Miscibility Studies of Hydroxypropyl Cellulose/Poly(vinyl pyrrolidone) in Dilute Solutions and Solid State

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ABSTRACT: The miscibility of hydroxypropyl cellulose (HPC) and poly(vinyl pyrrolidone) (PVP) blends in aqueous solutions was studied using viscosity, ultrasonic velocity, and refractive index techniques at 30°C. The interaction parameters ΔB, μ, and α calculated from viscosity using Sun and Chee methods indicated the miscibility of this blend. This was further confirmed by ultrasonic and refractive index results. The HPC/PVP blend films are prepared by solution casting method and are analyzed by differential scanning calorimetry, X-ray diffraction, Fou-rier transform infrared spectroscopy, and scanning electron microscopic techniques that confirmed the complete miscibility. This miscibility is due to the strong intermolecular H-bonding interactions between ─OH groups of HPC and C═O groups of PVP. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2289–2296, 2012

Key words: hydroxypropyl cellulose; poly(vinyl pyrrolidone); blends; miscibility

INTRODUCTION

To satisfy the growing needs of new materials with specific properties such as engineering materials, new polymers have been synthesized[1–3] and chemical modifications in conventional polymers have also been proposed.[4,5] However, the mixture of two or more polymers, forming a polymer blend, continues to be an economical method to obtain new polymeric materials.[6] The final properties of a polymeric blend will commonly depend on the properties of its polymeric components, its composition, and, mainly, on the miscibility of the constituent polymers.[7] In some cases, by synergistic effects, the blend can present better properties than the pure components.[6,7]

Several works on polymer–polymer miscibility have been developed in the last 20 years.[8,9] For such investigations, the techniques most commonly and widely used are electron microscopy,[10] spectroscopy,[11] thermal analysis,[12] and inverse gas chromatography.[13] Other techniques using alternative properties[14] or less expensive techniques, for instance, viscometry, ultrasonic velocity, and refractometry methods, have also been proposed.[15,16] Chee[17] and Sun et al.[18] suggested the viscometric method for the study of polymer–polymer miscibility. Paladhi and Singh[19,20] showed that the variation of ultrasonic velocity and viscosity with blend composition is linear for miscible blends and nonlinear for immiscible blends. Basav Raju et al.[21] also used refractive index method for the miscibility of polymer blends.

A combination of synthetic and natural polymers results in new materials, which have useful properties of natural component (e.g., good mechanical properties, easy processability, low production, and transformation costs) and biocompatibility typical for biopolymers.[22] These blends have already been used as biodegradable biomaterials,[23] drug delivery systems,[24] membranes,[25] and materials for agricultural application.[26]

Hydroxypropyl cellulose (HPC) is a cellulose derivative used as coatings, excipients, encapsulations, binding materials, foaming agents, protection colloids, flocculants, and so forth. For a wide variety of applications in food, drugs, paper, ceramics, plastics,[27] and so forth, cellulose ether–ester films are flexible and transparent, exhibit a moderate strength, and exhibit resistance to oil and fat migration.[28] They act as acceptable barriers to moisture and oxygen.[29,30] Blends based on HPC with natural or synthetic polymers were proposed to design new materials with enhanced properties and with wide range of applications.

Poly(vinyl pyrrolidone) (PVP) is an amorphous polymer; it has several pharmaceutical applications.[31] In addition, PVP is able to form complexes

with a wide range of compounds through hydrogen bond formation between its carbonyl group and the hydroxyl groups of water, alcohol, and hydroxyl-containing polymers such as poly(vinyl alcohol) (PVA).[32,33]

The aim of this research was to prepare and characterize polymeric films by blending of PVP with water-soluble polysaccharide (HPC) and to study the miscibility nature of these polymers through low-cost techniques and also advanced techniques. Both PVP and HPC exhibit lower critical solution temperature in aqueous solutions and it is interesting to know the nature of miscibility of this blend. HPC is a typical polysaccharide and contains a large amount of hydroxyl groups in its structure, which have proton-donating nature. The PVP molecules have carbonyl groups, which have proton-accepting nature, and form intermolecular hydrogen bonding.

MATERIALS AND METHODS

Materials

HPC (MW = 140,000) was purchased from Sigma Aldrich (St. Louis, Missouri, USA.) and PVP (M_W = 40,000) was purchased from S.D. Fine Chemicals (Mumbai, India) and were used without further purification. Bidistilled and deionized water, having almost zero conductivity, was used as a solvent.

Preparation of blend solutions

The 1 wt % of HPC and 1 wt % of PVP solutions were prepared by dissolving 1 g of each polymer in 100 mL of distilled water in two separate stoppered conical flasks. Eight different blend solutions of HPC and PVP were prepared by mixing HPC with PVP in the weight ratios of 0/100, 20/80, 40/60, 50/50, 60/40, 80/20, and 100/0. From each of these blend solutions, 0.1, 0.3, 0.5, 0.7, and 0.9 (w/v) concentrated solutions were used for the measurement of solution viscosity, ultrasonic velocity, and refractive index.

