# Ultrasonic, Refractometric, and Viscosity Studies of Some Polymer Blends in Solution

**A. VARADA RAJULU,[1] R. LAKSHMINARAYANA REDDY,[1] SIDDARAMAIAH[2]**

[1] Department of Polymer Science and Technology, Sri Krishnadevaraya University, Anantapur 515 003, India

[2] Department of Polymer Science and Technology, S. J. College of Engineering, Mysore 570 006, India

**ABSTRACT:** Miscibility studies of poly(vinyl pyrrolidone)–polystyrene and poly(vinyl pyrrolidone)–poly(methyl methacrylate) in mixed common solvent (dimethyl formamide + cyclohexanone) have been carried out in different percentages of the blend components. The ultrasonic velocity, viscosity, density, and refractive index have been measured at 30°C. The interaction parameters have been obtained using the viscosity data to probe the miscibility. The obtained results have been confirmed by the ultrasonic velocity, density, and refractive index. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1823–1827, 1998

**Key words:** polymer blends; ultrasonic velocity; viscosity; refractive index; miscibility

## INTRODUCTION

The blending of polymers is one of the simplest means to obtain a variety of physical and chemical properties from the constituent polymers.[1] The gain in newer properties depends on the degree of compatibility or miscibility of the polymers at a molecular level. There have been various techniques of studying the miscibility of the polymer blends.[2] Some of these techniques may be complicated, costly, and time-consuming. Hence, it is desirable to identify simple, low-cost, and rapid techniques to study the miscibility of polymer blends. Chee[3] and Sun et al.[4] have suggested a viscometric method for the study of polymer–polymer miscibility. Singh and Singh[5,6] have suggested the use of ultrasonic velocity and viscosity measurements for investigating the polymer miscibility. Paladhi and Singh[7,8] have shown that the variation of ultrasonic velocity and viscosity with

blend compositions is linear for miscible blends. Recently, Varada Rajulu et al.[9] have used an ultrasonic technique for the study of the miscibility of polymers. In the present study, the authors have measured the viscosity, ultrasonic velocity, density, and refractive index of poly(vinyl pyrrolidone)–polystyrene (PVP–PS) and poly(vinyl pyrrolidone)–poly(methyl methacrylate) (PVP–PMMA) blend solutions in 1 : 1 mixture of cyclohexanone and dimethyl formamide at 30°C in order to study the miscibility of the blend. This mixed solvent is found to be an effective one for the blends under study.

## EXPERIMENTAL

The blends of PVP–PS and PVP–PMMA of different compositions have been made by mixing solutions of the polymers in a mixed solvent of dimethyl formamide and cyclohexanone (taken in 1 : 1 ratio). PVP (M/s Laser Chemicals, India; $\bar{M}_V = 25{,}000$), PS (M/s G.S.F.C., India; $\bar{M}_V = 90{,}000$), and PMMA (M/s G.S.F.C., India; $\bar{M}_V$

**Table I   Ultrasonic Velocity, Density, and Refractive Index of PVP–PS and PVP–PMMA Blend Solutions in Mixed Solvent of Dimethyl Formamide and Cyclohexanone at 30°C**

| % of PVP in the Blend | Ultrasonic Velocity (m/s) | Density (g/cc) | Refractive Index |
|---|---|---|---|
| | PVP–PS Blend | | |
| 0.0 | 1413.06 | 0.9439 | 1.4325 |
| 20.0 | 1416.00 | 0.9438 | 1.4330 |
| 40.0 | 1416.16 | 0.9438 | 1.4330 |
| 60.0 | 1415.36 | 0.9438 | 1.4330 |
| 80.0 | 1417.60 | 0.9438 | 1.4330 |
| 100.0 | 1416.00 | 0.9437 | 1.4330 |
| | PVP–PMMA Blend | | |
| 0.0 | 1441.92 | 0.9517 | 1.4305 |
| 20.0 | 1408.16 | 0.9442 | 1.4320 |
| 40.0 | 1414.88 | 0.9448 | 1.4310 |
| 60.0 | 1416.00 | 0.9447 | 1.4300 |
| 80.0 | 1408.00 | 0.9424 | 1.4320 |
| 100.0 | 1416.00 | 0.9437 | 1.4330 |

= 98,000) have been employed in the present study. The total weight of the 2 components in the solution is always maintained at 1 g/dL. The ultrasonic velocity measurements have been performed by an ultrasonic interferometric technique.[10] The temperature is maintained at 30°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 densities of the solutions have been measured at 30°C by specific gravity bottle. The refractive index of the blend solutions has been measured with Abbe's refractometer with thermostated water circulation system[11] at 30°C. The relative viscosity of blend solutions has been measured at 30°C using an Ubbelohde suspended level viscometer.

## RESULTS AND DISCUSSION

The obtained values have been presented in Table I. Figure 1 shows the Huggin's plots for blends of PVP–PS and PVP–PMMA, in which the weight fraction of both the components has been maintained at 0.5. Chee[3] has given an expression for the interaction parameter when the polymers are

mixed in weight fractions of $W_2$ and $W_3$ as follows:

$$\Delta B = (b - \bar{b})/2W_2W_3 \tag{1}$$

where $\bar{b} = W_2b_{22} + W_3b_{33}$, in which $b_{22}$ and $b_{33}$ are the slopes of the viscosity curves for the pure components. The coefficient $b$ is related to the Huggin's coefficient $K_H$ as

$$b = K_H[\eta]^2 \tag{2}$$

For a ternary system,[3] the coefficient '$b$' is also given by

$$b = W_2^2b_{22} + W_3^2b_{33} + 2W_2W_3b_{23} \tag{3}$$

where $b_{23}$ is the slope of the viscosity curve for the blend solution.

