

Studies on the miscibility of hydroxy propyl methyl cellulose and poly(vinyl pyrrolidone) blends

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Received 19 June 2001; revised received 27 February 2002; accepted 3 April 2002

Compatibility of polyvinyl pyrrolidone (PVP) and hydroxypropyl methyl cellulose (HPMC) has been investigated by solution viscometric, ultrasonic, differential scanning calorimetric (DSC) methods and fourier transform infrared spectroscopic (FTIR) techniques. Ultrasonic velocity and adiabatic compressibility versus blend composition are plotted and found to be linear. The results obtained reveal that HPMC and PVP form a miscible blends in the entire composition range. FTIR spectroscopy demonstrated that there is strong intermolecular hydrogen bonding between carbonyl group of PVP and free hydroxyl group of HPMC.

In recent years great interest has been focused on polymeric blends due to their technological and pharmaceutical application^{1,2}. Compatibility of a certain order is essential in a polymer blend to achieve good thermal, mechanical and chemical stability. Thermodynamic miscibility in a polymer blends is due to favourable dispersion force interaction between segments of component polymer chains. Cellulosics/synthetic polymer blends are studied as models for strong intermolecular interactions such as hydrogen bonding. The individual components, HPMC and PVP have been used in drug delivery studies^{3,4}. Though there are several publications on interaction of PVP with organic and inorganic systems in blends and solutions with specific objectives. The interactions involving blending of HPMC with a proton donor polymer PVP has not been studied so far. Hence, as a part of the research programme on synthesis, characterization and applications of polymeric materials⁵⁻⁷, herein miscible blend system of HPMC and PVP is being reported and an attempt has been made to study the interaction involved in blending HPMC with a proton donor polymer PVP.

Experimental Procedure

Polymers used for the present study, PVP and HPMC were obtained from CDH (India).

Molecular weight of PVP is 12000 and that of HPMC is 100000.

Sample preparation and measurement

For viscometric studies dilute polymer solutions (1% w/v) were used. Stock solution of HPMC and PVP and their different blend compositions 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90 were prepared in water as a common solvent. Viscosity measurements were made using Ubbelohde viscometer and densities of dilute solutions were measured using pycnometer and those of concentrated solution by specific gravity bottle. For DSC and FTIR studies thin films of component polymers and their blends with a thickness in the order of microns were prepared by solution casting using water as the common solvent. Films were dried in vacuum for 48 h and were found to be transparent. The polymer solution of HPMC and PVP (5% w/v) were used. The relative compositions of the two polymers in the mixed solutions were 100/0, 70/30, 50/50, 30/70, 0/100 by weight. The blend solutions were poured into a petri dish kept on a flat tiled table that was leveled by spirit leveler. It was allowed to dry overnight at room temperature. The films were then peeled off, covered with aluminum foil and kept in the desiccators till further analysis. DSC measurements were done in MATTLER MODEL TA 4000DSC at the scan rate of 10°C/min under dry nitrogen.

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The ultrasonic velocity measurements were made with 3% w/v. solutions of homopolymers and their blends of compositions 0/100, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90, 100/0 (PVP/HPMC) at 28°C using ultrasonic INTERFEROMETER with a measuring frequency of 2MHz. The accuracy of measurement was $\pm 0.5\%$.

IR studies were made with SHIMIDZON FTIR. The samples dried by an infrared lamp were cut to a fine powder and mixed with KBr and was pressed to give a pellet to be used as the FTIR analysis samples.

Results and Discussion

From viscometric measurement, relative and reduced viscosities of homopolymers and their blends were found out at 28° and 50°C (Tables 1 & 2). A plot of reduced viscosity of the component polymers and their 30/70, 50/50, 70/30, blend compositions was plotted against concentrations. In the case of the

polymer blends comprising noncompatible polymer components, a sharp cross-over is observed and a significant decrease in slope occurs in the plot of reduced viscosity versus composition⁸. But in this case the plots were linear and no cross-over is seen showing that blends are compatible^{9,10} (Fig. 1).