Preparation of blend films

Blend films of HPC with PVP were prepared by solution casting method. Required amount of HPC was dissolved in distilled water by stirring over a magnetic stirrer (model 1103; Jenway, UK) for 24 h. To this, 20, 40, 50, 60, and 80 wt % (with respect to HPC) of PVP were added. Solutions were mixed uniformly and filtered to remove any foreign floating or suspended particles. The respective solution was poured onto a clean glass plate, leveled perfectly on a tabletop kept in a dust-free atmosphere,

and dried at room temperature. The dried films were peeled off carefully from the glass plate.

Techniques

Viscosity and density were measured at 30°C using Ubbelohde suspended-level viscometer (with the flow time 95 s for distilled water) and specific gravity bottle, respectively. The required temperature was maintained within ±0.05°C. The ultrasonic velocities of the blend solutions with different compositions, namely, 0/100, 20/80, 40/60, 50/50, 60/40, 80/20, and 100/0 by weight, were measured at 30°C using an ultrasonic interferometer. The constant temperature was maintained by circulating water from a thermostat with a thermal stability of ±0.05°C through the double-walled jacket of ultrasonic experimental cell. The experimental frequency was 2 MHz, and the velocity measurements were accurate to better than ±0.5%. The refractive indices of blend solutions with different compositions were measured directly with an Abbe's refractometer (digital) with thermostated water circulation system at 30°C. The accuracy of the refractive index measurement is ±0.02%.

Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectra of HPC, PVP, and their blend films were recorded on Bomen MB-3000 FTIR spectrometer. Blend films were characterized at room temperature from 4000 to 400 cm^{-1} at a scan rate of 21 cm^{-1}.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) curves of HPC, PVP, and their blend films of different compositions were recorded using TA instruments DSC (Model: SDT Q600; USA). The analysis of samples was performed at a heating rate of 20°C/min under N_2 atmosphere at a purge speed of 100 mL/min.

X-ray diffraction

The X-ray diffraction (XRD) patterns of the blend samples were recorded on an Intel diffractomer (Paris, France) with monochromatized Cu Kα radiation (scan speed of 1°/min in a 2θ range of 5°–40°) at room temperature.

Scanning electron microscopic analysis

The scanning electron microscopic (SEM) micrographs of the blend samples were obtained under high resolution (magnification: 300×, 5 kV) using JOEL JSM 840 SEM equipped with phoenix energy dispersive system.

RESULTS AND DISCUSSION

Viscosity studies

The absolute viscosity versus concentration curves for the blends of HPC and PVP of different compositions at 30°C in water are shown in Figure 1. It was well established earlier by many workers[34,35] that the variation of absolute viscosity versus concentration of blend composition plots are linear for compatible blends and nonlinear for incompatible blends. Based on these data, in the current study, the linear variation of the absolute viscosity with concentration for all the blend compositions in water was attributed to the miscibility nature of the blend.

The Huggin's plots of reduced viscosity against concentration of different compositions of HPC/PVP blends, HPC, and PVP at 30°C are shown in Figure 2 (curves a–g). From these graphs (Fig. 2, curves a–e), it is also clearly evident that the Huggin's curves are linear in nature and this may be attributed to the mutual attraction of macromolecules in solution that favors the polymer miscibility. A similar observation was made by Ravi Prakash et al.[36] from their viscometric investigations on intermolecular interactions between methyl cellulose/Poly(Ethylene Glycol) (PEG) in water.

