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# Miscibility Studies on Chitosan/Poly(vinyl alcohol) Blends

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Miscibility studies of chitosan (CHI)/poly(vinyl alcohol) (PVA) blend in buffer solution were carried out in several blend compositions (10/90, 20/80, . . . , 90/10). Viscosity, ultrasonic velocity, density and refractive were measured at 30, 40 and 50°C, respectively. Using viscosity data, the interaction parameters  $\mu$  and thermodynamic parameter  $\alpha$  were computed to determine the miscibility of the blend in solution. These values revealed that the blend is miscible when the chitosan content is more than 60% in the blend. The obtained results were further confirmed by the ultrasonic velocity, density and refractive index study.

**Keywords:** chitosan; poly(vinyl alcohol); blend; miscibility; viscosity; ultrasonic; refractive index

## 1 Introduction

In recent years there has been growing interest in modifying the existing polymers rather than synthesizing new polymers. The modifications are polymer blends, composites, copolymers and interpenetrating polymer network (IPN). Polymer blends are physical mixtures of structurally different homo or copolymers which interact through secondary forces with no covalent bonding between them. So blending of polymers is one of the simplest methods to obtain a variety of physical and chemical properties absent from that of the constituent polymers (1). However, the gain in newer properties of the blends depends on the degree of compatibility or miscibility of the polymers at the molecular level.

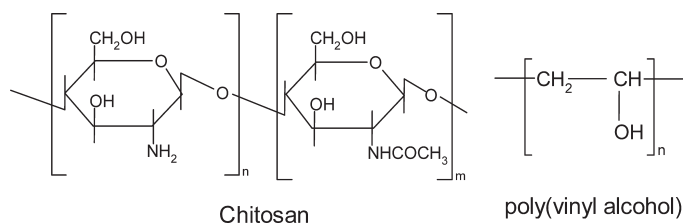
Many experimental and theoretical studies have been used to investigate the polymer-polymer miscibility. Some of the important techniques are thermal analysis, electron microscopy, dynamic mechanical studies and viscometric techniques (2–7). As some of these techniques are complicated, costly and time consuming; viscometric measurements provide an effective, quick and inexpensive technique to investigate polymer-polymer interaction. Hence this technique is used for many polymer pair to determine their miscibility (8–11). There are many criteria proposed by the researchers to determine polymer-polymer miscibility by viscometry such as plot of

reduced viscosity vs. composition, interaction parameter  $\mu$  and thermodynamic parameter  $\alpha$  (12, 13). Singh and Singh (14, 15) have suggested the use of ultrasonic velocity and viscosity measurements for investigating the polymer miscibility. Paladhi and Singh (16, 17) and Varada Rajulu et al. (18) have shown that the variation of ultrasonic velocity, viscosity, refractive index with blend composition is linear for miscible blends and non-linear for immiscible blends. Recently, Ravi Prakash et al. (19) have used viscosity, ultrasonic velocity and refractive index techniques to study the miscibility of a sodium alginate/poly(vinyl alcohol) blend.

Chitosan (CHI), (20–22) a copolymer of glucosamine and N-acetylglucosamine units linked by 1–4 glucosidic bonds. And, it is obtained by N-deacetylation of chitin, which is widely distributed in nature as the main component in the exoskeleton of crustaceans and it is one of the second most abundant biopolymer next to cellulose. Chitosan is a non-toxic, biocompatible and biodegradable cationic polymer and is found in various applications in pharmaceutical, medicine and food industries (23–25). It is also used as a chelating agent for removing heavy toxic metals in sewage (26). Poly(vinyl alcohol) (PVA) is a non-toxic, water soluble, biocompatible and biodegradable synthetic polymer which is widely used in biochemical and biomedical applications (27, 28). The structures of both CHI and PVA are shown in Scheme 1, respectively.

The authors selected these polymers, since they have a wide range of applications in pharmaceutical and cosmetic industries, and the mixtures of these polymers may be included in drug or cosmetic formulation, either in solution or in the solid state. Hence, this study is aimed to probe the miscibility windows of these two polymers in solution.

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Sch. 1. Chemical structures of chitosan and poly(vinyl alcohol).

