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Miscibility of Polycarbonate/ Polyvinylpyrrolidone and Polycarbonate/Polyethylene Oxide in Chloroform by Viscosity, Ultrasonic and Refractometric Methods

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Miscibility studies of polycarbonate/polyvinylpyrrolidone (PC/PVP) and polycarbonate/polyethylene oxide (PC/PEO) in common solvent chloroform were carried out in different percentages of the blend compositions. The viscosity, ultrasonic velocity, refractive index and density were measured at 30°C. The interaction parameters were obtained using the viscosity data to probe the miscibility. The obtained results were confirmed by the ultrasonic velocity, density and refractive index measurements.

Keywords: Polymer blends; viscosity; ultrasonic velocity; density; refractive index; miscibility

INTRODUCTION

The Polymer blends are formed by combining two or more polymers by mechanical or chemical methods of intimate mixing. The resulting polymeric systems often exhibit properties that are superior to any one of the component polymers alone. There has been a great deal of

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interest in the studies of these polymer systems generally known as polymeric alloys [1]. However, the manifestation of superior properties depends upon the miscibility of homopolymers on the molecular scale. In general there are three distinct types of blends, *i.e.*, totally miscible, partially miscible and immiscible. The miscibility results in altogether different morphology of the blends ranging from single phase system to two or multiphase systems. There have been various techniques of studying the miscibility of 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 the polymer blends. Chee [3] and Sun *et al.* [4], suggested viscometric method for the study of polymer-polymer miscibility. Singh and Singh [5, 6] suggested the use of ultrasonic velocity and viscosity measurements for investigating the polymer miscibility. Paladhi and Singh [7, 8] showed that the variation of ultrasonic velocity and viscosity with blend compositions is linear for miscible blends. Recently Varada Rajulu *et al.* [9] used the ultrasonic and refractometric techniques for the study of the miscibility of polymers. In the present study the authors measured the viscosity, ultrasonic velocity, density and refractive index of the polycarbonate/polyvinyl pyrrolidone (PC/PVP) and polycarbonate/polyethylene oxide (PC/PEO) blend solutions in chloroform at 30°C in order to study the miscibility of the blends.

EXPERIMENTAL

The blends of PC/PVP and PC/PEO of different compositions were prepared by mixing solutions of the polymers in chloroform. PC (M/S Viral Rasayana, Mumbai, India, $\bar{M}_v = 25,000$), PVP (M/S Laser Chemicals, India $\bar{M}_v = 25,000$) and PEO (M/S Aldrich chemicals, USA, $\bar{M}_v = 2,00,000$) were employed in the present study. The total weight of the two components in solution was always maintained at 1 g/dL. The ultrasonic velocities of the blend solutions were measured by an ultrasonic interferometric technique [10]. The temperature was maintained at 30°C by circulating water from a thermostat with a thermal stability of $\pm 0.05^\circ\text{C}$ through a double wall jacket of the ultrasonic experimental cell. The densities of the solutions were measured at 30°C by specific gravity bottle. The refractive indices of

blend solutions were measured with an Abbe's refractometer with a thermostated water circulation system at 30°C as described elsewhere [11]. The relative viscosities of blend solutions were measured at 30°C using a Ubbelohde suspended-level viscometer.

RESULTS AND DISCUSSION

The measured values of ultrasonic velocity, density, and refractive index of PC/PVP and PC/PEO blend solutions in chloroform at 30°C are presented in Table I. Figure 1 shows the Huggins plots for these blends in which the weight fraction of both the components were maintained at 0.5. Chee [3] gave the expression for the interaction parameter when the polymers are mixed in weight fractions of w_1 and w_2 as

$$\Delta B = \frac{b - \bar{b}}{2w_1w_2} \quad (1)$$

where $\bar{b} = w_1b_{11} + w_2b_{22}$

where b_{11} and b_{22} are the slopes of the viscosity curves for the pure

TABLE I Ultrasonic velocity, density and refractive index of PC/PVP and PC/PEO blend solutions in chloroform at 30°C

<i>% of PC in the blend</i>	<i>Ultrasonic velocity (m/s)</i>	<i>Density (g/cc)</i>	<i>Refractive index</i>
A. PC/PVP Blend			
0.0	972	1.3681	1.440
20.0	971.2	1.3699	1.441
40.0	971.5	1.3699	1.442
50.0	972.8	1.3746	1.439
60.0	978.4	1.3746	1.442
80.0	984.5	1.3755	1.438
100.0	967.4	1.4530	1.440
B. PC/PEO Blend			
0.0	980.6	1.3718	1.442
20.0	978.1	1.3837	1.441
40.0	973.3	1.3737	1.443
50.0	978.9	1.3457	1.442
60.0	980.6	1.3697	1.442
80.0	979.8	1.3737	1.442
100.0	967.4	1.4530	1.440

