Carbohydrate Polymers 74 (2008) 779–782

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Miscibility studies of HPMC/PVA blends in water by viscosity, density, refractive index and ultrasonic velocity method

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ARTICLE INFO

Article history:
Received 15 March 2008
Accepted 25 April 2008
Available online 1 May 2008

Keywords:
Blend
Density
Hydroxy propyl methylcellulose
Miscibility
Refractive index
Ultrasonic velocity
Viscosity

ABSTRACT

Hydroxy propyl methyl cellulose (HPMC)/polyvinyl alcohol (PVA) blends are edible polymer films used for food packing and directly in foodstuffs. However they are water-soluble in ordinary temperature and have good mechanical properties. The miscibility of HPMC/PVA blend in water was studied by viscosity, ultrasonic velocity, density and refractive index techniques at 30 and 50 °C. Using viscosity data, the interaction parameters μ and α were calculated. These values revealed that HPMC/PVA blend is miscible when the HPMC content is more than 60% in the blend at 30 and 50 °C. And also the result revealed that the change in temperature has no significant effect on the miscibility of HPMC/PVA polymer blend.

1. 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 process ability. Polymer blends are physical mixtures of structurally different polymers or co-polymers, which interact through secondary forces with no covalent bonding (Krause, 1978) 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 (Varenell, Runt, & Cdeman, 1983; Varnell & Coleman, 1981; Woo, Barlow, & Paw, 1986). There have been various techniques of studying the miscibility of the polymer blends (Cabanclas, Serrano, & Baselga, 2005; Crispim, Rubira, & Muniz, 1999; Jiang & Han, 1998; Patel, 2004; Ping,1997). 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 (1990) and Sun, Wang, and Fung (1992) have suggested a viscometric method for the study of polymer–polymer miscibility in solution. Singh and Singh (Singh, 1984; Singh & Singh, 1983) have suggested the use of ultrasonic velocity and viscosity measurements for investigating the polymer miscibility in solution. Palladhi and Singh (1994a, 1994b) have shown that the variation of ultrasonic velocity and viscosity with blend composition is linear for miscible blends and non-linear for immiscible blends. Recently, Varada Rajulu, Reddy, and Ranga Reddy (1998) have used ultrasonic and refractometric technique to study the miscibility of polymer blend.

As part of our research work, we have studied the miscibility of HPMC/PVA blend in water at different temperatures by viscosity, ultrasonic velocity, density and refractive index techniques (Demappa, Basavaraju, & Rai, 2006, 2007). We selected these polymers, because they have many pharmaceutical and biomedical applications (Jumel, Harding, & Hayter, 1996; Zeng, Fang, & Xu, 2004). Hydroxy propyl methyl cellulose (HPMC) is a polysaccharide prepared from cellulose. It contains both methyl and hydroxy propyl substitutes. Poly vinyl alcohol (PVA) is a synthetic water-soluble polymer with good film forming property, which offers good tensile strength (TS), flexibility and barrier properties to oxygen and aroma (Schellekens & Bastiansen, 1991). The structures of both HPMC and PVA are shown in Schemes 1 and 2, respectively.

2. Experimental

HPMC (E 15 LV premium; LOBA CHEMIE PVT LTD) and PVA ($\overline{M}_w = 12,500$; AR grade, Merck India Ltd., India) were used for this work. A dilute polymer solution of 1% w/v was prepared for viscometric studies. Stock solutions of homopolymers and the blends of HPMC/ PVA of different compositions, 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20 and 90/10, were prepared in water.

