Original Article

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

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Received 30 October 2013; accepted 16 November 2013

Abstract
Compatibility of Sodium carboxy methyl cellulose/ Poly (vinyl pyrrolidone) blends in solution was studied by viscosity, ultrasonic velocity and refractive index methods. Solution viscosity showed a linear variation with the blend composition upto 40% NaCMC, and non-linear beyond 40% NaCMC composition. From the viscosity data by using Chee and Sun et al., approaches, the interaction parameters μ, Δρ and α were also calculated to predict the compatibility of the blend solution. The results of these blends data suggested that NaCMC/PVP blend was immiscible when the NaCMC content was more than 40% in the blend. The results pertaining to variation of ultrasonic velocity (u) also supports the miscibility nature of these blends. This is further confirmed by refractive index results also. FT-IR, Differential Scanning Calorimetry (DSC), X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were also used to confirm the compatibility of NaCMC/PVP blends in the solid state (thin film). Experimental results showed that the blends of NaCMC and PVP are semicompatible.

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Keywords: Sodium carboxy methyl cellulose, Poly (vinyl pyrrolidone), compatibility, FTIR, DSC, X- RD, SEM.

1. INTRODUCTION

In search of new polymeric materials, either new monomers are polymerized or co-polymerization technique is used to tailor make a new product. An alternative method has been used to blend existing polymers to produce materials with desired properties. An obvious advantage of this approach is that usually requires little or no extra capital expenditure relative to new polymers. The miscibility between the constituents of polymer mixture is an important factor in the development of new materials based on polymeric blends[1]. During the past few years, researchers have paid considerable attention to the study of polymer blending [2-6].

Sodium Carboxymethyl cellulose (NaCMC) is an important industrial polymer with a wide range of applications in flocculation, drag reduction, detergents, textiles, paper, foods, drugs, and oil well drilling operation. NaCMC is a derivative of cellulose and formed by its reaction with sodium hydroxide and chloroacetic acid. It has a number of sodium carboxymethyl groups (CH₂COONa), introduced into the cellulose molecule, which promote water solubility. The various properties of NaCMC depend upon three factors: molecular weight of the polymer, average number of carboxyl content per anhydroglucose unit, and the distribution of carboxyl substituents along the polymer chains[7-9]. The most important properties of NaCMC are viscosity building and flocculation. Among all the polysaccharides, NaCMC is easily available, very cheap and has high shear stability. These properties made it responsible for its blend compatible studies[7-9].

Poly (Vinyl Pyrrolidone) (PVP) is a water-soluble polymer. PVP has beneficial effects on protection, viscosity, absorbency, solubilization and condensation, with its most significant feature being excellent solubility and biological compatibility. Additionally, PVP has low toxicity and is utilized in a broad range of areas, such as medical, food, cosmetics and health-related domains. However, issues concerned with the rigid but fragile nature of PVP and its lack of sturdiness have resulted in processing difficulties[10].

In continuation of our research work on polymer blend compatibility[11-13] and as the literature reveals that there were no reports on the compatibility of NaCMC/PVP blends, the authors thought of investigating their blend compatibility using a battery of techniques in solution (such as Viscosity, Ultrasonic velocity and Refractive Index) and in solid (FTIR, X-RD, SEM & DSC). Further the blends of natural/synthetic polymers useful for preparing polymers
2. MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1 Materials

Sodium carboxy methylcellulose (M_W = 90,000) was purchased from E. Merck (India) Limited, Mumbai, India. Poly (vinyl pyrrolidone) (M_W = 40,000) was purchased from s.d. fine chemicals, Mumbai, (India) and were used without further purification. Double distilled and deionized water having almost zero conductivity was used as a solvent.

2.2 Preparation of blend solutions

The 1% weight of NaCMC and 1% weight of PVP solutions were prepared by dissolving 1g of each polymer in 100 ml of distilled water in two separate stoppered conical flasks. Seven different blend solutions of NaCMC and PVP were prepared by mixing NaCMC 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.

2.3 Preparation of blend films

Blend films of NaCMC with PVP were prepared by solution casting method. Required amount of NaCMC was dissolved in distilled water by stirring over a magnetic stirrer (Jenway, model 1103, UK) for 24 h. To this 20, 40, 50, 60 and 80 (weight% with respect to NaCMC) of PVP were added. Solutions were mixed uniformly and filtered to remove any foreign floating or suspended particles. The respective solution was poured on to 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.

2.4 Techniques

Viscosity and density measurements were made at 30°C using Ubbelohde suspended level viscometer (with the flow time of 95 sec 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, viz, 0/100, 20/80, 40/60, 50/50, 60/40, 80/20 and 100/0 by weight were measured at 30°C using 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 2MHz 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%.