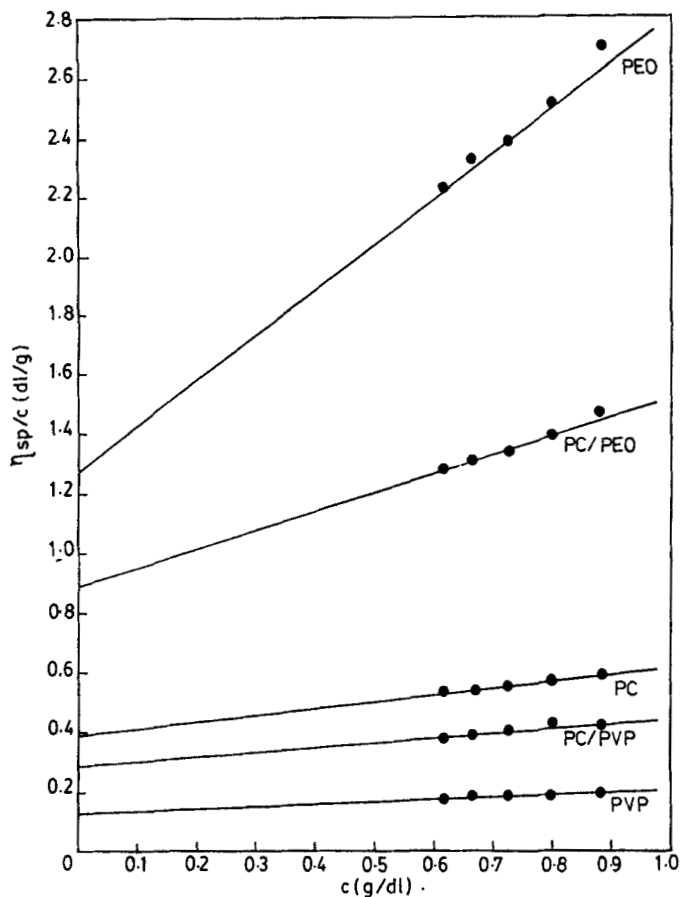


FIGURE 1 The variation of reduced viscosity with composition in PC/PVP and PC/PEO (equal weight fraction) blends in chloroform at 30°C.

components. The coefficient b is related to the Huggins coefficient k_H as

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

For ternary system, the coefficient b is also given by

$$b = w_1^2 b_{11} + w_2^2 b_{22} + 2w_1 w_2 b_{12} \quad (3)$$

where b_{12} is the slope of the viscosity curve for the blend solution.

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

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

where $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities for the pure component systems.

The blend is miscible if $\mu \geq 0$ and immiscible if $\mu < 0$ [3]. In the present study the value of μ for PC/PVP is computed to be -0.2041 indicating blend is immiscible. In the case of PC/PEO μ is found to be -0.3305 indicating its immiscible nature.

Recently Sun *et al.* [4] suggested a new equation for the determination of miscibility of polymers as follows:

$$\alpha = k_m - \frac{k_1[\eta]_1^2 w_1^2 + k_2[\eta]_2^2 w_2^2 + 2\sqrt{k_1 k_2}[\eta]_1[\eta]_2 w_1 w_2}{\{[\eta]_1 w_1 + [\eta]_2 w_2\}^2} \quad (5)$$

where k_1 , k_2 and k_m are the Huggins constants for individual pure components 1, 2 and blend respectively. While deriving this equation, the long-range hydrodynamic interactions are taken into account. Sun *et al.* [4] suggested that a blend will be miscible if $\alpha \geq 0$ and immiscible when $\alpha < 0$. In the present study the α value is found to be -1.8959 for PC/PVP system and -0.3192 for PC/PEO system. These two values are indicating that both the blends are immiscible.

In order to further confirm the miscibility of these blends, the variation of the ultrasonic velocity, density, and refractive index of the polymer blend solutions with composition are depicted in Figures 2, 3 and 4 respectively. From these figures, it is clearly evident that the variation is non-linear indicating a double phase for both PC/PVP and PC/PEO blends. Varada Rajulu *et al.* [9] used these techniques for the miscibility study of cellulose acetate/poly(methyl methacrylate) blend, where nonlinear variation of the ultrasonic velocity and refractive index with blend composition was attributed to the immiscible behavior of the blend. Similarly the linear variation of ultrasonic velocity with blend composition in the case of poly(methyl methacrylate)/poly(vinyl acetate) [6] was attributed to the miscible nature of the blend. Further it is observed that the ultrasonic velocity, density and