Chee and Sun interaction parameters

To quantify the miscibility of the polymer blends, Chee suggested that the general expression for interaction parameter when polymers are mixed in weight fractions w_1 and w_2 is as follows:
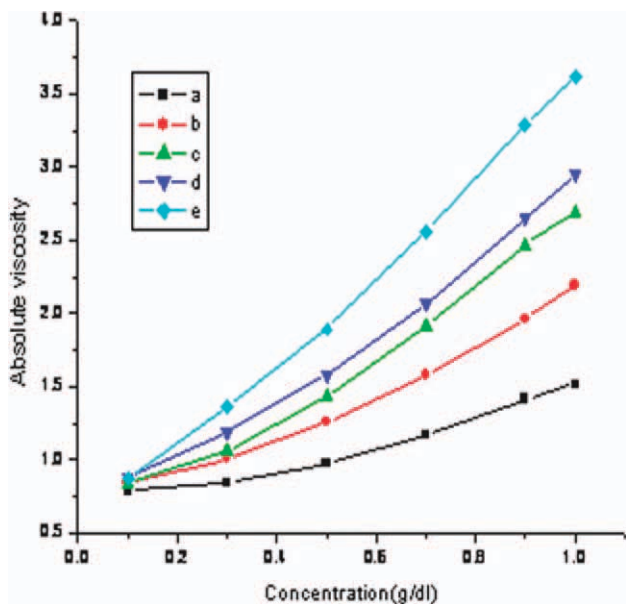
Figure 1 Plots of absolute viscosity versus concentration for 1% w/v HPC/PVP of 20/80 (a), 40/60 (b), 50/50 (c), 60/40 (d), and 80/20 (e). [Color figure can be viewed in the online issue, which is available at wileyonline library.com.]
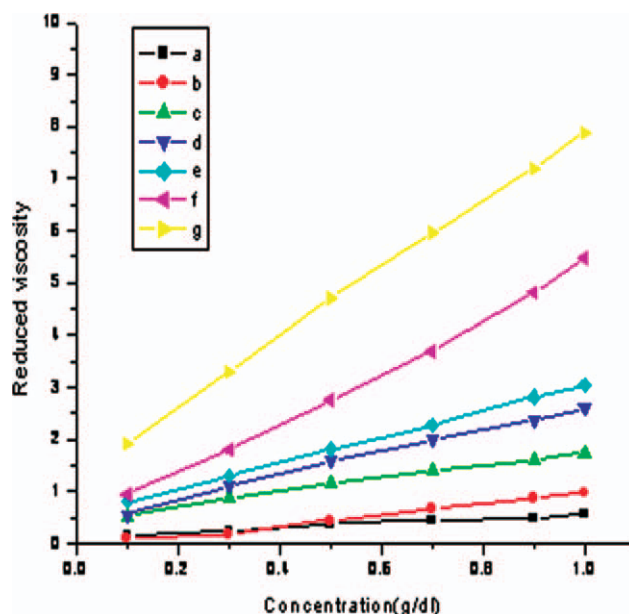
Figure 2 Reduced viscosity versus concentration curves for pure PVP (a), HPC/PVP blends 20/80 (b), 40/60 (c), 50/50 (d), 60/40 (e), and 80/20 (f), and pure HPC (g). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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

where $\bar{b} = w_1 b_{11} + w_2 b_{22}$, 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

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

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

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

where η_1 and η_2 are the intrinsic viscosities for the pure component solutions. Sun et al.[18] have suggested a new formula for the determination of polymer miscibility as follows:

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

**Chee and Sun's Interaction Parameters for Compositions
of 1% (w/v) HPC/PVP Blends in Water at 30°C**

HPC/PVP blends composition	Chee's differential interaction parameters		Sun's miscibility parameter $\alpha \times 10^2$
	ΔB	μ	
20/80	0.0553	3.0714	0.1774
40/60	0.1166	0.8060	0.0645
50/50	0.0697	0.6359	0.1215
60/40	0.0484	0.7003	0.0448
80/20	0.0422	5.1086	0.4428

where α is the interaction parameter, and K_1, K_2, and K_m are the Huggin's constants for individual components 1, 2, and the blend, respectively.

It is observed from Table I that the values of ΔB, μ, and α are positive for all the compositions of HPC/PVP blends. In general, if ΔB, μ, and α are positive for any poly-blend system, it is considered as a miscible one, whereas if these values are negative, the poly-blends are considered as immiscible. Based on these data and the values given in Table I, HPC/PVP blends show miscibility nature for all poly-blend compositions. A similar observation was made by Guru et al.[37] in the case of xanthan gum/PVP blends. To further confirm this observation, we measured the ultrasonic velocity (v) and refractive index (n) of the blend under consideration at various compositions at 30°C. The variation of the ultrasonic
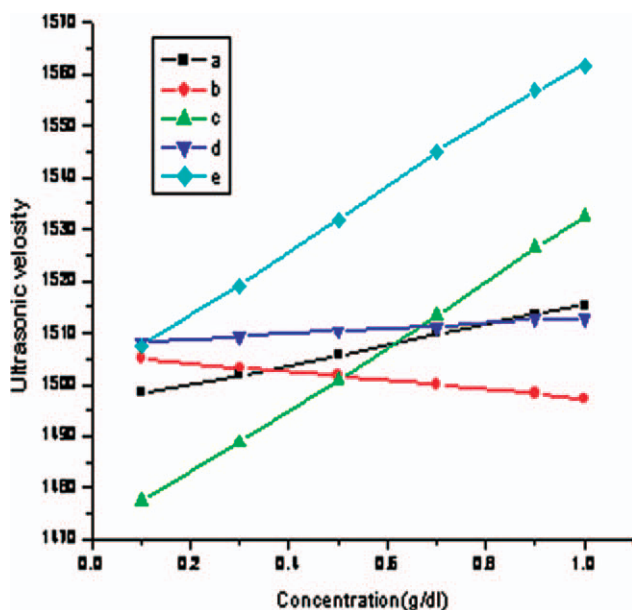
Figure 3 Ultrasonic velocity versus concentration curves for HPC/PVP blends of 20/80 (a), 40/60 (b), 50/50 (c), 60/40 (d), and 80/20 (e). [Color figure can be viewed in the online issue, which is available at wileyonline library.com.]
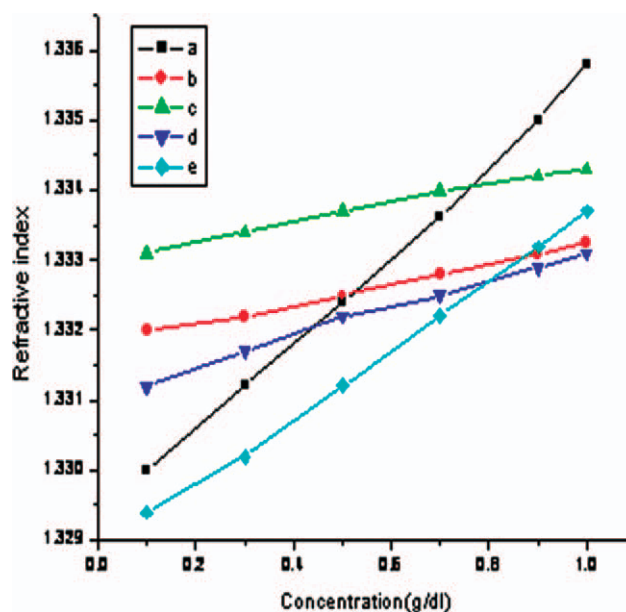
Figure 4 Refractive index versus concentration curves for HPC/PVP blends of 20/80 (a), 40/60 (b), 50/50 (c), 60/40 (d), and 80/20 (e). [Color figure can be viewed in the online issue, which is available at wileyonline library.com.]