Using these values, Chee[3] has defined a more effective parameter, as follows:

$$\mu = \Delta B/\{[\eta]_3 - [\eta]_2\}^2 \tag{4}$$

where $[\eta]_2$ and $[\eta]_3$ are the intrinsic viscosities for the pure component solutions. The blend is miscible if $\mu \geq 0$ and immiscible[3] if $\mu < 0$. In the present study, the values of $\mu$ for PVP–PS and PVP–PMMA systems are computed as $-0.1596$ and $-0.7344$, respectively, indicating that the blends are immiscible. But recently, Sun et al.[4] have suggested a new formula for the determination of miscibility for polymers as follows:

$$\alpha = K_m - \frac{K_1[\eta]_1^2W_1^2 + K_2[\eta]_2^2W_2^2 + 2K_1K_2[\eta]_1[\eta]_2W_1W_2}{\{[\eta]_1W_1 + [\eta]_2W_2\}^2} \tag{5}$$

where $K_1$, $K_2$, and $K_m$ are the Huggin's constants for the individual (pure) components 1 and 2 and the blend, respectively. While deriving this equation, the long-range hydrodynamic interactions are taken into account. Sun et al.[4] have suggested that a blend will be miscible if $\alpha \geq 0$ and immiscible when $\alpha < 0$. In the present study, the $\alpha$ values are found to be $+0.8360$ and $-0.4828$ for PVP–PS and PVP–PMMA blends, respectively. These values indicate that the blend of PVP–PS is miscible, whereas PVP–PMMA is immiscible. But the $\mu$ values [eq. (4)] indicate that both the blends under study are immiscible.

**Figure 1** The variation of reduced viscosity with composition in PVP–PS and PVP–PMMA (equal weight fraction) in mixed solvent (dimethyl formamide + cyclohexanone) at 30°C.

In order to confirm the miscibility or otherwise of these blends and the validity of equation (5), the variation of the ultrasonic velocity ($v$), density ($\rho$), and refractive index ($n$) of the polymer blend solutions with composition have been shown in Figures 2, 3, and 4, respectively. From these figures, it is clearly evident that the variation is linear for PVP–PS and nonlinear for PVP–PMMA showing a single phase for PVP–PS and a double phase for PVP–PMMA blend. Varada Rajulu et al.[9] have used these techniques for the miscibility study of a cellulose acetate–poly(methyl methacrylate) blend where nonlinear variation of the ultrasonic ve-

**Figure 2** Variation of ultrasonic velocity with the composition of PVP–PS and PVP–PMMA blends in a mixed solvent (dimethyl formamide + cyclohexanone) at 30°C.

locity with the blend composition has been attributed to the immiscible nature of the blend. Similarly, the linear variation of ultrasonic velocity with blend composition in the case of poly(methyl methacrylate)–poly(vinyl acetate)[6]



**Figure 3** Variation of density with composition of PVP–PS and PVP–PMMA blends in a mixed solvent (dimethyl formamide + cyclohexanone) at 30°C.



**Figure 4** The variation of the refractive index with the composition of PVP–PS and PVP–PMMA blends in a mixed solvent (dimethyl formamide + cyclohexanone) at 30°C.

has been attributed to the miscible nature of the blend. Further, Singh et al.[12] have pointed out that the variation of $v$ and $\rho$ with blend composition is linear for miscible blends, whereas the curves depicting this variation for immiscible blends are found to have S or inverted S shapes. In the present case, the variation of $v$, $n$, and $\rho$ with blend composition for PVP–PS is found to be linear, whereas the curves are S-shaped for PVP–PMMA blend. These observations clearly indicate that the blend PVP–PS is miscible, whereas PVP–PMMA is immiscible. The same information is found when equation (5) is employed to compute $\alpha$ values. Thus, these observations confirm the validity of equation (5). Further, it is also observed that the ultrasonic velocity, density, and refractive index of the PVP–PMMA blend is varying larger than those of the pure components. This observation further indicates that the blend is immiscible. But the ultrasonic velocity, density, and refractive index of the PVP–PS blend are not varied much more than those of the pure components. This observation indicates that the blend is miscible.

## REFERENCES

1. R. K. Gupta, I. D. Gaba, C. P. Pande, Y. P. Singh, and R. P. Singh, in *Polyimides,* Vol. 1, Plenum Press, New York, 1987, pp. 547–554.
2. S. Krause, in *Polymer Blends,* D. R. Paul and N. Seymour, Eds., Academic Press, New York, 1978.
3. K. K. Chee, *Eur. Polym. J.,* **26,** 423 (1990).
4. Z. Sun, W. Wang, and Z. Fung, *Eur. Polym. J.,* **28,** 1259 (1992).
5. Y. P. Singh and R. P. Singh, *Eur. Polym. J.,* **20,** 201 (1984).
6. Y. P. Singh and R. P. Singh, *Eur. Polym. J.,* **19,** 535 (1983).
7. R. Paladhi and R. P. Singh, *J. Appl. Polym. Sci.,* **51,** 1559 (1994).
8. R. Paladhi and R. P. Singh, *Eur. Polym. J.,* **30,** 251 (1994).
9. A. Varada Rajulu, R. Lakshminarayana Reddy, and R. N. V. Ranga Reddy, *Acustica,* **83,** 1 (1997).
10. A. Varada Rajulu and P. Mabu Sab, *Eur. Polym. J.,* **32,** 257 (1996).
11. A. Varada Rajulu and P. Mabu Sab, *Eur. Polym. J.,* **34,** 31 (1998).
12. Y. P. Singh, S. Das, S. Maiti, and R. P. Singh, *J. Pure Appl. Ultrason.,* **3,** 1 (1981).