2.4.1 Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectra of NaCMC, PVP and their blend films were taken using Bomen MB-3000 FTIR spectrometer. Blend films were characterized at room temperature from 4000 to 400 cm⁻¹ under a N₂ atmosphere at a scan rate of 21 cm⁻¹.

2.4.2 Differential scanning calorimetry

DSC curves of NaCMC, PVP and their blend films of different compositions were recorded using TA instruments differential scanning calorimeter (Model:SDT Q600, USA). The analysis of samples was performed at heating rate of 20°C/min under N₂ atmosphere at a purge speed of 100ml/min.

2.4.3 X-ray diffraction

The X-ray diffraction (XRD) patterns of the blend samples were obtained with an intel diffractometer (Paris, France) with monochromatized Cu Kα radiation (scan speed of 1°/min in a 20 range of 5°-40°) at room temperature.

2.4.4 Scanning electron microscopic analysis

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

![Figure 1: Plots of absolute viscosity Vs concentration for 1% (w/v) NaCMC/PVP blends of 20/80(a), 40/60(b), 50/50(c), 60/40(d) and 80/20(e).](image-url)
composition plots are linear for compatible blends and non-linear for incompatible blends. On this basis in the present study, it is noticed that the absolute viscosity varies linearly with the concentration of blend composition upto 40/60 NaCMC/PVP blends and varies non-linearly beyond this composition. This indicates that the polymer blends of NaCMC/PVP are found to be miscible when NaCMC content is less than 40% and immiscible beyond this composition.

The Huggins plots of reduced viscosity against concentration of different NaCMC/PVP blend compositions, NaCMC and PVP in water at 30°C are shown in the Figs. 2(a) to 2(g). From these graphs (Fig. 2(a) to 2(g), it is also noticed that a linear variation for the blends upto 40/60 NaCMC/PVP. But the curves composed of two regions with varying slopes for the blends beyond 40/60 NaCMC/PVP blends. The change in the slope of the curve may be attributed to the mutual attractions of macromolecules in solution which favors the polymer miscibility. But later above 40/60 NaCMC/PVP blends the reduced viscosity Vs concentration of blends shows non-linear variation which is an indication of mutual repulsion of macromolecules in solution which inturn favors the polymer immiscibility. A similar observation was also made by Naveen Kumar et al. [13] in case of Acacia/poly(vinyl alcohol) blend compatibility by viscosity method.

\[ b = w_1^2 b_{11} + w_2^2 b_{22} + 2 w_1 w_2 b_{12} \]  \hspace{1cm} (3)

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

\[ \mu = \frac{\Delta B}{(\eta_2 - \eta_1)^2} \]  \hspace{1cm} (4)

where \( \eta_1 \) and \( \eta_2 \) are the intrinsic viscosities for the pure component solutions. Recently, Sun have suggested a new formula for the determination of polymer miscibility as follows:

\[ \alpha = K_m - \frac{K_1 \eta_1^2 w_1 + K_2 \eta_2^2 w_2 + 2 \eta_1 \eta_2 K_1 \eta_2 w_1 w_2}{\eta_1 w_1 + \eta_2 w_2} \]  \hspace{1cm} (5)

Where \( K_1, K_2 \) and \( K_m \) are the Huggin’s constants for individual components 1, 2 and the blend, respectively. It is observed from the Table 1 that the values of \( \Delta B, \mu \) and \( \alpha \) are positive upto 40/60 NaCMC/ PVP blend compositions and negative beyond this composition. In general [3,4] if \( \Delta B, \mu \) and \( \alpha \) 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 one. Based on this, it is concluded from the present study, as per the values given in the Table 2 that NaCMC/PVP blend shows miscibility nature when the NaCMC content is less than 40% and immiscible more than 40% of NaCMC. To confirm this further, we have measured the ultrasonic velocity (u) and refractive index (n) of the blend under consideration at various compositions at 30°C. The variation of the ultrasonic velocity (in Fig. 3) and refractive index (fig. 4) with the concentration of different blend compositions are shown respectively.

**Figure 2:** Reduced viscosity Vs Concentration curves for Pure PVP(a), NaCMC/PVP blends 20/80(b), 40/60(c), 50/50(d), 60/40(e) 80/20(f) and Pure NaCMC(g).