## 2 Experimental

Chitosan with a degree of deacetylation 80.3% (viscosity of 190 Cps,  $\bar{M}_v = 2.7 \times 10^5$  Da) was received as a gift sample from India Sea Foods, Cochin, India, and PVA  $\bar{M}_w = 1,25,000$ , LR grade, (S.D. Fine Chem. Ltd., Boisar, India) were employed in the present study. Stock solutions of homopolymers and the blends of CHI/PVA of different blend compositions-10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 40/30, 80/20 and 90/10 were prepared by mixing a solution of the polymers in a buffer solution (20) (0.1 M acetic acid + 0.2 M sodium acetate). The total weight of the two components in the solution was always maintained at 1 g/dL. A dilute polymer solution of 1% w/v was prepared for viscometric studies. Using an Ubbelohde suspended level dilution viscometer (USLV), the viscosity measurements were made at 30, 40 and 50°C, respectively. The ultrasonic velocity measurements were carried out by an interferometric technique (18) employing an ultrasonic interferometer (Mittal Enterprises, New Delhi, India). During the experiment, the temperature is maintained by circulating water from a thermostat with a thermal stability of  $\pm 0.05^\circ\text{C}$  through the double wall jacket of the ultrasonic experimental cell. The experimental frequency was 2-MHz and the velocity measurements were accurate to better than  $\pm 0.5\%$ . The densities of the solutions were measured using a specific gravity bottle. The refractive index of the blend solutions were measured with an Abbe's refractometer with a thermostat water circulation system (18). The accuracy of the refractive index measurements was  $\pm 0.02\%$ .

## 3 Results and Discussion

Chitosan exhibits a polyelectrolyte property in solution, due to the presence of free amino groups in its backbone. Therefore, in the absence of salt, there is an abnormal increase in the viscosity of the more dilute solution because of an increase in volume due to charge repulsion and it thereby stretches out of the molecule (21). To overcome this difficulty, a buffer solution of 0.1 M acetic acid + 0.2 M sodium acetate was chosen as a solvent, which suppresses the repulsion of like charges in dilute solution, so that the viscosity behavior will be normal (20, 21).

The Huggin's plots for the pure components and their blends at 30, 40 and 50°C are shown in Figures 1, 2 and 3,

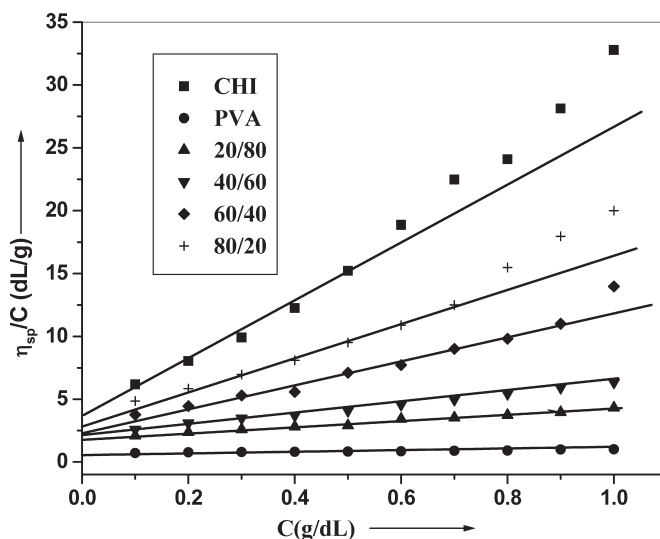


Fig. 1. Huggin's plot for 1% w/v CHI/PVA blend in buffer solution at 30°C.

respectively. It is evident from the figure that the reduced viscosity decreases as the temperature increases. The figure also indicates a considerably higher slope variation for 80/20 and 60/40 CHI/PVA blend compositions. This may be attributed to the mutual attraction of macromolecules in solution, which leads to the increase of hydrodynamic volume. Hence, the CHI/PVA blend is found to be miscible only when the CHI content is more than 60% in the blend. Below this critical concentration, a sharp decrease in the slope is observed in the Huggin's plot which is due to the phase separation.

To quantify the miscibility of the polymer blends, Chee (12) suggested a general expression for the interaction

