

MISCIBILITY STUDIES OF POLYSTYRENE/ POLYETHER SULFONE BLENDS BY VISCOSITY, ULTRASONIC VELOCITY AND POLARIZED OPTICAL MICROSCOPIC METHODS

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Abstract: The solutions of polystyrene and poly ether sulfone blends of different compositions were prepared in a common solvent. The miscibility of these blends was probed by 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 favorable for preparing polymer alloys using a suitable compatibilizer.

Keywords - Polymer blends, Polystyrene, Polyether sulfone, Miscibility, Ultrasonic velocity, Viscosity, Optical microscopy.

I. INTRODUCTION

For comfortable living, man always wants to have newer materials with improved properties. Owing to their unique properties, such as high strength to weight ratio, ease of preparation, light weight etc, polymers find many applications in our daily life. But for specific needs, a single polymer alone may not meet the demands. In such cases, blending of two or more polymers or copolymers is usually carried out. The properties of the resulting blends depend on the miscibility of their components at molecular level. A miscible blend can be used as a tailor made polymer system whereas; an immiscible can be converted into a polymer alloy with a suitable compatibilizer. The polymer alloys usually possess superior properties to those of the corresponding homopolymers.

Various techniques are available to study the polymer miscibility. They are – Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA), Scanning Electron Microscopy (SEM), Nuclear Magnetic Resonance (NMR) etc. But these techniques are complicated and time consuming. In order to employ simple, rapid and low cost techniques, the author used viscosity, ultrasonic velocity, refractive index, density and polarized optical microscopy.

Chee[1] and Sun et al. [2] used the viscometric method for the study of the polymer–polymer miscibility. Singh and Singh [3] suggested the use of ultrasonic velocity and viscosity measurements for investigating polymer–polymer miscibility. Singh [4] and Singh et al. [5] showed that the variation of ultrasonic velocity and viscosity with blend composition is linear for miscible blends and non- linear for immiscible blends. Recently, Varada Rajulu et al. [6-12] used viscosity, ultrasonic velocity, refractive index, density and polarizing optical microscopic techniques and probed the miscibility of several polymer blends. In the present study, the author employed these techniques to investigate the miscibility of polystyrene (PS) / polyether sulfone (PES) blend. The author selected PS and PES because PS is a rigid polymer whereas PES is a film forming membrane polymer.

II. MATERIALS AND METHODS

The blends of PS/ PES of different compositions were prepared by mixing solutions of the respective polymers in DMF. PS (M/s Rishab Polymers, $\overline{Mn} = 70,000$) and PES (M/s Aldrich, $\overline{Mn} = 100000$) were employed in the present study. The total weight of the two components was always maintained at 2g/dl for making the stock solutions. The ultrasonic velocities of the blend solutions were measured by ultrasonic interferometric technique⁵. The temperature was maintained at 35 °C by circulating water from a thermostat with a thermal stability of +0.05 °C through the double wall jacket of the ultrasonic experimental cell. The relative viscosities of the blend solutions were measured at 35 °C using an Ubbelohde Suspended Level Viscometer. The polarizing optical micrograms of the blend films cast for all compositions were recorded using a microprocessor controlled Carl Zeiss polarizing microscope.

III. RESULTS AND DISCUSSIONS

The measured values of reduced viscosity for PS, PES and PS/PES (blend in which the weight fraction of PS and PES each is 0.5) in DMF at 35 °C are presented in table 1.

Table 1: Reduced viscosities of PS, PES and their blend (0.5: 0:5 compositions) in DMF at 35 °C

Concentration (g/dl)		Reduced Viscosity (η_{sp} / C) (dl / g)	
	PS	PES	PS/PES
1.43	0.3973	0.4340	0.3425

1.54	0.4225	0.4807	0.3355
1.67	0.4296	0.4661	0.3377
1.82	0.4603	0.5770	0.3476
2.00	0.4716	0.5683	0.3477

The Huggin's plot for this blend in which the weight of both the components was maintained at 0.5 is presented in Fig. 1.

