



Miscibility Studies of Poly(Vinylpyrrolidone)/Poly(Vinyl Alcohol) Blends in Water by Viscosity, Density, Refractive Index and Ultrasonic Velocity Methods

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ABSTRACT

Poly(vinylpyrrolidone) (PVP)/poly(vinyl alcohol) (PVA) are water-soluble polymer blends; they are used for food packaging, biomedical, and pharmaceutical applications. The miscibility of PVP/PVA blends in water was studied by viscosity, density, ultrasonic velocity, and refractive index techniques at 30°C and 50°C. Using viscosity data, the interaction parameters such as ΔB , μ and α were calculated. These values revealed that PVP/PVA blends are miscible at all compositions both at 30°C and 50°C. In addition, Fourier transform infrared studies and scanning electron microscope analysis were the supporting evidence for miscibility of this system. In addition, adiabatic compressibility (β_{ad}), acoustical impedance (Z) and intermolecular free length (L_f) were also computed.

Key words: Blends, Miscibility, Interactions, Ultrasonic velocity, Refractive index.

1. INTRODUCTION

In the development of polymer blends, the miscibility between the polymers is a very important factor [1,2]. Polymer-polymer miscibility by ultrasonic velocity and density measurements methods were investigated by Paladhi and Singh [3,4]. Ultrasonic methods have the added advantages of being less costly with more efficiency comparable to other methods. The use of ultrasonic is a tool in interdisciplinary sciences in increasing the effect of ultrasound in polymerization reactions, organic synthesis, electropolymerization, electroplating, electrosynthesis has been exploited to good effect.

2. EXPERIMENTAL

poly(vinyl alcohol) (PVA) ($M_w = 1, 25,000$, AR grade, Merck India Ltd.; India) and poly(vinylpyrrolidone) (PVP) purchased from Loba, Chem, Mumbai, India, were used for this work. A dilute polymer solution of 1% w/v was prepared for viscometric studies. A stock solution of homopolymer and blends of PVP/PVA of different compositions 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20 and 90/10 was prepared in water. Viscosity measurement at 30°C and 50°C were made using Ubbelohde suspended level viscometer with flow time of 96 s for distilled water.

3. RESULTS AND DISCUSSIONS

The Huggin's plots for the pure components and their blends at 30°C and 50°C are shown in Figure 1a and b, respectively. Figure 1 indicates the considerable higher slope variation. Hence, PVP/PVA blend is found to be miscible, at all compositions both at 30°C and 50°C. The miscibility of the polymer blends is predicted by the Chee's [5] and Sun *et al.* [6] interactions parameters, ΔB and μ using the formulae as follows (Table 1):

$$\Delta B = \frac{b - b^-}{2w_1w_2}$$

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

Where, $b^- = w_1b_{11} + w_2b_{22}$ in which b_{11} and b_{22} are the slopes of the viscosity curves for the pure components.

$B = w_1^2b_{11} + w_2^2b_{22} + 2w_1w_2b_{12}$, Where, b_{12} is the slope for the blend solution of pure component solutions.

The blend is miscible when $\mu \geq 0$ and immiscible when $\mu < 0$. Recently, Sun *et al.* have suggested a new formula for the determination of polymer miscibility

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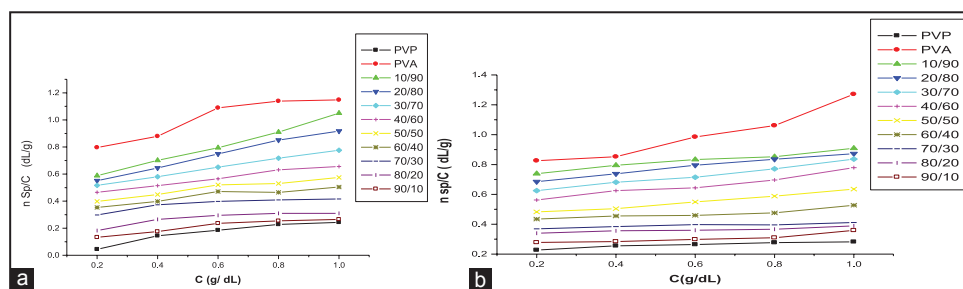


Figure 1: Huggin's plots for 1% w/v poly(vinylpyrrolidone)/poly(vinyl alcohol) blends in water at 30°C and at 50°C.