velocity and refractive index with the blend composition is shown in Figures 3 and 4, respectively.

It was already established[15,38] that the variation is linear for miscible blend and nonlinear for immiscible blend. In the current case, the variation is found to be linear for all compositions, and this observation is in confirmation with μ and α values. Hence, the current study indicates the existence of miscibility over entire composition range due to possible H-bonding interactions taking place between the carbonyl groups of PVP and the hydroxyl groups of HPC as shown in the Scheme 1. A similar observation was made by Demappa et al.[15] in the case of miscibility of hydroxy propyl methyl cellulose (HPMC)/PVA blends.

MISCIBILITY STUDIES OF BLEND FILMS BY CHARACTERISTIC TECHNIQUES
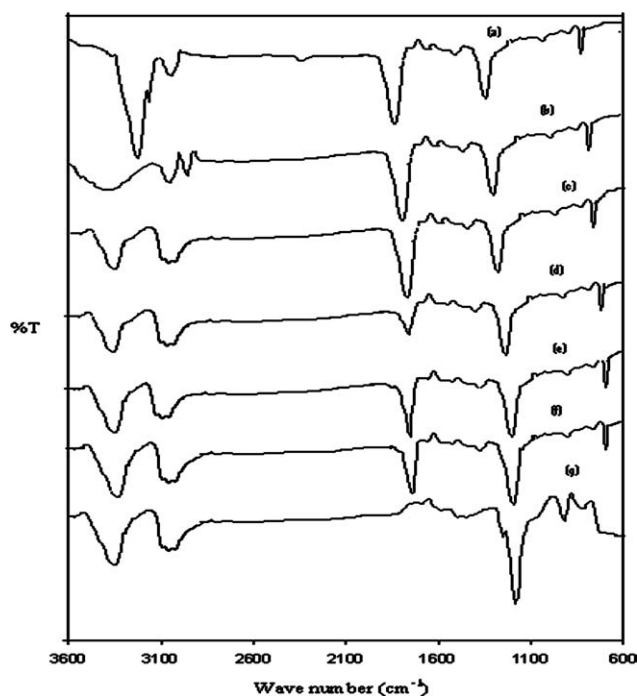
FTIR spectroscopy studies

The formations of a miscible polymer blend require the presence of specific interactions between the two polymers.[39] Infrared spectroscopic study is often used to determine the interactions between the counterpart polymers of a blend. In the current study, the type of hydrogen bonding within HPC/PVP polymer blends may be complicated,[40–43] because there are several groups that can from hydrogen bonds in HPC.