**3.2 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:

\[ \Delta B = \frac{b - \bar{b}}{2w_1 w_2} \]  \hspace{1cm} (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 \( K_n \) as

\[ b = K_n \eta^2 \]  \hspace{1cm} (2)

for ternary systems, the coefficient \( b \) is also given by

\[ b = \frac{w_1^2 b_{11} + w_2^2 b_{22} + 2 w_1 w_2 b_{12}}{w_1 + w_2} \]  \hspace{1cm} (3)

These graphs show both the linear and non-linear regions. It was already established [16-18] 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 NaCMC content is less than 40% is in confirmation with \( \Delta B, \mu \) and \( \alpha \) values. So, the present study indicates the existence of miscibility windows when the NaCMC content is less than 40% due to the H-bonding interactions taking place between the carbonyl groups of PVP and the hydroxyl groups of NaCMC as shown in the scheme1.
A similar observation was observed by S. K. Rai et al. [19] from their miscibility studies of HPMC/Pullulan blends in water. Polymer-polymer miscibility is generally known to be enhanced by specific interactions between the polymer pairs. In the present study, the reason why miscibility shows a tendency to increase with the increasing weight fraction of PVP is specific interactions like dipole-dipole interaction or H-bonding should be responsible for the miscibility observed between NaCMC and PVP in solution. It can be proposed that favorable interactions occur between hydroxyl groups of NaCMC and carbonyl groups of PVP. Considering the structure of NaCMC, it is strongly expected that intra and intermolecular H-bonding will form between the polymer segments. Under the conditions where miscibility is exhibited between NaCMC and PVP, the interactions between the two polymers should be enough to overcome the intra and inter molecular H-bonding among NaCMC chains themselves. This is the possible reason for the blends up to 40/60 NaCMC/PVP blends which shows the miscibility as the weight fraction of PVP in the blend composition decreases i.e., above the 40/60 NaCMC/PVP blends the probability for a NaCMC chain to establish H-bonding interaction with a chain of its own kind (intra molecular interactions) increases, since PVP chains become less available in the medium for bonding. Consequently immiscibility between the two polymers is observed at the low weight fractions of PVP i.e., above the 40/60 NaCMC/PVP blends. Under these conditions, the NaCMC/PVP blends show miscibility up to 40/60 NaCMC/PVP blends whereas these blends show immiscibility beyond this composition.

3.3 Miscibility Studies of Blend Films by Characteristic Techniques

3.3.1 Fourier Transform Infrared Spectroscopy Studies

FTIR spectroscopy has been widely used by many researchers to study the formation of blends [20-22]. FTIR spectrum provides information regarding intermolecular interaction via analysis of FTIR spectra corresponding to stretching or bending vibrations of particular bands, and the positions at which these peaks appear depends directly on the force constant or bond strength. Hydrogen bonding or other secondary interactions between chemical groups on the dissimilar polymers should theoretically cause a shift in peak position of the participating groups. This kind of behavior is exhibited by miscible blends that show extensive phase mixing. Hydrogen bonding interactions usually move the stretching frequencies of participating groups, e.g., O-H towards lower numbers usually with increased intensity and peak broadening. The shift in peak position will depend on the strength of the interaction. The formation of strong hydrogen bonds between NaCMC and PVP was demonstrated by FTIR spectroscopy from the shifts of absorption bands showing hydroxyl stretching vibrations, which were sensitive to the hydrogen bonds formed during blending. The broad transmission bands at 3600-3100cm⁻¹ produced by stretching of the hydroxyl groups in the spectrum of NaCMC can be remarkably distinguished. It can be seen from the spectrums that the peak intensity and peak shape were clearly different and these differences were induced by the different blend ratios. The broad band in the pure NaCMC spectrum at 3500-3200 cm⁻¹, with a maximum at 3460 cm⁻¹, was assigned to stretching vibrations of the –OH groups in the range of 3500-3200cm⁻¹. The difference among the curves in Figure 5, a little broadening or shifting or peaks at 3500-3200cm⁻¹ was observed in the 20/80 and 40/60 (NaCMC/PVP) blend compositions when they were compared with that of pure NaCMC, which suggested that a relative low amount of

FTIR spectra NaCMC (a), NaCMC/PVP (80/20) (b), NaCMC/PVP (60/40) (c), NaCMC/PVP (50/50)(d), NaCMC/PVP (40/60)(e), NaCMC/PVP (20/80)(f), PVP (g).
interaction was presented between the polymers indicating the miscibility nature of this pair of polymers up to 40/60 (NaCMC/PVP). But in the case of 50/50, 60/40, 80/20 NaCMC/PVP blends there was no shifting in the peak, which indicates that no interactions in between NaCMC and PVP. This further confirms that immiscibility nature of these blends beyond 40/60 NaCMC/PVP blends.