as follows:

$$\alpha = K_m - \frac{K_1[\eta]_1^2 w_1^2 + K_2[\eta]_2^2 + 2\sqrt{K_1 K_2}[\eta]_1[\eta]_2 w_1 w_2}{\{[\eta]_1 w_1 + [\eta]_2 w_2\}^2}$$

Where, K_1 , K_2 and K_m are the Huggin's constants for individual components 1, 2 and the blends, respectively. Here, the blend will be miscible when $\alpha \geq 0$ and immiscible when $\alpha < 0$. The computed values of μ and α are found to be positive when all the PVP/PVA compositions at 30°C and 50°C. As the long-range hydrodynamic interactions are considered the value α in equation (5) is more accurate than equation (4). Similar observations made by Fadnis [7] and Illiger and Fadnis [8] for hydroxypropyl methylcellulose (HPMC)/PVA and HPMC/PEG blends, where μ was found to be negative and α was found to be positive. We are conformed by measured the ultrasonic velocity, density, refractive index, and viscosity data. The adiabatic compressibility (β_{ad}) [9] of different blend composition was evaluated using the equation.

$$\beta_{ad} = \frac{1}{v^2 \rho}$$

Where, v is the velocity of sound and ρ is the density of blend solution. The acoustical impedance (Z) was calculated using the formula;

$$Z = \rho U$$

Where, ρ is the density of the mixture and U is the ultrasonic velocity of the mixture. The intermolecular free length (L_f) was calculated using the formula;

$$L_f = K \beta^{1/2}$$

Where, $K = 1.98 \times 10^{-6}$, the Jacobson constant.

3.1. Fourier Transform Infrared (FTIR) Spectral Analysis

The FTIR spectra of pure PVP, pure PVA, and PVP/PVA blends are in the spectral range 4000-600 cm^{-1} as shown in Figure 2. In pure PVA, it is observed

Table 1: Interaction parameters.

Composition	Interaction parameters		
	ΔB	M	α
10/90	0.167 (0.0073)	0.3781 (0.027)	167.54 (2.076)
20/80	0.1431 (0.0164)	0.3236 (0.061)	8.54 (3.75)
30/70	0.0007 (0.00079)	0.00158 (0.0029)	- (3.144)
40/60	0.0806 (0.00395)	0.1822 (0.0147)	9.54 (4.44)
50/50	0.3652 (0.0016)	0.8258 (0.00592)	14.45 (6.64)
60/40	1.558 (0.1358)	3.524 (0.5029)	21.49 (5.29)
70/30	0.125 (0.235)	0.2826 (0.8703)	23.93 (6.45)
80/20	0.01203 (0.0669)	0.0272 (0.2477)	76.24 (6.23)
90/20	0.24 (0.003)	0.5427 (0.01148)	8.86 (2.16)

that a broad and intense band at 3306 cm^{-1} , which corresponds to O-H stretching vibration. The band at 2940 cm^{-1} is attributed to asymmetric stretching vibration of CH_2 group. The vibration band is observed at about 1644 cm^{-1} attributed to C = O stretching of PVP and PVA [7,8]. In the spectra of pure PVP, a broad peak is observed at 1018 cm^{-1} , which is due to the outer face vibration oscillation of the hydroxyl group and the peaks centered at 1440 cm^{-1} and 1289 cm^{-1} are assigned to the inner face bending vibrations of the -OH group. A prominent peak is observed at 1716 cm^{-1} , which is also seen in 50:50 ratio [9-11].

3.2. Scanning Electron Microscope (SEM) Studies

The surface morphology of PVP and PVA films was homogeneous. It is also noticed from SEM studies that the morphology of the blends shows homogeneous nature as observed in the case of pure PVP and pure PVA. No phase separation is observed in the SEM images of all the compositions of the blends compared