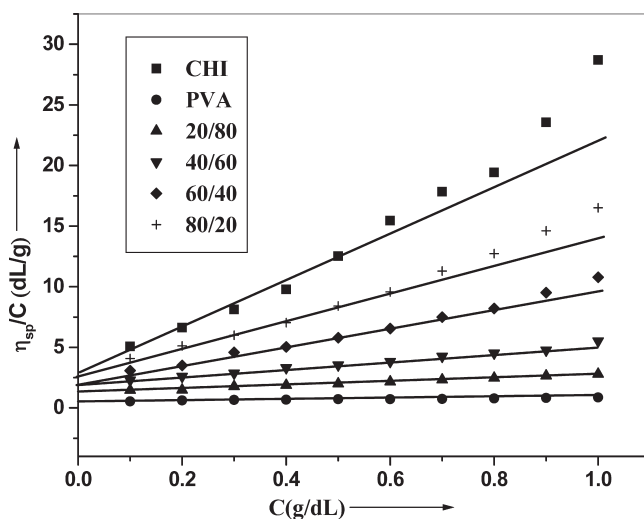
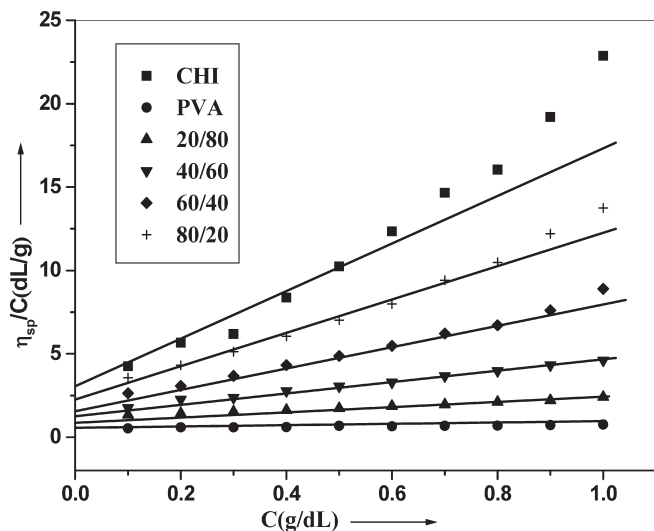


Fig. 2. Huggin's plot for 1% w/v CHI/PVA blend in buffer solution at 40°C.



**Fig. 3.** Huggin's plot for 1% w/v CHI/PVA blend in buffer solution at 50°C.

parameter when polymers are mixed in weight fractions  $w_1$  and  $w_2$  as:

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

where,  $\bar{b} = w_1b_{11} + w_2b_{22}$ , in which  $b_{11}$  and  $b_{22}$  are the slopes of the viscosity curves for the pure components. The coefficient  $b$ , which reflects the binary interactions between polymer segments is related to the Huggin's coefficient  $K_H$  as:

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

For ternary systems, (12) the coefficient 'b' is also given by:

$$b = w_1^2b_{11} + w_2^2b_{22} + 2w_1w_2b_{12} \quad (3)$$

where,  $b_{12}$  is slope for the blend solution. Using these values, Chee (12) defined a more effective interaction parameter  $\mu$ , 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 solutions. The blend is miscible when  $\mu \geq 0$  and immiscible (12) when  $\mu < 0$ . The values of  $\mu$ , calculated with the above expression at 30, 40 and 50°C, are represented in Table 1.

Recently, Sun et al. (13) proposed an additional criteria,  $\alpha$  for polymer-polymer miscibility in terms of a thermodynamic parameter and suggested a new formula for the determination of polymer miscibility as follows:

$$\alpha = K_m - \frac{K_1[\eta]_1^2w_1^2 + K_2[\eta]_2^2w_2^2 + 2\sqrt{K_1K_2}[\eta]_1[\eta]_2w_1w_2}{\{[\eta]_1w_1 + [\eta]_2w_2\}^2} \quad (5)$$

where,  $K_1$ ,  $K_2$  and  $K_m$  are the Huggin's constants for individual components 1, 2 and the blend, respectively. The long-range hydrodynamic interactions were considered while deriving this equation. Sun et al. (13) have suggested that a blend will be miscible when  $\alpha \geq 0$  and immiscible when  $\alpha < 0$ .

The computed values of  $\mu$ , are found to be negative when the chitosan content is up to 60% and then positive beyond this value. However,  $\alpha$  is found to be negative when the chitosan content is up to 50% and then positive beyond this value at 30, 40 and 50°C, respectively; the data are given in Table 1.

A similar observation was made by Varada Rajulu et al. (29) in the case of Epoxy/Unsaturated Polyester Resin blends, where  $\mu$  was found to be negative and  $\alpha$  was found to be positive. They confirmed the miscibility of such blends by other methods. They further established that the equation for  $\alpha$  is more accurate than the equation for  $\mu$ , as the long range interactions are taken into account.