For predicting compatibility ultrasonic measurement were made. Sound waves provide useful tool for investigation of miscibility of polymer blends in liquid state. Ultrasonic velocity measurements were performed on blend solution by ultrasonic Interferometric technique^{11,12}. The polymers and the blend solutions were taken in required concentrations. A measuring frequency of 2MHz was used. The experimental cell had a double wall jacket and thermostated water was circulated, wavelength and then velocity was determined. The velocity in solutions of the PVP/HPMC blend is plotted against the percentage of PVP and the plots are found to be linear (Fig.2) showing the compatibility. For

Table 1—Relative viscosity data for HPMC/PVP blends

Composition of HPMC/PVP	Relative viscosity for 1% blend solution	
	28° C	50° C
100/0	5.800	3.3043
90/10	5.242	3.0760
80/20	4.925	2.7717
70/30	4.608	2.5489
60/40	4.502	2.5108
50/50	4.576	2.2173
40/60	3.802	2.1695
30/70	3.451	1.9402
20/80	3.192	1.8315
10/90	2.902	1.6847
0/100	2.597	1.5271

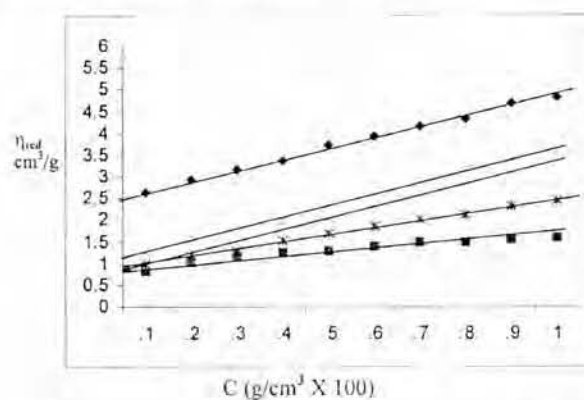


Fig. 1—Reduced viscosity versus concentration for PVP, HPMC and HPMC/PVP blends.

Table 2—Relative viscosity and reduced viscosity data for HPMC, PVP and their blends in water at 28°C

Conc. (C) g/100 cm ³	HPMC		PVP		HPMC/PVP (50/50)		HPMC/PVP (70/30)		HPMC/PVP (30/70)	
	η _{rel}	η _{red} cm ³ g ⁻¹	η _{rel}	η _{red} cm ³ g ⁻¹	η _{rel}	η _{red} cm ³ g ⁻¹	η _{rel}	η _{red} cm ³ g ⁻¹	η _{rel}	η _{red} cm ³ g ⁻¹
1	5.800	4.800	2.597	1.597	4.576	3.576	4.608	3.608	3.440	2.440
0.9	5.206	4.673	2.395	1.545	3.853	3.170	4.054	3.100	3.070	2.300
0.8	4.467	4.334	2.184	1.480	3.320	2.900	3.559	3.199	2.701	2.126
0.7	3.923	4.171	2.038	1.482	2.820	2.600	3.043	2.919	2.402	2.003
0.6	3.347	3.913	1.842	1.403	2.380	2.300	2.543	2.572	2.114	1.856
0.5	2.869	3.739	1.646	1.293	2.021	2.043	2.168	2.336	1.836	1.673
0.4	2.340	3.350	1.500	1.250	1.750	1.875	1.798	1.997	1.608	1.521
0.3	1.945	3.150	1.358	1.195	1.467	1.557	1.432	1.775	1.391	1.304
0.2	1.586	2.934	1.206	1.032	1.298	1.494	1.326	1.630	1.239	1.195
0.1	1.265	2.650	1.081	0.815	1.110	1.100	1.125	1.250	1.097	0.978

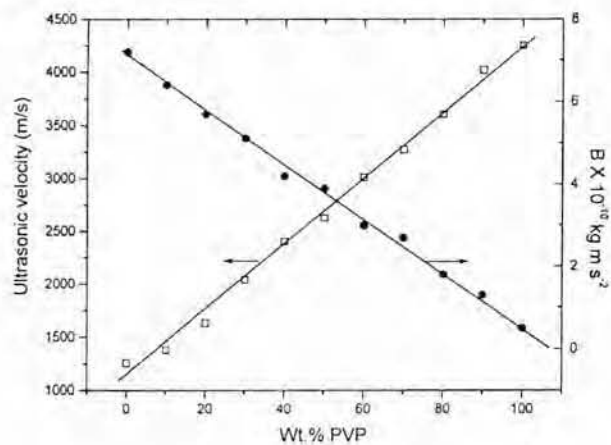


Fig. 2—Ultrasonic velocity and adiabatic compressibility versus composition of PVP-HPMC blends.