FTIR analysis was based on the identification of absorption bands associated with the vibrations of
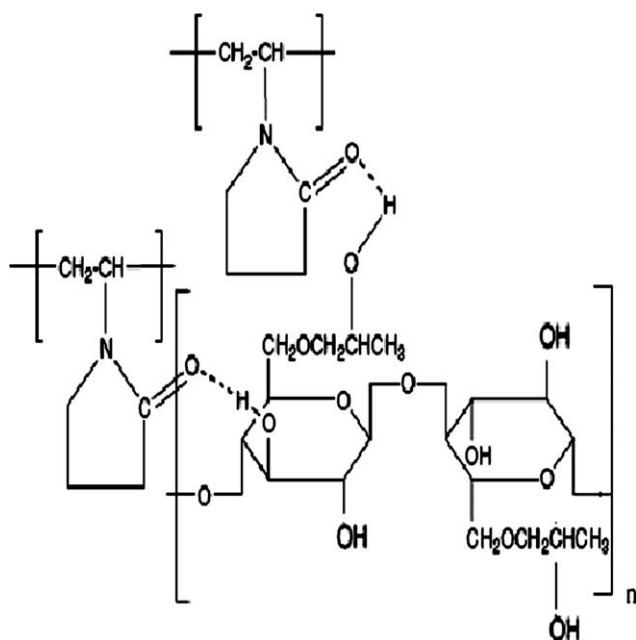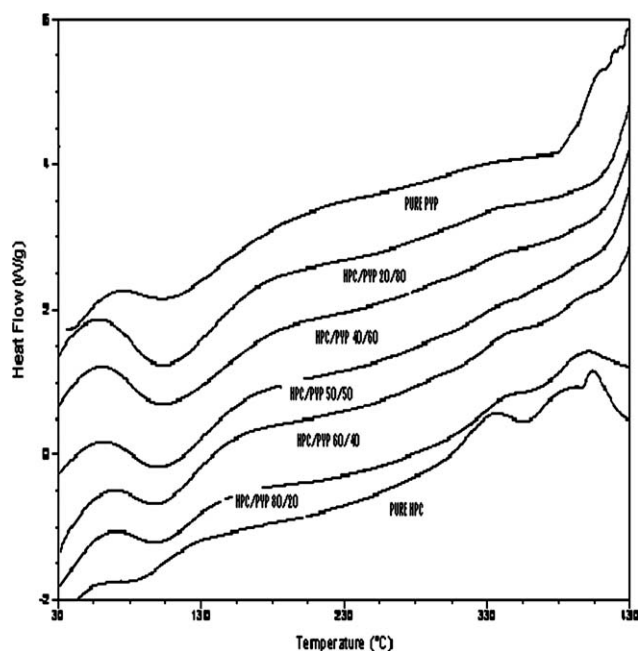
Scheme 1 Hydrogen bonding between the carbonyl groups of PVP and the hydroxyl groups of HPC.

functional groups present in HPC and PVP. Figure 5 shows the FTIR transmittance spectra for pure HPC, PVP, and the HPC/PVP poly-blend samples as functions of wave numbers in the range of 4000–500 cm^{-1}. The formation of strong hydrogen bonds between HPC and PVP was demonstrated by FTIR spectroscopy from the shifts of absorption bands

Figure 6 DSC thermograms of HPC, PVP, and their blend membranes.