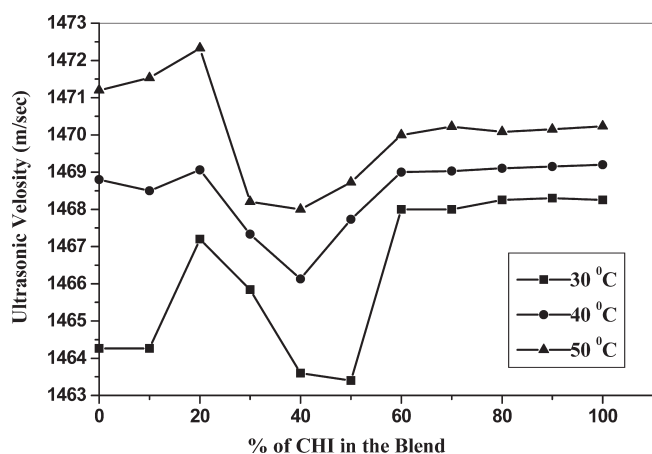
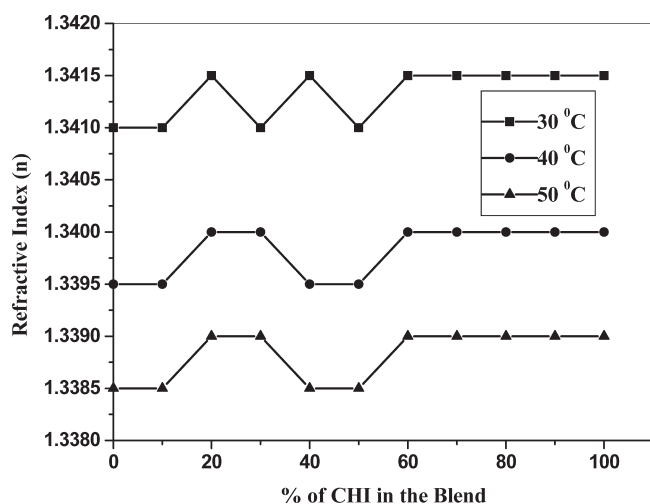
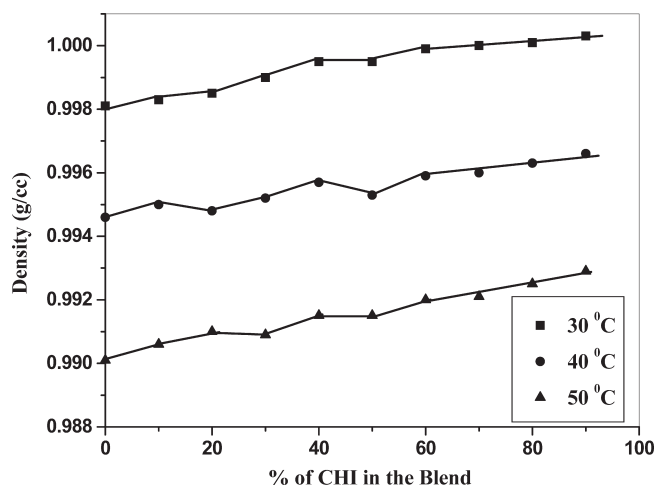
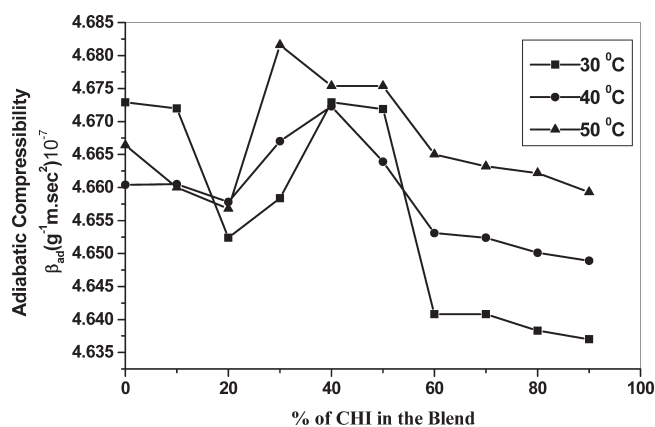
To confirm this further, we have measured the ultrasonic velocity ( $v$ ), density ( $\rho$ ) and refractive Index ( $n$ ) of the blend under consideration of various compositions at 30, 40 and 50°C; the values are presented in Table 2. The variation of the ultrasonic velocity, density and refractive index with the blend composition is shown in Figures 4, 5 and 6, respectively.

