Miscibility Studies on Chitosan/Hydroxypropylmethyl Cellulose Blend in Solution by Viscosity, Ultrasonic Velocity, Density, and Refractive Index Methods

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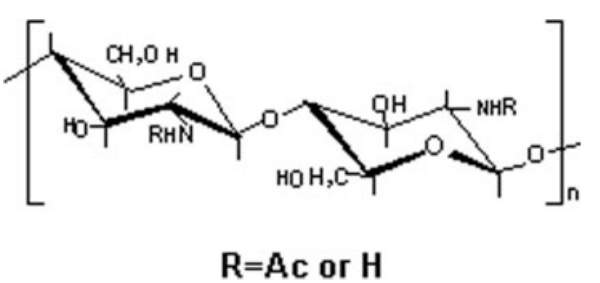
ABSTRACT: The miscibility studies of chitosan (CHI)/hydroxypropylmethyl cellulose (HPMC) blend in buffer solution (0.1*M* acetic acid + 0.2*M* sodium acetate) were carried out by viscosity, ultrasonic velocity, density, and refractive index methods at 30, 40, and 50°C, respectively. Using viscosity data, the interaction parameter μ and α were computed. These values revealed that the blend is miscible when the CHI content is more than 50% in the blend. The obtained results were further confirmed by ultrasonic velocity, density, and refractive index study. And also the result revealed that the change in temperature has no significant effect on the miscibility of CHI/HPMC polymer blends. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2738–2742, 2006

Key words: blend; chitosan; density; miscibility; refractive index; ultrasonic velocity; viscosity

INTRODUCTION

The importance of polymer blending has been increased in recent years, because of the preparation of polymeric materials with desired properties, low basic cost, and improved processability. Polymer blends are physical mixtures of structurally different polymers or copolymers, which interact through secondary forces with no covalent bonding[1] that are miscible at molecular level. The basis of polymer–polymer miscibility may arise from any specific interaction, such as hydrogen bonding, dipole–dipole forces, and charge transfer complexes for homopolymer mixtures.[2–4] There have been various techniques of studying the miscibility of the polymer blends.[5–9] Some of these techniques are 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[10] and Sun et al.[11] have suggested a viscometric method for the study of polymer–polymer miscibility in solution. Singh and Singh[12,13] have suggested the use of ultrasonic velocity and viscosity measurements for investigating the polymer miscibility in solution. Paladhi and Singh[14,15] have shown that the variation of ultrasonic velocity and viscosity with blend composition is linear for miscible blends. Recently, Varada Rajulu et al.[16] have used an ultrasonic and refractometric technique to study the miscibility of polymer blend. As part of our research work, we have studied the miscibility of CHI/HPMC blend in buffer solution at different temperatures by viscosity, ultrasonic velocity, density, and refractive index techniques. We selected these polymers, because it has many pharmaceuticals and biomedical applications.[17,18]

Chitosan (CHI),[19] a family of polysaccharide, is a partially deacetylated chitin, which consists of 2-acetamido-2-deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-D-glucopyranose (GlcN) residues, and may be considered as a binary heteropolysaccharide. The GlcN units carry positive charges in acidic media. Hydroxypropylmethyl cellulose (HPMC) is a polysaccharide prepared from cellulose. It contains both methyl and hydroxypropyl substitutes. The structures of both CHI and HPMC are shown in Schemes 1 and 2, respectively.



Scheme 1 Schematic representation of chitosan, R = acetyl of H, depending on the degree of acetylation.

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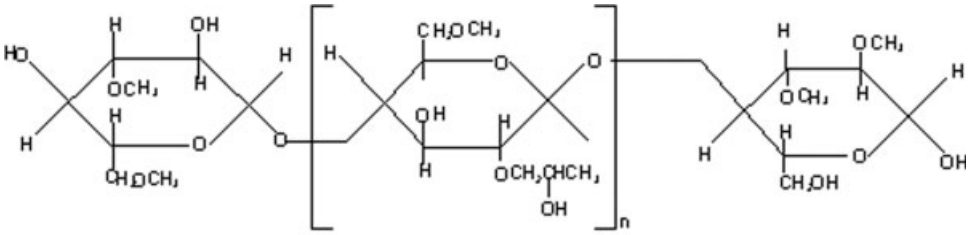

$$C_6H_{16}O_6(C_{10}H_{12}O_6)_\eta C_6H_{16}O_6$$

Scheme 2 Schematic representation hydroxypropylmethyl cellulose.