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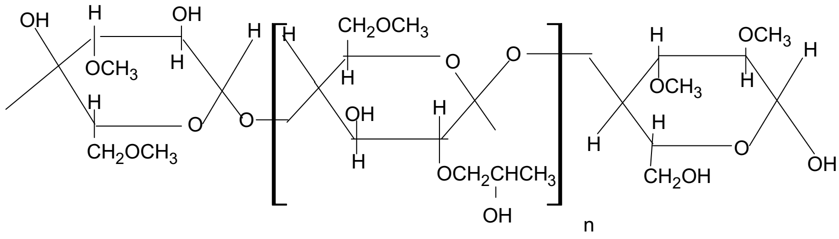
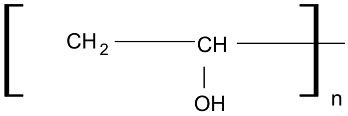
doi:10.1016/j.carbpol.2008.04.036



$C_8H_{16}O_8\ (C_{10}H_{18}O_8)_n\ C_8H_{16}O_8$

Scheme 1. Schematic representation of hydroxy propyl methyl cellulose.



Scheme 2. Poly(vinyl alcohol).

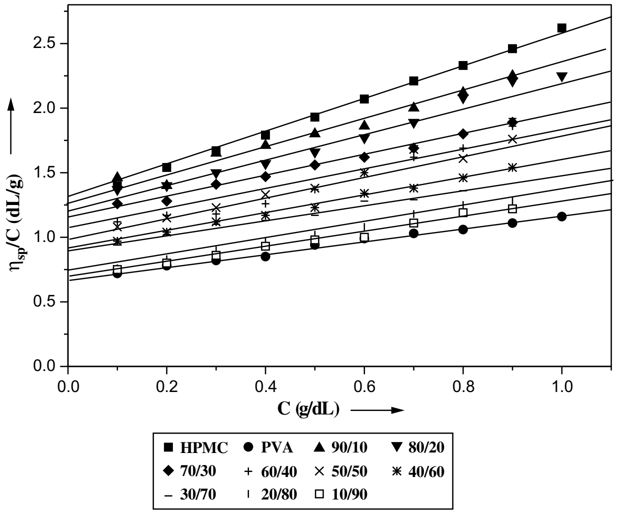


Fig. 1. Huggin's plots for 1% w/v HPMC/PVA blend in water at 30 °C.

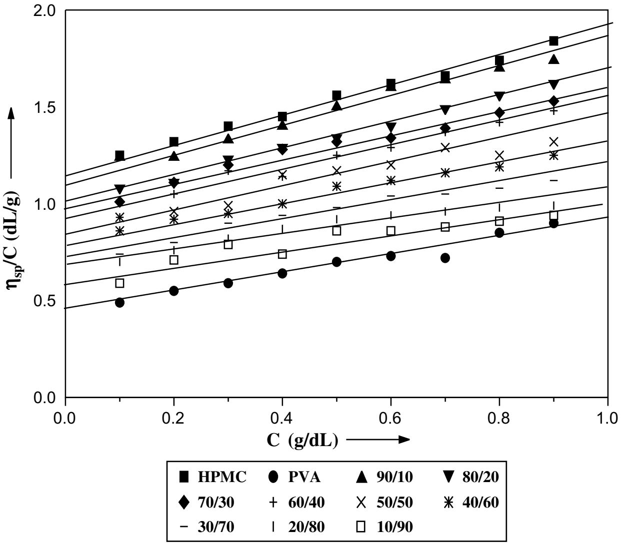


Fig. 2. Huggin's plots for 1% w/v HPMC/PVA blend in water at 50 °C.

Viscosity measurements at 30 and 50 °C were made using an Ubbelohde suspended level viscometer with the flow time of 96 s for distilled water. The total weight of the two components in the solution was always maintained at 1 g/dL. And the different temperatures were maintained in a thermostat bath, with a thermal stability of ±0.05 °C. The ultrasonic velocity measurements were performed by an ultrasonic interferometric technique (Vararda Rajulu & Mabusab, 1996). The temperatures were maintained at 30 and 50 °C by circulating water from a thermostat, with a thermal stability of ±0.05 °C, through the double–walled 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 and 50 °C by specific gravity bottle. The refractive indices of the HPMC/ PVA blend solutions were measured using an Abbe's refractometer, with a thermostat water-circulation system (Varada Rajulu & Mabusab, 1998) at 30 and 50 °C (Singh & Singh, 1984). The accuracy of the refractive index measurements are ±0.02%