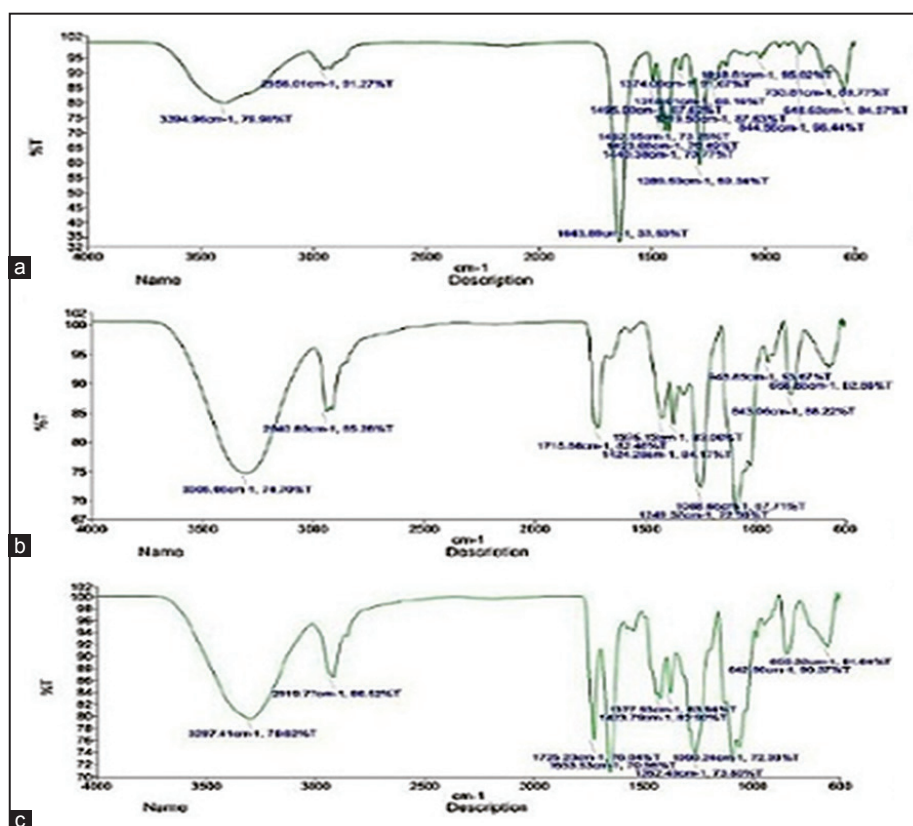


Figure 2: Fourier transform infrared spectra of (a) Poly(vinylpyrrolidone) (PVP), (b) poly(vinyl alcohol) (PVA), (c) PVP/PVA blends.

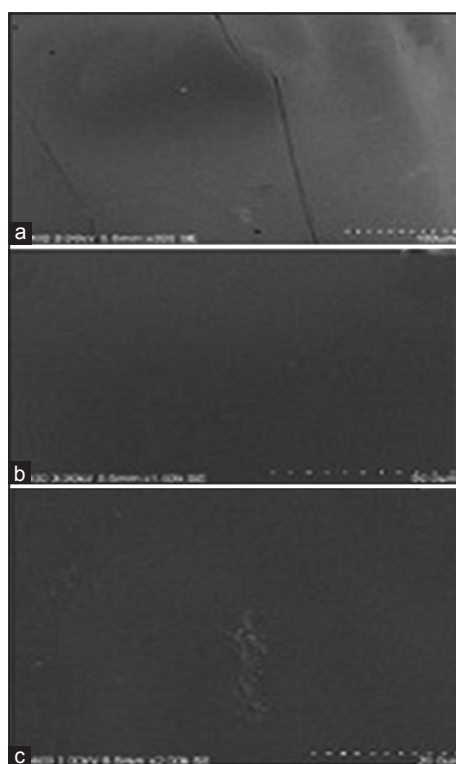


Figure 3: Scanning electron microscope images of (a) Poly(vinylpyrrolidone) (PVP), (b) poly(vinyl alcohol) (PVA) and (c) PVP/PVA blends.

to SEM images of pure compounds (Figure 3).

4. CONCLUSION

Using viscosity, ultrasonic velocity, density and refractive index methods, it is concluded that the polymer blend of PVP/PVA is found to be miscible at all compositions of blends at both 30°C and 50°C, respectively. It is also observed that temperature has no significant effect on the miscibility of these blends even though the reduced viscosity, density, ultrasonic velocity decreases slightly. Adiabatic compressibility increases negligibly and the refractive index has no significant effect on the temperature. Thus before mentioned techniques are simple, low cost, rapid and efficient methods in exploring the miscibility windows of PVP/PVA blend in solution.

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***Bibliographical Sketch**



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