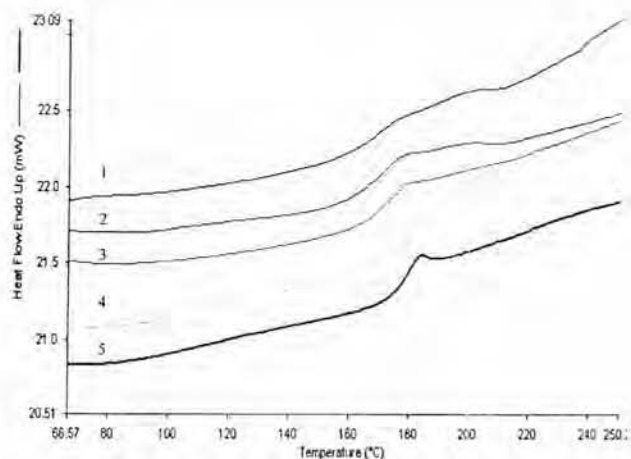


Fig. 3—DSC thermogram of PVP/HPMC blends.

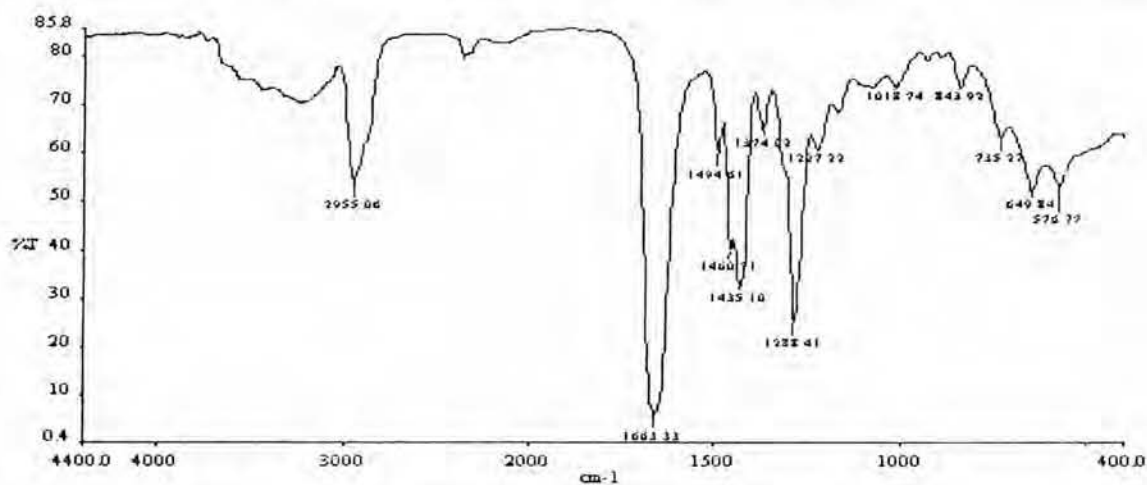


Fig. 4—FTIR spectra of PVP.

