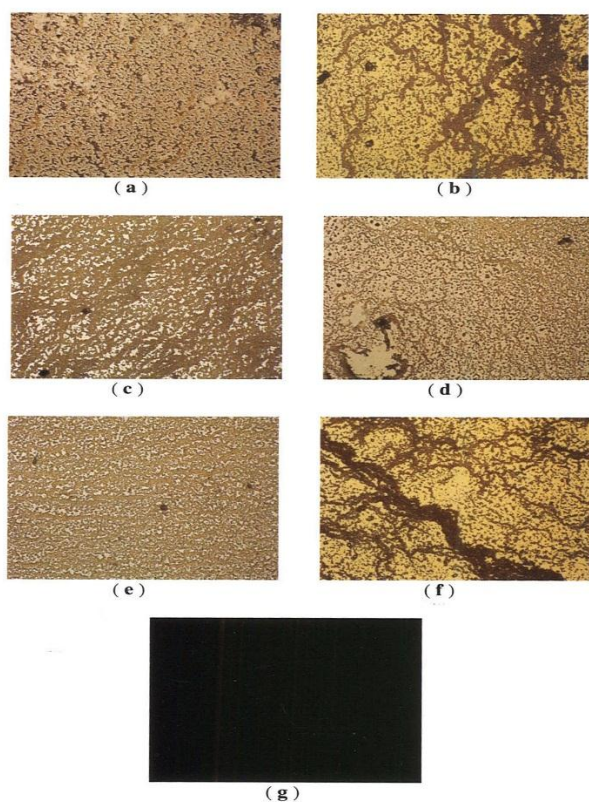


Fig. 3 Polarized Optical Micrographs of PVP/ PES blends with the weight fraction of PVP – (a) 0.0; (b) 0.2; (c) 0.4; (d) 0.5; (e) 0.6; (f) 0.8 ; (g) 1.0.

From these micrograms, it is clearly evident that the components of PVP and PES exist as two phases. This clearly indicates that the blend is immiscible in nature. Chattopadhyaya and Benerjee [17] also used polarizing microscopic technique to confirm the miscibility or otherwise of the blends in film form. These studies provide us a clue that the combination of PVP and PES can be converted in to a polymer alloy by suitable compatibilisation.

In order to explain the immiscible nature of PVP/ PES blend basing on thermodynamics, the solubility parameters of constituent polymers were calculated using Van Krevelen group additive method [18]. The computed values of solubility parameters PVP and PES Van Krevelen method [18] are found to be $19.2 J^{1/2} / cm^{3/2}$ and $21.5 J^{1/2} / cm^{3/2}$ respectively. The difference between these two values is found to be $2.3 J^{1/2} / cm^{3/2}$ (2.3 H). As per thermodynamic criterion, the components in a mixture are miscible only when the difference in their solubility parameters is less than $2 J^{1/2} / cm^{3/2}$ (2H). As in the present case, this value exceeded 2H and hence the blend is an immiscible one.

CONCLUSIONS

The viscosity, ultrasonic velocity and polarized optical microscopic techniques indicated that the blends of PVP/ PES are immiscible in nature. The computed values of Hildebrand (solubility) parameters also confirmed the immiscible nature of the blends under study. Thus PVP and PES are suitable homopolymers to prepare polymer alloys.

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