showing hydroxyl stretching vibrations, which were sensitive to the hydrogen bonds formed during blending. The broad transmission bands at 3600–3100 cm^{-1} produced by stretching of the hydroxyl groups in the spectrum of HPC can be remarkably distinguished. It can be seen from the spectra that the peak intensity and the peak shape were clearly different and that these differences were induced by the different blend ratios. The presence of hydrogen
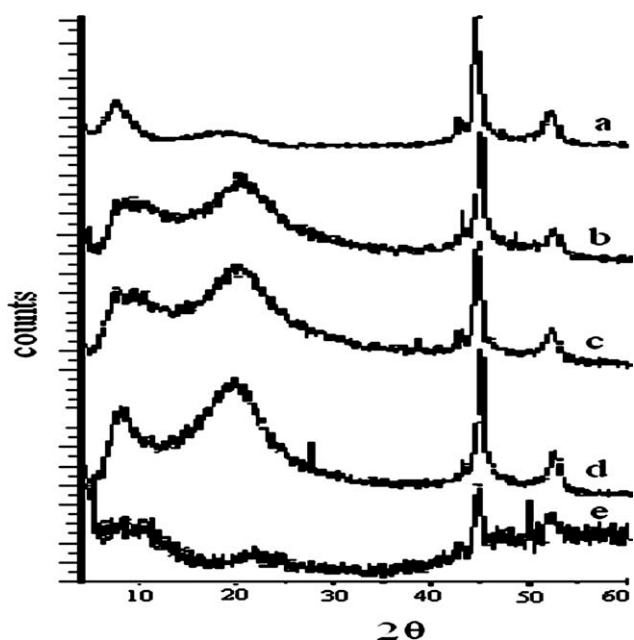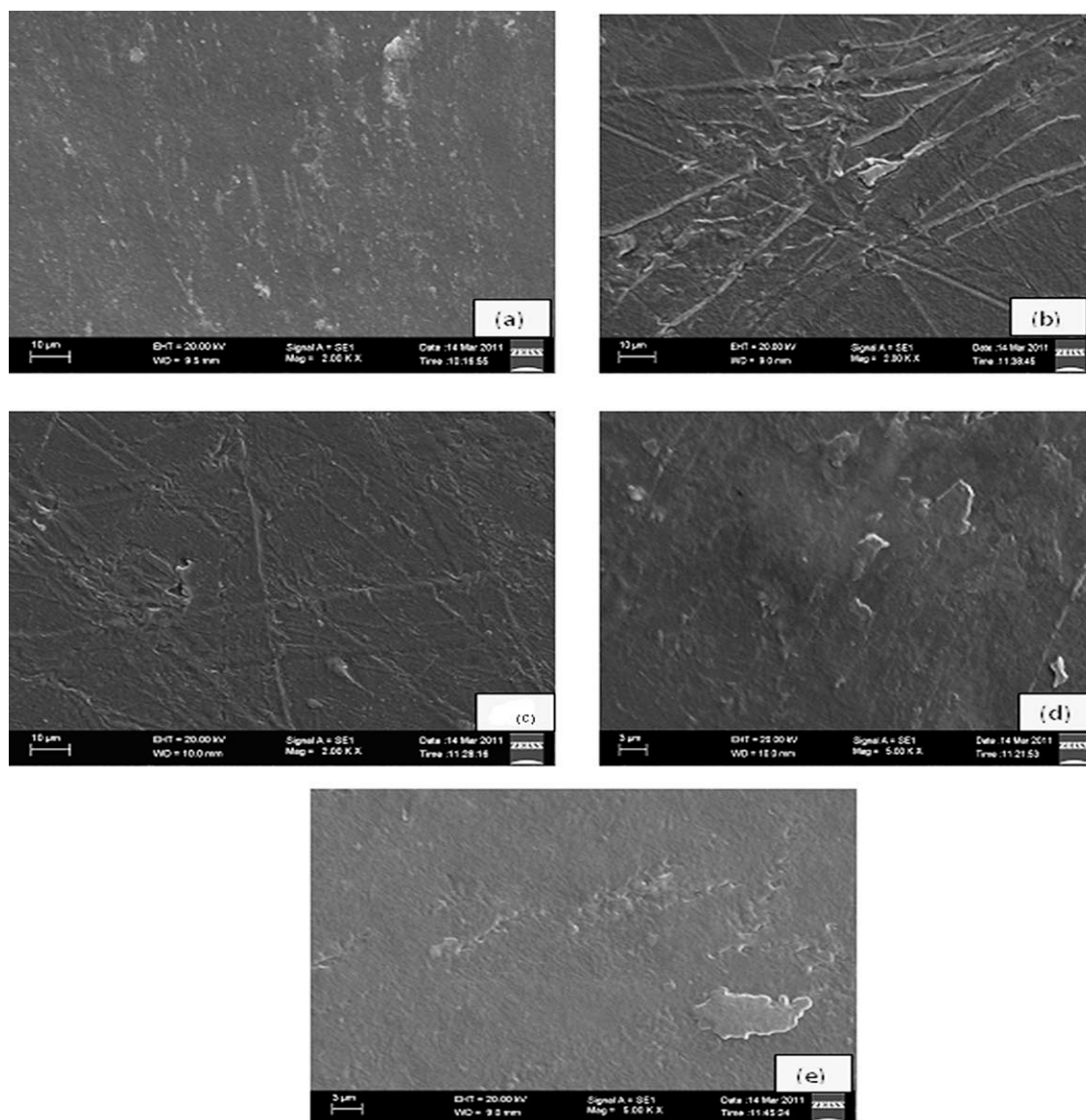

Figure 5 FTIR spectra of PVP (a), HPC/PVP 20/80 (b), HPC/PVP 40/60 (c), HPC/PVP 50/50 (d), HPC/PVP 60/40 (e), HPC/PVP 80/20 (f), and HPC (g).

Figure 7 X-ray diffraction patterns of HPC (a), HPC/PVP 80/20 (b), HPC/PVP 50/50 (c), HPC/PVP 20/80 (d), and PVP (e).