EXPERIMENTAL

The blends of CHI/HPMC of different compositions were prepared by mixing solution of the polymers in buffer solution.[19] (pH = 5.12) Commercial grade chitosan (CHI), with the degree of acetylation at 80.3%, was kindly provided by India Sea Foods (Cochin, India), and HPMC (LR grade, Loba Chemi, Mumbai, India) was employed in the present study. The total weight of the two components in solution was always maintained at 1 g/dL. Stock solutions of homopolymers and the blends of CHI/HPMC of different blend compositions, 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, and 90/10, were prepared in buffer solution. Viscosity measurements were made at 30, 40, and 50°C, using Ubbelohde-suspended level viscometer, with the flow time of 96 s for distilled water. And the different temperatures were maintained in a thermostat bath, with a thermal stability of ±0.05°C. The ultrasonic velocity measurement was performed by an ultrasonic interferometric technique.[20] The temperature is maintained at 30, 40, and 50°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 experimental frequency was 2 MHz, and the velocity measurements were accurate to better than ±0.5%. The densities of the solutions were measured at 30, 40, and 50°C by a specific gravity bottle. The refractive index of the blend solutions were measured using Abbe's refractometer, with a thermostat water circulation system[21] at 30, 40, and 50°C. The accuracy of the refractive index measurements was ±0.02%.

RESULTS AND DISCUSSION

CHI exhibits a polyelectrolyte property in solution, because of the presence of free amino groups in its backbone. In the absence of salt, there is an abnormal increase in the viscosity of the more dilute solution, because of an enlarged effective volume due to charge repulsion, and thereby it stretches out of the molecule.[22] To overcome this difficulty, a buffer

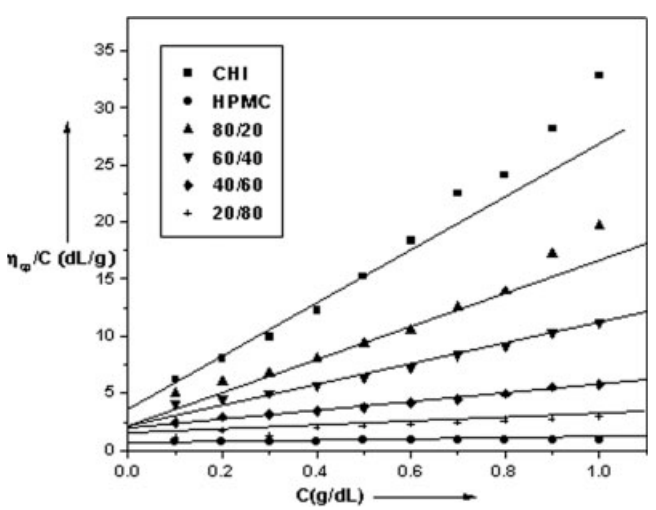

Figure 1 Huggin's plot for 1% w/v CHI/HPMC blend in buffer solution at 30°C.

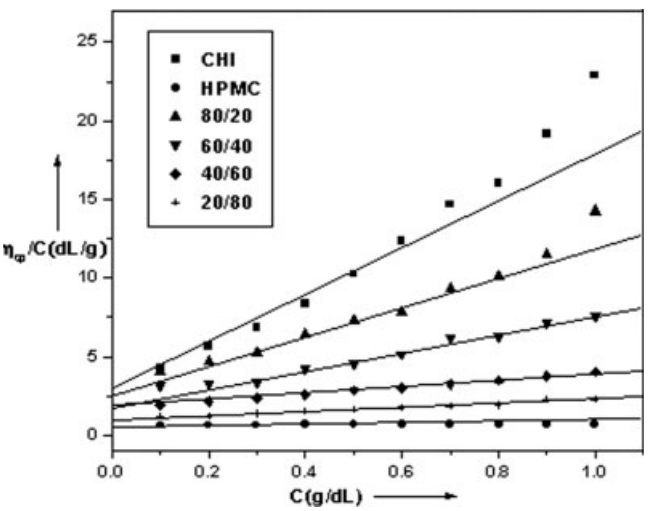

Figure 2 Huggin's plot for 1% w/v CHI/HPMC blend in buffer solution at 40°C.