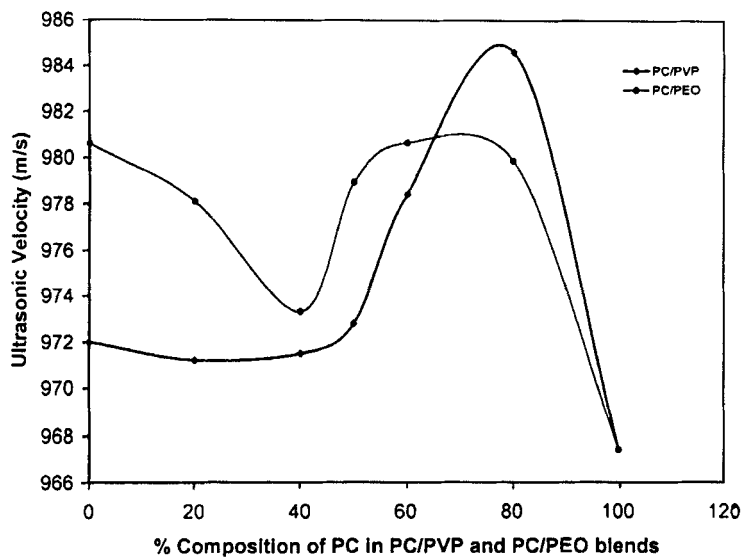


FIGURE 2 The variation of ultrasonic velocity with composition in PC/PVP and PC/PEO blends in chloroform at 30°C.

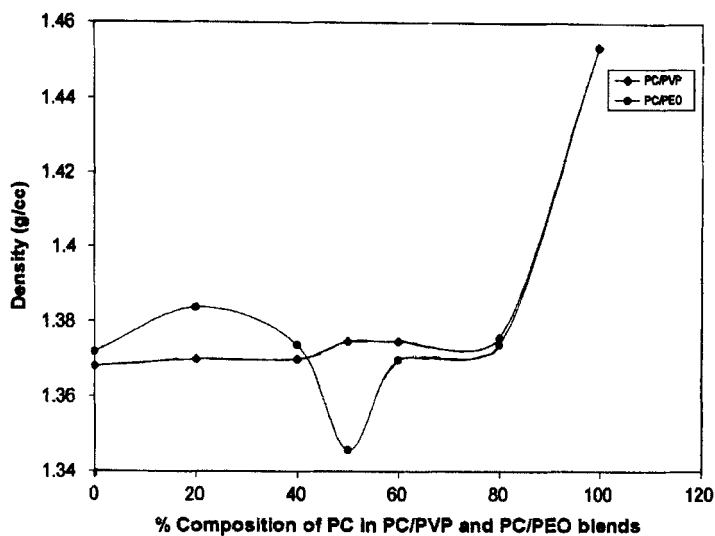


FIGURE 3 The variation of density with composition in PC/PVP and PC/PEO blends in chloroform at 30°C.

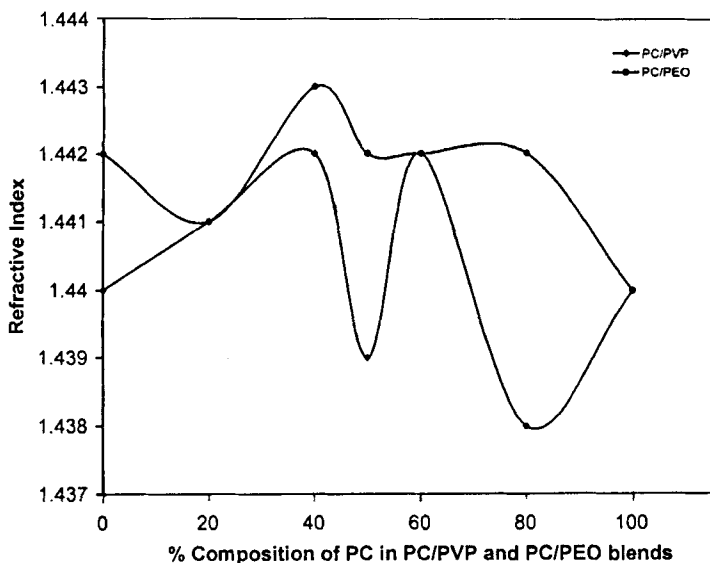


FIGURE 4 The variation of refractive index with composition in PC/PVP and PC/PEO blends in chloroform at 30°C.

refractive index of PC/PVP and PC/PEO are varying much than those of the pure components. These observations indicate that both PC/PVP and PC/PEO blends are immiscible.

CONCLUSIONS

Using viscosity, ultrasonic velocity, refractive index and density methods, the polymer blends for polycarbonate/polyvinyl pyrrolidone and polycarbonate/polyethylene oxide blends are found to be immiscible.

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