3.3.2 Differential Scanning Calorimetry Studies
DSC was carried out to determine the compatibility of the polymer blend system under study. Special care must be taken during DSC measurements since NaCMC and PVP are apt to absorb moisture which strongly effects the DSC measurements. DSC thermograms of NaCMC, PVP and their blend films are displayed in Figure 6. DSC thermograms show two sharp exothermic peaks at 360°C and 470°C for the pure NaCMC, at 340°C and 440°C for the pure PVP. Similar two sharp peaks are obtained in the range of 355°C-420°C for the blend films of 20/80 and 40/60 blends of NaCMC/PVP. This indicates that some interactions are taking place in between NaCMC and PVP indicating the miscibility nature of this pair of polymer up to 40/60 (NaCMC/PVP). But in case of NaCMC/PVP polymer blends beyond 40/60 (NaCMC/PVP) i.e. for 50/50, 60/40 and 80/20 (NaCMC/PVP) blend films show only one broad exothermic peak, so that in these compositions there is no interaction taking place in between NaCMC and PVP. Hence we can conclude that 20/80, 40/60 blend films are compatible and 50/50, 60/40, 80/20 NaCMC/PVP blend films are incompatible.

3.3.3 X-Ray Diffraction Studies
The typical X-RD patterns of PVP, NaCMC and their blend compositions (20/80, 50/50 and 80/20 (NaCMC/PVP)) are shown in Figure 7. For the pure NaCMC, there were two peaks around 2θ=21.5° and 44.6°. The diffractograms of PVP showed 2θ=11.7°, 21.8° and 44.6°, which indicates that there are no or weak interactions present between NaCMC/PVP molecules in these blend films. Because here each component shows its own crystal region and X-RD patterns are expressed as simple mixed patterns. It indicates that there is no interaction between NaCMC and PVP molecules in the 50/50 and 80/20 (NaCMC/PVP) blends. This confirms the immiscibility nature of these blends when NaCMC content is more than 40 % in the blend. From these evidences we can further conclude that 20/80 NaCMC/PVP blend is miscible and 50/50, 80/20 blend compositions are immiscible. The X-RD results also support the conclusions drawn from the other techniques carried out for this system.

3.3.4 Scanning Electron Microscopy Studies
Figure 8 shows the SEM images of NaCMC (a), PVP (b) and their blend membranes NaCMC/PVP (80/20) (c), NaCMC/PVP (60/40) (d), NaCMC/PVP (50/50)(e), NaCMC/PVP (40/60) (f). The surface morphology of NaCMC and PVP films were homogeneous. The bright strips presented in the image of pure PVP (b). With the addition of PVP to NaCMC the morphologies of the blended films changed dramatically. Phase separation is observed in the 50/50 and 80/20 (NaCMC/PVP) blend films, but no phase separation is visible in the case of 20/80 (NaCMC/PVP) blend. Hence we can conclude that the blend of 20/80 (NaCMC/PVP) is compatible, whereas blends 50/50 and 80/20 (NaCMC/PVP) are immiscible in nature. These results also supporting the earlier conclusions stating that (NaCMC/PVP) is a semi compatible blend.
Figure 8: SEM images of NaCMC (a), PEG (b), (20/80) NaCMC /PEG (c), (50/50) NaCMC /PEG (d), (80/20) NaCMC /PEG (e).

4.0 CONCLUSIONS

The miscibility behavior of sodium carboxy methyl cellulose (NaCMC)/Poly (vinyl pyrrolidone) (PVP) blends in water has been studied by viscometric, ultrasonic velocity and refractive index techniques at 30°C. Using viscometric data the interaction parameters $\Delta B$, $\mu$ suggested by Chee and $\alpha$ suggested by Sun are calculated. All these parameters are positive in the blends when the NaCMC content is 40% and negative in the blends when the NaCMC content is greater than 40%. It indicates that these blends are immiscible when NaCMC content is more than 40% in the blend whereas the blend are miscible when NaCMC content is less than 40% in the blends. The miscibility may be due to hydrogen bond formation between hydroxyl groups of NaCMC and carbonyl groups of PVP. This is further confirmed by ultrasonic and refractive index results.

NaCMC/PVP blend films prepared by solution casting using water as solvent are also characterized by FTIR, DSC, X-RD and SEM to support the miscibility data obtained from above simple methods. Analytical technique results support the miscibility window obtained by simple solution techniques.

5.0 ACKNOWLEDGEMENTS

Two of the authors (P. Kumara Babu & K. Chowdoji Rao) are thankful to UGC, New Delhi for sanction financial support (UGC letter No. F.No. 39-684/2010(SR), Dt: 12th Jan 2011) to covering the research work.

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Source of support: University Grants Commission, India (UGC letter No. F.No. 39-684/2010(SR), Dt: 12th Jan 2011); Conflict of interest: None declared