Figure 8   SEM images of HPC (a), PVP (b), 20/80 HPC/PVP (c), 50/50 HPC/PVP (d), and 80/20 HPC/PVP (e)

bond structures in some blends could be inferred from the peak shape and peak intensity of the absorption band of the hydroxyl stretching vibrations in the FTIR spectra.[44] The broad band in the pure HPC spectrum at 3600–3100 cm^{-1}, with a maximum at 3460 cm^{-1}, was assigned to stretching vibrations of the ─OH groups. The difference among the curves in Figure 5, that is, a little broadening or shifting or a peak at 3600–3100 cm^{-1} was observed in the transmission band of the HPC/PVP blends when compared with that of pure HPC, which suggest that a relative low amount of interaction was present between the polymers. The hydroxyl stretching vibration band was shifted to a lower wave number with increasing amounts of PVP. This could be associated with the hydrogen-bonded hydroxyl groups in HPC. The bands of hydroxyl stretching vibrations had a 6- to 14-cm^{-1} red-shift relative to a

free hydroxyl, and the bands of hydroxyl stretching vibrations varied markedly with hydrogen bonding interactions between the ─OH belonging to HPC and the C=O belonging to PVP. However, the free and associated hydroxyl groups in macromolecules shifted to equilibrium via hydrogen bonds. The greater the amount of free hydroxyls in the structure of the HPC chains, the stronger are the hydrogen bonds between the blending constitutes and the vice versa.

DSC studies

Figure 6 displays the DSC thermograms of HPC, PVP, and their different blend membranes. The polymer–polymer compatability is determined by the melting temperature (T_m) of the blend and its comparison with the T_m of component polymers. If

the components are crystalline in nature, then the depression in the melting temperature can also be used to study the blend compatability.[45,46] In the current study, DSC was used to estimate the T_m of the blends to investigate the compatability of PVP and HPC blends. From Figure 6 we can observe that T_m of HPC and PVP are 353°C and 380°C, respectively. From Figure 6 we can observe that as the PVP content increases, the T_m of polymer blend decreases. This indicates that the T_m values of the blends are in between the pure polymer values. This further confirms the miscibility of all compositions of polymer blends under study.

XRD studies

XRD was performed to investigate how the crystalline portion of PVP might be influenced by mixing it with HPC. The scanning of the samples was carried out with an X-ray diffractometer at room temperature. The typical XRD patterns of PVP, HPC, and their blend compositions are shown in Figure 7. For the pure HPC (curve a), there were two peaks around $2\theta = 8.5°$ and 44.6°. The diffraction model of PVP was shown at $2\theta = 5.1°$ and 44.6°. The peak at $2\theta = 8.5°$ in HPC/PVP blends became weak and disappeared with increasing PVP content in the blend. The peak of HPC/PVP blend films [HPC/PVP 80/20 (curve b), HPC/PVP 50/50 (curve c), and HPC/PVP 20/80 (curve d)] around $2\theta = 8.5°$ slightly shifted toward $2\theta = 8.9°$–9.8°. These evidences further conclude that strong interactions occurred between HPC/PVP molecules in the blend to indicate miscibility of these polymers. If there were no interactions between HPC and PVP molecules in the blend films, each component would have its own crystal region in the blend films and the XRD patterns would have expressed as simple mixed patterns. Thus, the XRD studies also support that HPC/PVP blends under study are miscible.

SEM studies

A common qualitative technique for the estimation of blend compatibility is visual identification. Figure 8 shows the SEM images of HPC (curve a), PVP (curve b), and their blends of different compositions 20/80 (curve c), 50/50 (curve d), and 80/20 (curve e). From Figure 8, it is noticed that the surface morphology of HPC (curve a) and PVP (curve b) films were homogeneous. The bright strips are present in the image of pure PVP (curve b). With the addition of HPC to PVP, the morphology of the blend films changed dramatically. The bright strips present in the PVP film disappeared; however, no obvious phase separation boundary was visible. Hence, we

conclude that the blends of different formulations are miscible in nature.

CONCLUSIONS

The miscibility of HPC/PVP blends in water has been carried out by solution methods such as viscosity, ultrasonic velocity, and refractive index at 30°C. Using viscosity data, interaction parameters ΔB, μ, and α were computed. These values revealed that the blend is miscible in all compositions. This is further confirmed by ultrasonic velocity and refractive index measurements. The prepared films of HPC/PVP blends are also characterized using FTIR, DSC, XRD, and SEM to support the miscibility data obtained from the abovementioned simple methods. The miscibility of the HPC/PVP blends can be attributed to the hydrogen bonding between the —OH groups of HPC and the C=O groups of PVP.