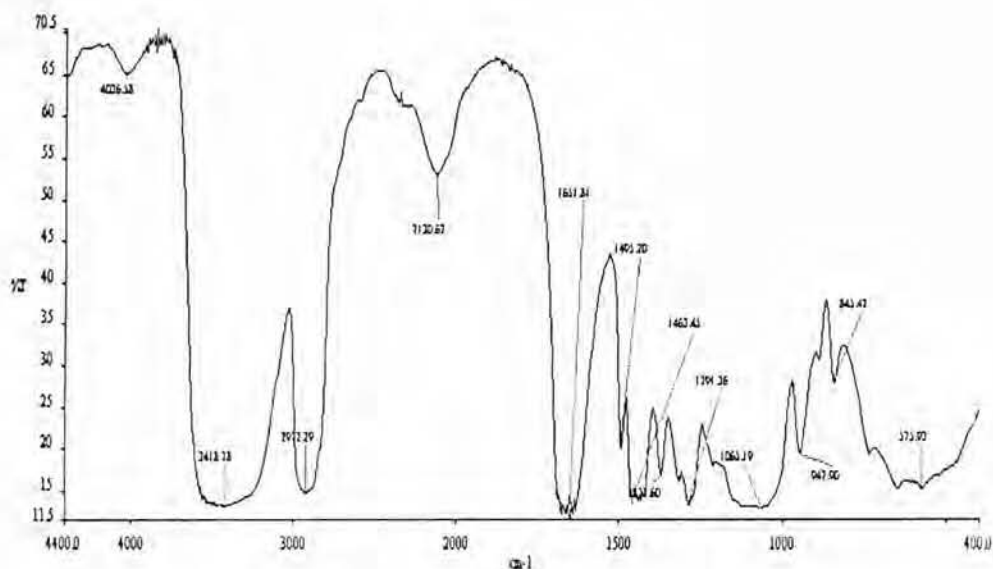


Fig. 5—FTIR spectra of HPMC/PVP (50/50) Blend.

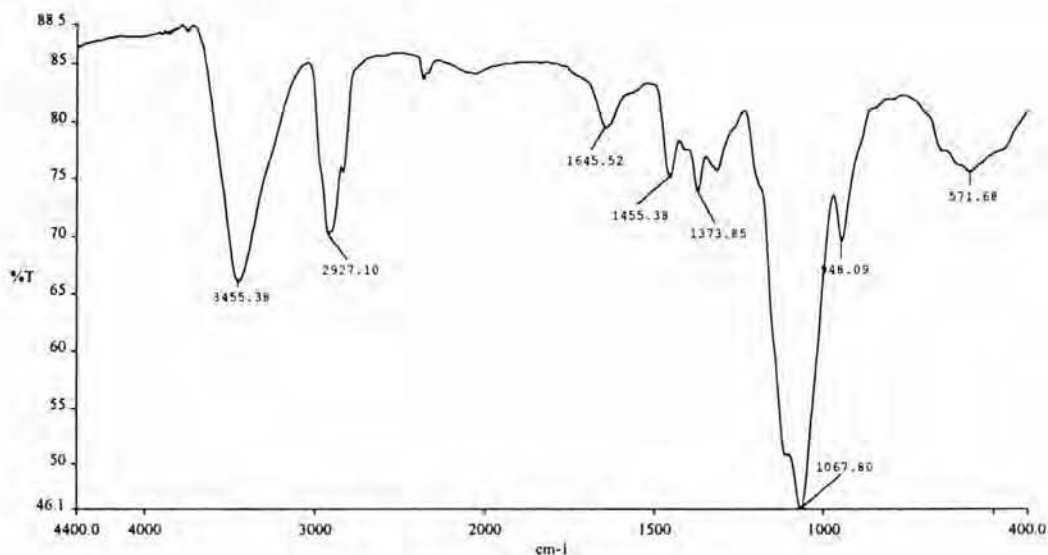


Fig. 6—FTIR spectra of HPMC.

incompatible blends the curves will be non linear because of the presence of voids at the interface between two immiscible polymers which cause excess attenuation^{13,14}. Adiabatic compressibility also varies with blend composition linearly indicating compatibility (Fig. 2).

The glass transition temperature (T_g) values for, pure HPMC, PVP/HPMC blends with compositions of 30/70, 50/50, 70/30 and pure PVP respectively in C are: 169.7, 172.7, 175.4, 181 and 182.1 (Fig. 3). Blends exhibit single T_g intermediate to those of PVP and HPMC, which indicate that blends are compatible over whole range of composition¹⁵.

FTIR investigation was performed on PVP, HPMC and their blends with a composition ratio 50:50 and the spectrums are compared (Figs 4-6). It is found that stretching vibration bands of both O-H groups in pure HPMC at 3455.38 cm^{-1} and C=O group in pure PVP at 1663.33 cm^{-1} , shift observably in the HPMC/PVP blends to the direction of lower wave number 3418.28 and 1651.81 cm^{-1} respectively.

The shift of carbonyl stretching band and hydroxyl stretching band in the blend may result from intermolecular hydrogen bonding and contribute to enhancement of the state of miscibility of blends^{16,17}.

Conclusion

The blends of HPMC/PVP are miscible over whole range of composition because of strong intermolecular interaction based on strong hydrogen bonding. Thus simple measurement of viscosity, ultrasonic velocity, DSC and FTIR studies give information regarding the miscibility of the blends.

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