3. Results and discussion

PVA exhibits a polyelectrolyte property in solution, in presence of surfactants, complexing agents, salts, buffer. HPMC, however, is known to be a flexible non-ionic polymer, which obeys the classical Huggin's equation. The Huggin's plots for the pure components and their blends at 30 and 50 °C are shown in Figs. 1 and 2 and Tables 1 and 2, respectively. The figure indicates the considerable higher slope variation for 80/20 and 60/40 HPMC/PVA blend compositions. This may be attributed to the mutual attraction of macromolecules in solution, because of the increase of hydrodynamic and thermodynamic interaction. Hence HPMC/PVA blend is found to be miscible, only when the HPMC 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 because of the phase separation.

To quantify the miscibility of the polymer blends Chee (1990) suggested that the general expression for interaction parameter when polymers are mixed in weight fractions w_1 and w_2 is as follows:

$$\Delta B = \frac{b - \bar{b}}{2w_1w_2} \tag{1}$$

where $\bar{b} = w_1b_{11} + w_2b_{22}$ in which, b_{11} and b_{12} 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

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

where b_{12} is the slope for the blend solution. Using these values, Chee Chee (1990) defined a more effective parameter as follows:

Table 1
Reduced viscosity data for HPMC/PVA and their blends in solution at 30 °C

Conc. (g/dL)	η_{sp}/C (dL/g) at 30 °C									
	HPMC	PVA	HPMC/PVA blend composition							
			90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80	10/90
0.1	1.40	0.72	1.46	1.37	1.26	1.12	1.08	0.97	0.94	0.76	0.75
0.2	1.54	0.78	1.40	1.40	1.28	1.17	1.15	1.04	1.02	0.83	0.80
0.3	1.67	0.82	1.65	1.50	1.41	1.18	1.23	1.12	1.10	0.90	0.86
0.4	1.79	0.83	1.71	1.57	1.47	1.26	1.33	1.32	1.13	0.97	0.93
0.5	1.93	0.94	1.80	1.66	1.56	1.37	1.38	1.23	1.17	1.02	0.98
0.6	2.07	0.99	1.86	1.77	1.62	1.50	1.50	1.34	1.28	1.08	1.00
0.7	2.21	1.03	2.00	1.89	1.69	1.62	1.68	1.38	1.29	1.18	1.11
0.8	2.33	1.06	2.12	2.08	1.80	1.69	1.61	1.46	1.36	1.25	1.19
0.9	2.46	1.11	2.25	2.21	1.89	1.86	1.76	1.54	1.92	1.28	1.22

Table 2
Reduced viscosity data for HPMC/PVA and their blends in solution at 50 °C

Conc. (g/dL)	η_{sp}/C (dL/g) at 50 °C									
	HPMC	PVA	HPMC/PVA blend composition							
			90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80	10/90
0.1	1.25	0.49	1.24	1.08	1.01	0.93	0.93	0.86	0.74	0.70	0.59
0.2	1.32	0.55	1.24	1.11	1.11	1.05	0.96	0.92	0.80	0.76	0.71
0.3	1.40	0.59	1.33	1.23	1.20	1.17	0.99	0.95	0.90	0.82	0.79
0.4	1.45	0.64	1.40	1.29	1.28	1.14	1.15	1.1	0.94	0.87	0.74
0.5	1.56	1.70	1.50	1.34	1.32	1.25	1.17	1.09	0.98	0.92	0.86
0.6	1.62	0.73	1.60	1.40	1.34	1.29	1.20	1.12	1.04	0.94	0.86
0.7	1.66	0.72	1.64	1.49	1.39	1.367	1.29	1.16	1.05	0.96	0.88
0.8	1.74	0.85	1.70	1.56	1.47	1.42	1.25	1.19	1.08	0.98	0.91
0.9	1.84	0.90	1.74	1.62	1.53	1.48	1.32	1.25	1.12	0.99	0.94

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

where $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities for the pure component solutions. The blend is miscible when $\mu \geqslant 0$ and immiscible when $\mu < 0$ (Chee, 1990). The values of μ, calculated with the aforementioned expression at 30 and 50 °C are represented in Table 3.