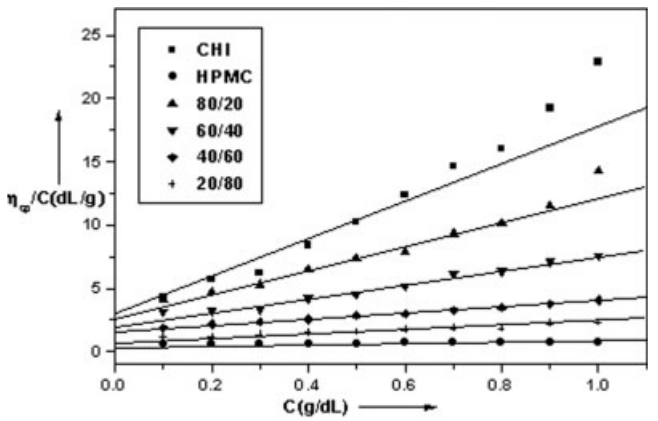

Figure 3 Huggin's plot for 1% w/v CHI/HPMC blend in buffer solution at 50°C.

solution of 0.1*M* CH_3COOH and 0.2*M* CH_3COONa, having a pH of 5.12, was chosen as a solvent, which suppresses the repulsion of like charges in dilute solution, so that the viscosity behavior will be normal.[19,23] HPMC, however, is known to be a flexible nonionic polymer, which obeys the classical Huggin's equation. The Huggin's plots for the pure components and their blends at 30, 40, and 50°C are shown in Figures 1–3, respectively. The figure indicates the considerable higher slope variation for 80/20 and 60/40 CHI/HPMC blend compositions. This may be attributed to the mutual attraction of macromolecules in solution, because of the increase of hydrodynamic and thermodynamic interaction. Hence, the CHI/HPMC blend is found to be miscible, only when the CHI content is more than 50% in the blend. Below this critical concentration, a sharp decrease in the slope is observed in the Huggin's plot because of the phase separation.

To quantify the miscibility of the polymer blends Chee[10] suggested that the general expression for interaction parameter when polymers are mixed in weight fractions w_1 and w_2 is as follows:

$$\Delta B = \frac{b - \overline{b}}{2\, w_1 w_2} \tag{1}$$

where $b = w_1 b_{11} + w_2 b_{22}$, in which b_{11} and b_{22} 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 ternary systems, the coefficient b is also given by

$$b = w_1^2\, b_{11} + w_2^2\, b_{22} + 2\, w_1 w_2\, b_{12} \tag{3}$$

where b_{12} is the slope for the blend solution. Using these values, Chee[10] defined a more effective parameter as follows:

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

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[5] when $\mu < 0$. The values of μ, calculated with the aforementioned expression at 30, 40, and 50°C, are represented in Table I.

Recently, Sun et al.[11] have suggested a new formula for the determination of polymer miscibility as follows:

$$\alpha = K_m - \frac{K_1[\eta]_1^2 w_1^2 + K_2[\eta]_2^2\, w_2^2 + 2\sqrt{K_1\, K_2}\,[\eta]_1[\eta]_2 w_1\, w_2}{\{[\eta]_1\, w_1 + [\eta]_2\, w_2\}^2} \tag{5}$$

where, K_1, K_2, and K_m are the Huggin's constants for individual components 1 and 2 and the blend, respectively. The long-range hydrodynamic interactions are considered while deriving this equation. Sun et al.[11] have suggested that a blend will be miscible when $\alpha \geq 0$ and immiscible when $\alpha < 0$.

The computed values of μ are found to be negative when the CHI content is up to 60% and then positive beyond this value. However, α is found to be negative when the CHI content is up to 40%, and then positive beyond this value at 30, 40, and 50°C, respectively, and the datas are given in Table I. As the long-range hydrodynamic interactions are considered in the equation for α, eq. (5) is more accurate than does eq. (4).

A similar observation was made by Varada Rajulu et al.[24] in case of polyvinyl pyrrolidone/polystyrene blends, where μ was found to be negative and α was found to be positive. They confirmed the miscibility of such blends by other methods.

TABLE I
Interaction Parameters μ and α of CHI/HPMC Blend in Buffer Solution of Different Compositions at 30, 40, and 50°C

Composition CHI/HPMC	At 30°C		At 40°C		At 50°C	
	μ	α	μ	α	μ	α
10/90	−1.08	−0.43	−1.49	−1.18	−1.27	−1.55
20/80	−1.01	−0.43	−1.37	−0.87	−2.3	−0.54
30/70	−0.90	−0.42	−1.35	−0.86	−1.00	−0.94
40/60	−0.85	−0.58	−1.10	−0.80	−1.15	−1.08
50/50	−0.60	0.14	−0.64	0.12	−0.51	1.81
60/40	−0.25	0.10	−0.46	0.32	−0.22	0.46
70/30	0.03	0.58	0.06	0.73	0.16	0.89
80/20	0.23	0.08	0.41	0.32	0.55	0.19
90/10	0.87	0.25	1.23	0.93	1.24	0.31