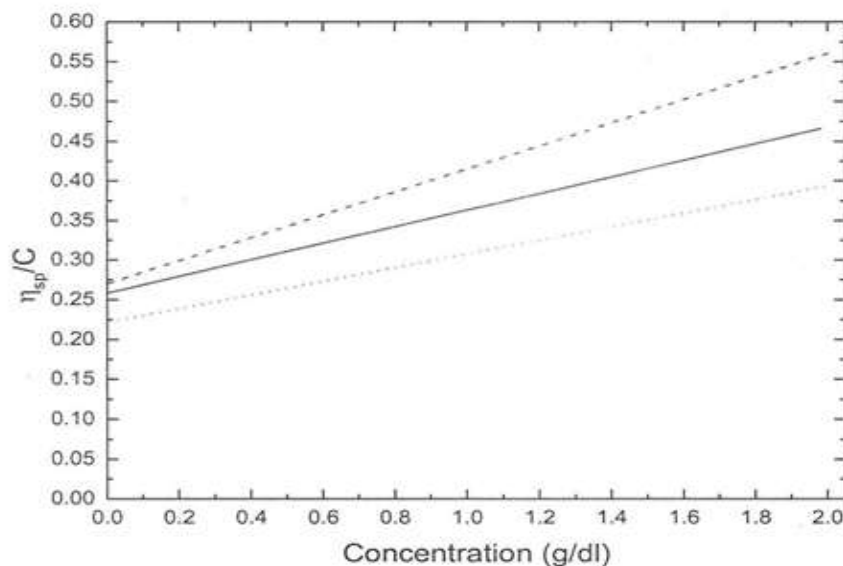


Fig. 1 Reduced viscosity vs concentration graph for PS (0.5)/PES (0.5) blend Composition (--- PES; ___ PS/ PES Blend; and ... PS)

In the same figure, the Huggin's plots for the constituent homopolymers are also presented. In order to probe the miscibility of the PS/ PES blends, the equations suggested by Chee [1] and Sun et al. [2] (Eqns. 1 and 2 respectively) were utilized and the interaction parameters μ and α were calculated.

$$\mu = \frac{\Delta B}{\{[\eta]_2 - [\eta]_1\}^2} \quad \dots(1)$$

Here $\Delta B = W_1^2 b_{11} + W_2^2 b_{22} + 2 W_1 W_2 b_{12}$ in which W_1 and W_2 are the weight fractions of the two polymers, b_{11} and b_{22} and b_{12} are the slopes of the Huggin's plots of the two polymers and b_{12} is that of the blend. $[\eta]_1$ and $[\eta]_2$ are intrinsic viscosities for pure component solutions.

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

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. (2)], the long range hydrodynamic interactions are taken into account. Sun et al. [2] suggested that the blend would be miscible if $\alpha \geq 0$ and immiscible when $\alpha < 0$.

The μ and α values for blends of different compositions are presented in Table 2.

Table 2: Interaction parameters μ and α for PS/ PES blends of different compositions

Weight fraction of PS/ PES Blend	μ	α
0.2/0.8	-30.84	-1.912
0.4/0.6	-22.82	-1.816
0.5/0.5	-26.28	-2.310
0.6/0.4	-30.26	-2.242
0.8/0.2	-04.47	-5.783

From this table, it can be seen that μ and α for PS/ PES blends of all compositions are negative. This 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 was measured. The variation of ultrasonic velocity of PS/ PES polymer blends with composition is depicted in Fig. 2.

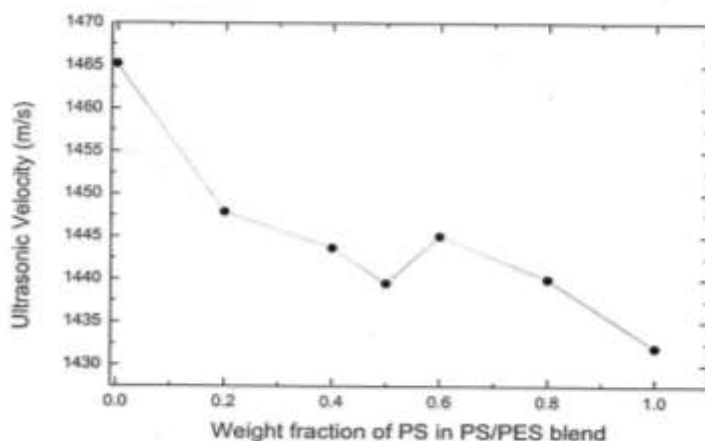


Fig. 2 The variation of ultrasonic velocity with weight fraction of PS in PS/ PES Blend in DMF at 35 °C

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 [3] 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 PS/PES blend, the authors used the solid – state technique, viz., polarized optical microscopy. The micrograms of the PS/PES blends of different compositions are presented in Fig. 3.

From these micrograms, it is evident that the components of PS and PES exist as two phases in the blend. This clearly indicates that the blends is immiscible in nature. Chattopadhyaya and Benerjee [13] 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 PS and PES can be converted in to a polymer alloy by suitable compatibilization.

In order to explain the immiscible nature of PS/ PES blend basing on thermodynamics, the solubility parameters were calculated using Van Krevelen group additive method [14]. The computed values of solubility parameters (Hildebrand parameters) of PS and PES are found to be $19.1 J^{1/2} / cm^{3/2}$ and $21.5 J^{1/2} / cm^{3/2}$ respectively. The difference between these two values is 2.4 H (where H is the Hildebrand Unit = $1 J^{1/2} / cm^{3/2}$). As per thermodynamic criterion [14] the components in a mixture are miscible only when the difference in their solubility parameters is less than 2H. As in this case, the value exceeded 2H, the blends under study became immiscible.