**Table 1.** Interaction parameters  $\mu$  and  $\alpha$  of CHI/PVA blends at 30, 40 and 50°C

Composition CHI/PVA	At 30°C		At 40°C		At 50°C	
	$\mu$	$\alpha$	$\mu$	$\alpha$	$\mu$	$\alpha$
10/90	-1.0765	-0.8550	-1.1761	-1.2344	-1.2202	-0.1450
20/80	-0.8670	-0.7547	-1.0187	-0.8017	-1.1105	-1.1207
30/70	-0.8331	-0.5121	-0.9764	-0.6247	-0.9688	-0.8161
40/60	-0.7129	-0.3228	-0.8552	-0.9404	-0.7797	-0.3932
50/50	-0.5584	-0.4897	-0.5811	-0.1511	-0.5907	-0.5831
60/40	-0.0965	0.8023	-0.2175	0.4404	-0.2126	0.2005
70/30	0.6575	0.2140	0.0469	0.1735	0.1654	1.2536
80/20	0.3143	0.2791	0.3114	0.1262	0.5434	0.6308
90/10	0.6624	0.3306	0.8403	0.1060	1.3941	1.1348

**Table 2.** Ultrasonic velocity, density and refractive index of CHI/PVA blend in solution at 30, 40 and 50°C

% of CHI in the blend	Ultrasonic velocity (m/s)			Density (g/cc)			Refractive index ( <i>n</i> )		
	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
0.0	1464.26	1468.80	1471.20	0.9981	0.9946	0.9901	1.3410	1.3395	1.3385
10.0	1464.26	1468.50	1471.53	0.9983	0.9950	0.9906	1.3410	1.3395	1.3385
20.0	1467.20	1469.06	1472.33	0.9985	0.9948	0.9910	1.3415	1.3400	1.3390
30.0	1465.84	1467.33	1468.20	0.9990	0.9952	0.9909	1.3410	1.3400	1.3390
40.0	1463.60	1466.13	1468.00	0.9995	0.9957	0.9915	1.3415	1.3495	1.3385
50.0	1463.40	1467.73	1468.73	0.9995	0.9953	0.9915	1.3410	1.3395	1.3385
60.0	1468.00	1469.00	1470.00	0.9999	0.9959	0.9920	1.3415	1.3400	1.3390
70.0	1468.00	1469.03	1470.22	1.0000	0.9960	0.9921	1.3415	1.3400	1.3390
80.0	1468.25	1469.10	1470.08	1.0001	0.9963	0.9925	1.3415	1.3400	1.3390
90.0	1468.30	1469.15	1470.15	1.0003	0.9966	0.9929	1.3415	1.3400	1.3390
100	1468.25	1469.20	1470.23	1.0004	0.9970	0.9931	1.3415	1.3400	1.3390

**Fig. 4.** Effect of temperature on the variation of ultrasonic velocity with composition of 1% w/v of CHI/PVA blend in solution.**Fig. 6.** Effect of temperature on the variation of refractive index with composition of 1% w/v of CHI/PVA blend in solution at 30, 40 and 50°C.**Fig. 5.** Effect of temperature on the variation of density with composition of 1% w/v of CHI/PVA blend in solution at 30, 40 and 50°C.**Fig. 7.** Effect of temperature on the variation of adiabatic compressibility with composition of 1% w/v of CHI/PVA blend in solution at 30, 40 and 50°C.

The adiabatic compressibility  $\beta_{ad}$  [18] of different blend compositions was evaluated by using the equation:

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

where,  $v$  is the velocity of sound and  $\rho$  is the density of blend solutions.

The variation of adiabatic compressibility at 30, 40 and 50°C is as shown in Figure 7. The graphs show both linear and nonlinear regions. Hence, it has already been established that the variation will be linear for miscible blends and nonlinear for immiscible blends (14, 15). This observation is in agreement with  $\mu$  and  $\alpha$  values.

Therefore, in the present case, the variations are found to be linear when the CHI content is more than 60% in the blend. This may be due to the CHI, which is a rigid polymer with coil conformation and PVA is a flexible polymer and as the molecular weight of CHI is higher than PVA it may act as a pseudo solvent for the low molecular weight PVA by entangling around the short flexible PVA chains. As the fraction of PVA in the mixture increases and the fraction of CHI decreases, the possibility of chain entanglement, which may lead to miscibility, decreases. Hence, miscibility is observed for the blend CHI/PVA when the CHI concentration is more than 60% in the blend.

#### 4 Conclusions

Based on viscosity, ultrasonic velocity, density and refractive index measurements, it is concluded that the polymer blends of CHI/PVA is miscible when the CHI content is more than 60% in the blend at all temperatures. Below this critical CHI concentration, the blends were found to be immiscible. It may be due to some specific interaction between the carbonyl groups in the CHI and the hydroxy groups in the PVA, which may lead to the miscibility of the blend. Further, the temperature has no significant effect on the miscibility of these blends even though the reduced viscosity, density, refractive index and adiabatic compressibility decreases and the ultrasonic velocity increases as the temperature increases. Hence, the CHI/PVA blend in solution at 30, 40 and 50°C is semi-compatible in nature. Thus, simple measurements like viscosity, ultrasonic velocity, density, and refractive index studies give information regarding the miscibility of the blends in solution.

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