TABLE II
Ultrasonic Velocity, Density, and Refractive Index Data for CHI/HPMC Blend in Solution of Different Compositions at 30, 40, and 50°C

% of CHI in the blend	Ultrasonic velocity (m/s)			Density (g/cc)			Refractive index (*n*)		
	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
0.0	1469.06	1471.20	1472.80	0.9980	0.9945	0.9905	1.3400	1.3390	1.3380
10.0	1469.60	1470.80	1472.50	0.9983	0.9950	0.9901	1.3400	1.3390	1.3380
20.0	1468.60	1470.55	1472.20	0.9980	0.9945	0.9909	1.3405	1.3395	1.3385
30.0	1466.90	1469.00	1470.73	0.9987	0.9957	0.9915	1.3400	1.3390	1.3380
40.0	1466.66	1468.48	1469.60	0.9995	0.9961	0.9913	1.3405	1.3395	1.3385
50.0	1468.00	1469.61	1471.10	0.9992	0.9957	0.9918	1.3410	1.3400	1.3390
60.0	1468.00	1469.60	1471.00	0.9993	0.9959	0.9919	1.3410	1.3400	1.3390
70.0	1468.00	1469.60	1471.05	0.9997	0.9962	0.9923	1.3410	1.3400	1.3390
80.0	1468.26	1469.62	1471.20	0.9998	0.9963	0.9927	1.3410	1.3400	1.3390
90.0	1468.30	1469.57	1471.11	0.9999	0.9969	0.9928	1.3410	1.3400	1.3390
100.0	1468.25	1469.60	1471.23	1.0004	0.9970	0.9931	1.3410	1.3400	1.3390

To confirm this further, we have measured the ultrasonic velocity (v), density (ρ), and refractive index (n) of the blend under consideration at various compositions, at 30, 40, and 50°C. These values are presented in Table II.

The variation of the ultrasonic velocity, density, and refractive index with the blend composition is shown in Figures 4–6, respectively. The adiabatic compressibility β_{ad}[25] of different blend compositions was evaluated by using the equation

$$\beta_{ad} = \frac{1}{V^2\rho} \tag{6}$$

where, V is the velocity of sound and ρ is the density of blend solutions, and the values are given in Table III. The variation of adiabatic compressibility at 30, 40, and 50°C is shown in Figure 7, respectively. The graphs show both linear and nonlinear regions. It was already established[10,12] that the variation is linear for miscible blend and nonlinear for immiscible blend. In the present case, the variation is found to be linear when the CHI content is more than 50% at 30, 40, and 50°C, respectively. This observation is in confirmation with μ and α values. So the present study indicates the existence of miscibility windows when the CHI content is more than 50% in the blend. This is because the specific interaction between the polymer segments is more when the CHI content is more than 50%, thereby, leading to miscibility of the blend. And below this composition, there will not be much interaction between the polymer segments, which leads to immiscibility of the polymer blend. Here, the miscibility of the blend

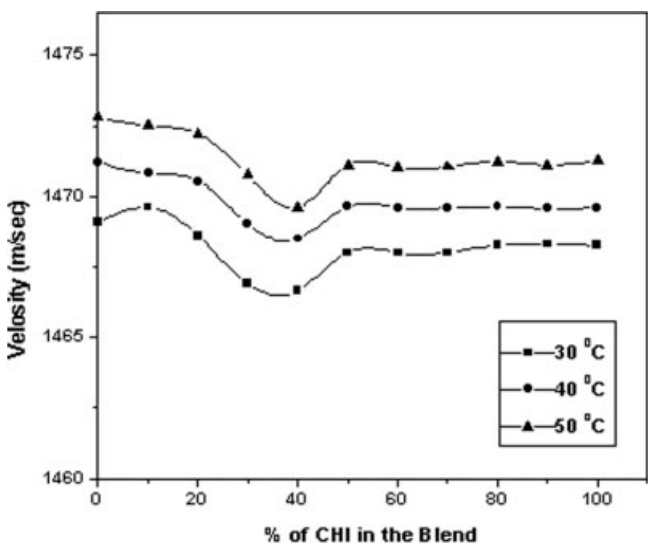

Figure 4 Effect of temperature on the variation of ultrasonic velocity with the composition of 1% w/v of CHI/HPMC blend in solution.