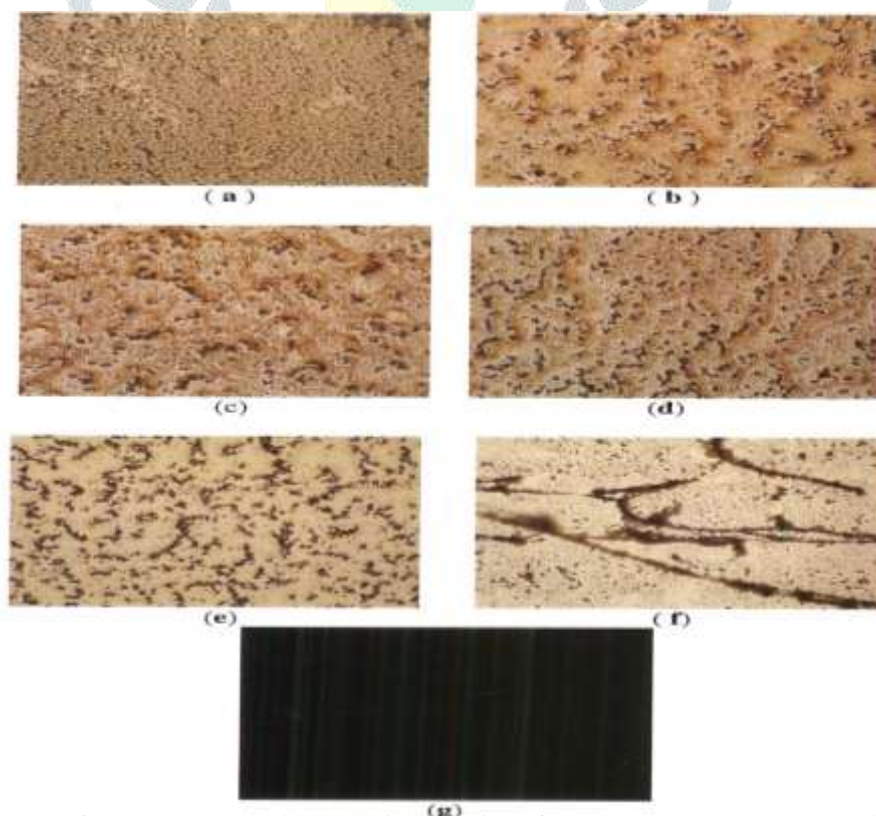


Fig. 3 Polarized Optical Micrographs of PS/ PES blends with the weight fraction of PS – (a) 0.0; (b) 0.2; (c) 0.4; (d) 0.5; (e) 0.6; (f) 0.8 ; (g) 1.0

IV. CONCLUSIONS

From the viscosity, ultrasonic velocity, refractive index, density and polarizing optical microscopic techniques, the blends of PS/PES were found to be immiscible. The computed solubility parameters further supported these observations.

REFERENCES

- [1] Chee, K.K. 1990. Determination of polymer-polymer miscibility by viscometry. *European Polymer Journal*, 26(4): 423-426.
- [2] Sun, Z., Wang, W. and Feng, Z. 1992. Criterion of polymer-polymer miscibility determined by viscometry. *European Polymer Journal*, 28(10): 1259–1261.
- [3] Singh, Y. P. and Singh, R. P. 1983. Compatibility studies on solid polyblends of poly(methyl methacrylate) with poly(vinyl acetate) and polystyrene by ultrasonic technique. *European Polymer Journal*, 19(6): 529-533.
- [4] Singh, Y. P. and Singh, R. P. 1984. Compatibility studies on polyblends of PVC with chlororubber-20 and its graft polyblends by ultrasonics. 20(2): 201-205.
- [5] Singh, Y. P., Das, S., Maiti, S. and Singh, R. P. 1981. *Journal of Pure and Applied Ultrasonics*, 3: 1.
- [6] Varada Rajulu, A, Babu Rao, G. and Lakshminarayana Reddy, R. 2001. *J Polym Mater*, 19: 217.
- [7] Varada Rajulu, A., Lakshminarayana Reddy, R., Babu Rao, G., He, J. and Zhang, J. 2001. *J Appl Polym Sci*, 81: 557.
- [8] Varada Rajulu, A., Babu Rao, G. and Lakshminarayana Reddy, R. 2001. *J. Pure Appl. Ultrason.*, 23: 33.
- [9] Varada Rajulu, A., Ganga Devi, L. and Babu Rao, G. 2003. *J Appl Polym Sci*, 89: 2970.
- [10] Varada Rajulu, A. and Lakshminarayana Reddy, R. 2000. *Int J Polym Anal Charact*, 5: 467.
- [11] Varada Rajulu, A. and Lakshminarayana Reddy, R. 2000. *Int J Polymeric Mater*, 47: 469.
- [12] Varada Rajulu, A., Lakshminarayana Reddy, R., Raghavendra, S. M. and Akheel Ahmed, S. 1999. *Eur Polym J*, 35: 1183.
- [13] Chatopadhyay, S. and Banerjee, A. N. 1991. *J Poly. Mater*, 8: 351.
- [14] Van Krevelen, D.W. 1990. *Properties of Polymers – Their correlation with chemical structure: Their numerical estimation and prediction from additive group contributions*. Polymer Science and Technology. (Elsevier, Amsterdam).