Recently, Sun et al. (1992) have suggested a new formula for the determination of polymer miscibility as follows:

$$\alpha = K_m - \frac{K_1[\eta]_1^2 w_1^2 + K_2[\eta]_2^2 w_2^2 + 2\sqrt{K_1K_2}[\eta_1][\eta_2]w_1w_2}{\{[\eta]_1 w_1 + [\eta]_2 w_2\}^2} \tag{5}$$

where K_1, K_2 and K_m are the Huggin's constants for individual components 1, 2 and the blend, respectively. The long-range hydrodynamic interactions are considered while deriving this equation. Sun et al. (1992) have suggested that a blend will be miscible when $\alpha \geqslant 0$ and immiscible when $\alpha < 0$.The computed values of μ and α are found to be negative when the HPMC content is up to 50% and then positive beyond this value at 30 and 50 °C, respectively, and the data are given in Table 3. As the long-range hydrodynamic interactions are considered in the equation for α, Eq. (5) is more accurate than Eq. (4). A similar observation was made by VaradaRajulu, Siddaramaiah and Reddy (1998) and Jayaraju, Raviprakash, Keshavayya, and Rai (2006) in case of polyvinyl pyrrolidone/polystyrene and chitosan/hydroxypropyl methyl cellulose 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. 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 and 50 °C. These values are presented in Table 3. The variation of the density, refractive index and ultrasonic velocity, with the blend composition is shown in Figs. 3 and 4, respectively. The adiabatic compressibility β_{ad} (Varada Rajulu, Rao, & Naidu, 1990) 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 3. The variation of adiabatic compressibility at 30 and 50 °C is shown in Fig. 4. The graphs show

Table 3
Interaction parameters, density, refractive index, ultrasonic velocity and adiabatic compressibility of HPMC/PVA blend at 30 and 50 °C

Composition (%)	30 °C		50 °C		Density		Refractive index		Ultrasonic velocity		Adiabatic compressibility	
HPMC/PVA	μ	α	μ	α	30 °C	50 °C	30 °C	50 °C	30 °C	50 °C	30 °C	50 °C
10/90	−0.8056	−0.0494	−0.2721	−0.7105	1.0358	1.0315	1.341	1.34	9926	7807.4	9.7988	15.9044
20/80	−0.7134	−0.113	−0.0163	−0.3806	1.0352	1.0284	1.342	1.339	7962.3	11863.3	15.2369	6.9091
30/70	−1.3101	−0.2436	−0.1264	−0.3537	1.034	1.0288	1.341	1.339	9930	9876	9.808	9.9656
40/60	−0.4994	−0.0211	−0.0862	−0.324	1.0345	1.0305	1.34	1.338	7935	10515	15.3523	8.7767
50/50	−0.1099	−0.3728	−0.0114	−0.1274	1.0332	1.03	1.342	1.34	9946	11871	9.784	6.8895
60/40	2.2681	0.0886	0.0571	0.0106	1.0338	1.0304	1.342	1.34	7992.7	11835	15.1417	8.7767
70/30	3.51	0.178	0.1693	0.0114	1.0345	1.0308	1.342	1.34	7993	11847	15.1303	6.912
80/20	3.64	0.0122	0.0996	0.207	1.0352	1.0316	1.342	1.34	7939	11828	15.3265	6.9289
90/10	3.8225	0.008	0.2369	0.0162	1.0356	1.032	1.342	1.34	7981	11847	15.1597	6.904