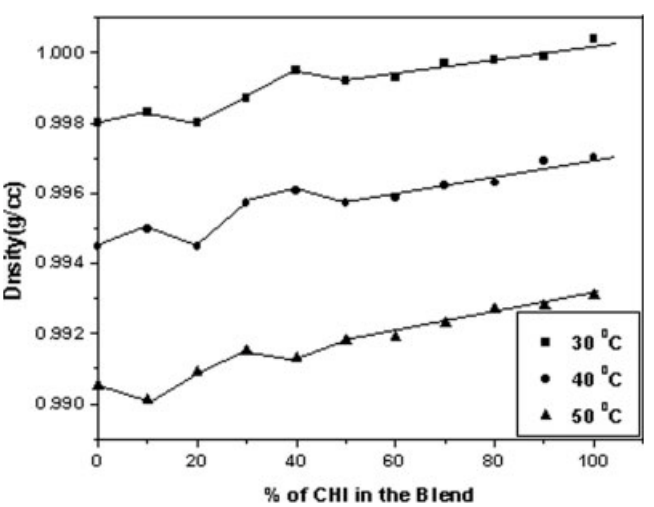

Figure 5 Effect of temperature on the variation of density, with the composition of 1% w/v of CHI/HPMC blend in solution at 30, 40, and 50°C.

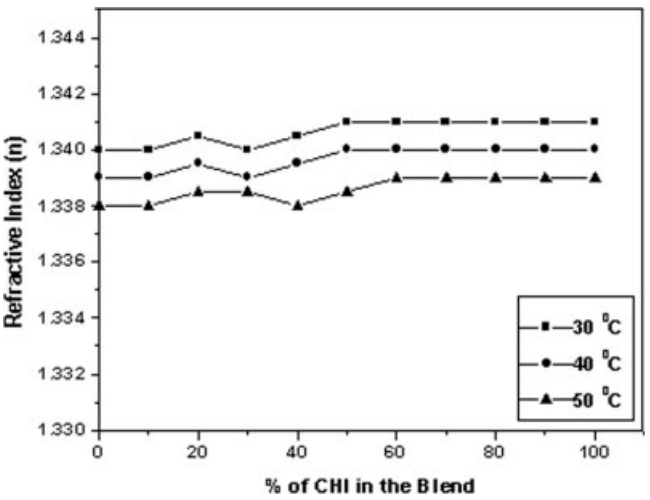

Figure 6 Effect of temperature on the variation of refractive index with the composition of 1% w/v of CHI/HPMC blend in solution at 30, 40, and 50°C.

TABLE III
Adiabatic Compressibility of CHI/HPMC Blend Solutions at 30, 40, and 50°C

% of CHI in the Blend	Adiabatic compressibility β_{ad} (10^{-7} g^{-1} m sec^2)		
	30°C	40°C	50°C
0.0	4.643	4.646	4.654
10.0	4.638	4.646	4.658
20.0	4.646	4.650	4.656
30.0	4.653	4.654	4.663
40.0	4.651	4.655	4.671
50.0	4.644	4.650	4.659
60.0	4.644	4.649	4.659
70.0	4.642	4.648	4.657
80.0	4.640	4.647	4.654
90.0	4.639	4.645	4.654
100.0	4.637	4.644	4.652

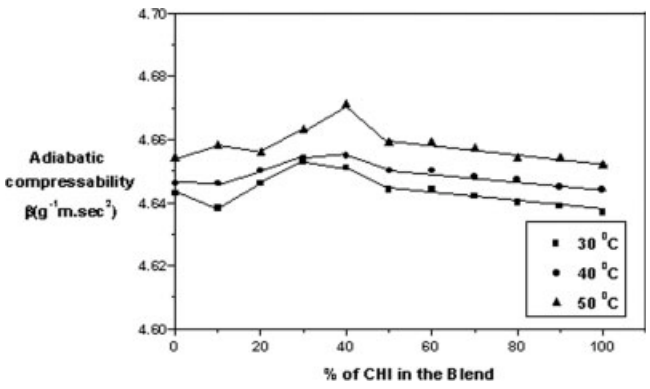

Figure 7 Effect of temperature on the variation of adiabatic compressibility with the composition of 1% w/v of CHI/HPMC blend in solution at 30, 40, and 50°C.

may be due to some specific interaction like H-bonding between CHI and HPMC.

CONCLUSIONS

Using viscosity, ultrasonic velocity, density, and refractive index methods, it is concluded that the polymer blend of CHI/HPMC is found to be miscible, when the CHI content is more than 50% in the blend at 30, 40, and 50°C, respectively. Below this critical CHI concentration, the blends were found to be immiscible. The miscibility of the blend in the case of CHI/HPMC is independent of the changes in temperature. Thus the aforementioned techniques are simple, low cost, rapid and efficient methods in exploring the miscibility windows of CHI/HPMC blend.

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