References

1. Lipscomb, G. G.; Banerjee, T. Polym Adv Technol 1993, 5, 708.
2. Pinnau, I. Polym Adv Technol 1993, 5, 733.
3. Stadler, R.; Auchra, C.; Bekmann, J.; Krape, U.; Voigt-Martin, I.; Leibler, L. Macromolecules 1995, 28, 3080.
4. Gagnon, K. D.; Lenz, R. W.; Farris, R. J. Polymer 1994, 35, 4368.
5. Ohya, Y.; Okawa, K.; Murata, J.; Ouchi, T. Angew Makromol Chem 1996, 240, 263.
6. Utracki, L. A. Polymer Alloys and Blends; Hanser Publishers: Munich, 1989.
7. Olabisi, O.; Robeson, L. M.; Shaw, M. T. Polymer–Polymer Miscibility; Academic Press: New York, 1979.
8. Cowie, J. M. G. Miscibility. In Encyclopedia of Polymer Science and Engineering; Mark, H. F. Ed.; Wiley: New York, 1985; p 455.
9. Paul, D. R.; Barlow, J. W.; Keskula, H. Polymer Blends; Academic Press: New York, 1973.
10. Inoue, T.; Ougizawa, T. J Macromol Sci Chem 1989, 26, 147.
11. Colemann, M. M.; Printer, P. C. Appl Spectrosc Rev 1984, 23, 255.
12. Hourston, D. J.; Zhang, H. X.; Song, M.; Pollock, M.; Hammiche, A. Thermochim Acta 1997, 23, 294.
13. Mandal, B. M.; Bhattacharya, C.; Bhattacharya, N. S. J Macromol Sci Chem 1989, 26, 175.
14. Muniz, E. C.; Vasquez, P. A. M.; Bruns, R. E.; Nunes, S. P.; Wolf, B. A. Makromol Chem Rapid Commun 1992, 13, 45.
15. Fadnis, C.; Illiger, S. R.; Rao, K. P.; Demappa, T. Carbohydr Polym 2008, 74, 779.
16. Sashidhara, G. M.; Guruprasad, K. H.; Vararadarajulu, A. Eur Polym J 2002, 38, 611.
17. Chee, K. K. Eur Polym J 1990, 26, 423.
18. Sun, Z.; Wang, W.; Fung, Z. Eur Polym J 1992, 28, 1259.
19. Paladhi, R.; Singh, R. P. J Appl Polym Sci 1994, 28, 1559.
20. Paladhi, R.; Singh, R. P. J Appl Polym Sci 1994, 30, 251.
21. Basav Raju, K. C.; Demappa, T.; Rai, S. K. Carbohydr Polym 2006, 74, 779.
22. Cascone, M. G.; Barbani, N.; Cristallini, C.; Giusti, P.; Ciradelli, G.; Lazzeri, L. J Biomater Sci Polym Edn 2001, 12, 267.

23. Azevado, H. S.; Gama, F. M.; Reis, R. L. Biomacromolecules 2003, 4, 1703.
24. Cascone, M. G.; Sim, B.; Downes, S. Biomaterials 1995, 16, 596.
25. Yang, J. M.; Su, W. Y.; Leu, T. L.; Yang, M. C. J Membr Sci 2004, 236, 39.
26. Chiellini, E.; Cinelli, P.; Imam, S. H.; Mao, L. Biomacromolecules 2001, 2, 1029.
27. Cascone, M. G.; Silvio, L. D.; Sim, B.; Downes, S. J Mater Sci: Mater Med 1994, 5, 770.
28. Psomiadou, E.; Arvanitoyannis, I.; Yamamoto, N. Carbohydr Polym 1996, 31, 196.
29. Hagenmaier, R. D.; Shaw, P. E. J Agric Food Chem 1990, 38, 799.
30. Hanlon, J. F. Handbook of Package Engineering; Technomic: Lancaster, PA, 1992; p 1.
31. Weber, H. A.; Molenaar, A. P. U.S. Pat.3,557 (1970).
32. Mosakala, E. J.; Varnell, D. F.; Coleman, M. Polymer 1985, 26, 228.
33. Goh, S. H.; Siow, K. S. Polym Bull 1990, 23, 205.
34. Coleman, M. M.; Zarian, J. J Polym Sci Polym Phys Ed 1979, 17, 83.
35. Flory, P. J. Principles of Polymer Chemistry; Cornell University Press: Itheca, NY, 1953.
36. Ravi Prakash, S. D.; Rama, H. V.; Rai, S. K. J Appl Polym Sci 2003, 90, 33.
37. Guru, G. S.; Prasad, T.; Siva Kumar, H. R.; Rai, S. K. J Polym Environ 2010, 18, 135.
38. Rai, S. K.; Jayaraju, J.; Raviprakash, S. D.; Kesavayya, J. J Appl Polym Sci 2006, 102, 2738.
39. Paul, D.; Newman, S. Polymer Blend; Academic Press: New York, 1978; Vol.1.
40. Mucha, M.; Jiekielna, J.; Wieczorek, A. Macromol Symp 1999, 144, 391.
41. Kolhe, P.; Kannan, R. M. Biomacromolecules 2003, 4, 173.
42. Jiang, W. H.; Han, S. J. J Polym Sci Part B: Polym Phys 1998, 36, 1275.
43. Fang, L.; Goh, S. H. J Appl Polym Sci 2000, 76, 1785.
44. Cai, T.; Hu, Z. B. Macromolecules 2003, 36, 6559.
45. Nishil, T.; Wang, T. T. Macromolecules 1975, 8, 909.
46. Imken, R. L.; Paul, D. R.; Barlow, J. W. Polym Sci Eng 1976, 16, 593.