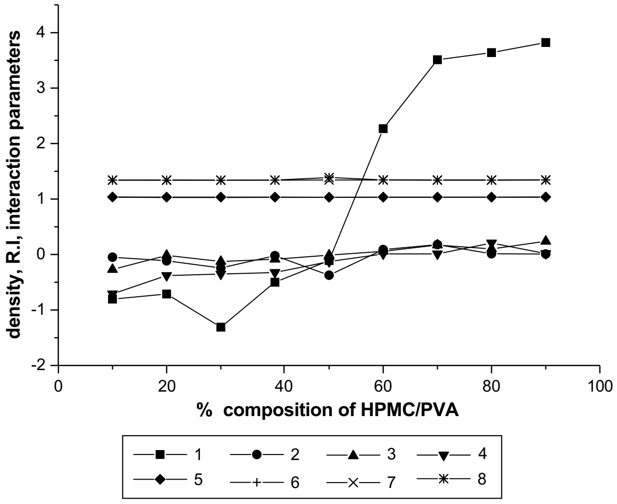


Fig. 3. Effects of density, R.I, Interaction parameters. (1 and 2) Interaction parameters μ and α at 30 °C, respectively. (3 and 4) Interaction parameters μ and α at 50 °C, respectively. (5 and 6) Densities at 30 and 50°C, respectively. (7 and 8) Refractive indices at 30 and 50 °C, respectively.

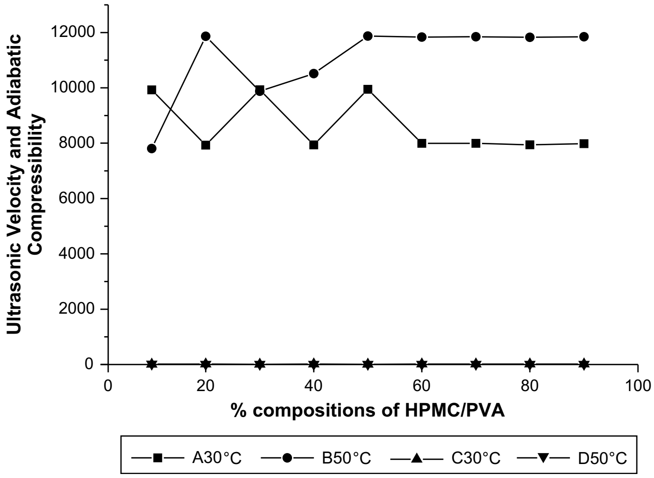


Fig. 4. Effect of Ultrasonic velocity and adiabatic compressibility. (A and B) The ultrasonic velocities at 30 and 50 °C. (C and D) Adiabatic compressibility at 30 and 50 °C.

both linear and non-linear regions. It was already established (Cabanclas et al. and Sun et al.) that the variation is linear for miscible blend and non-linear for immiscible blend. In the present case, the variation is found to be linear when the HPMC content is more than 60% at 30 and 50 °C, respectively. This observation is in confirmation with μ and α value. So the present study indicates the existence of miscibility windows when the HPMC content is more than 60% in the blend. This is because, the specific interaction between the polymer segments is more when the HPMC content is more than 60%, there by, 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 may be due to some specific interaction like H-bonding between HPMC/PVA.

4. Conclusion

Using viscosity, Ultrasonic velocity, density and refractive index methods, it is concluded that the polymer blend of HPMC/PVA is found to be miscible, when the HPMC content is more than 60% in the blend at 30 and 50 °C, respectively. Below this HPMC concentration, the blends were found to be immiscible. The miscibility of the blend in the case of HPMC/PVA is independent of the changes in temperature. Thus afore mentioned techniques are simple, low cost, rapid and efficient methods in exploring the miscibility windows of HPMC/PVA blend in solution.

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