



Miscibility Studies of ZnO Nanoparticles Incorporated CMC/PVA Nanocomposite Films

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ABSTRACT

In this work, the miscibility studies of carboxymethylcellulose/poly (vinyl alcohol) CMC/PVA blends were studied by viscosity, refractive index, density, and ultrasonic interferometer techniques. The values of molecular interaction parameters such as ΔB , μ , and α were revealed that CMC/PVA blend is miscible when the PVA content is higher than 50%. The films of CMC/PVA blends were characterized by Fourier-transform infrared techniques. ZnO nanoparticles were prepared by precipitation method and incorporated to CMC/PVA blends films. The micro structural properties of the ZnO nanoparticles incorporated to CMC/PVA blend films were characterized using X-ray diffraction techniques. Immiscible CMC/PVA polyblends were found to be miscible at all compositions of CMC/PVA blends when ZnO nanoparticles incorporated to polymer composite films.

Key words: Blends, miscibility, interactions, ultrasonic velocity, refractive index, nanoparticles.

1. INTRODUCTION

In the development of polymer blends, the miscibility between the polymers is a very important factor.[1,2] Polymer-polymer miscibility by ultrasonic velocity and density measurement methods were investigated by Paladhi and Singh.[3,4] Ultrasonic methods have the added advantages of being less costly with more efficiency comparable to other methods. The use of ultrasonic velocity is a tool in interdisciplinary sciences in increasing the effect of ultrasound in polymerization reactions, organic synthesis, electropolymerization, electroplating, and electrosynthesis has been exploited to good effect.

2. EXPERIMENT

Poly(vinyl alcohol) (PVA) (MW = 1, 25,000, AR grade, Merck India Ltd.; India) and carboxymethylcellulose (CMC) sodium salt purchased from Loba Chem., Mumbai, India, were used for this work. The blends of CMC/PVA of different compositions 0/100, 10/90, 30/70, 50/50, 70/30, 90/10, and 100/0 were prepared by mixing the aqueous solutions of the homo polymers. A dilute polymer solution of 0.015% w/v was prepared for viscosity, density, and refractive index methods. Viscosity and density measurements at room temperature were made using Ubbelohde suspended level viscometer and specific gravity bottle, respectively. The required temperature was

maintained within $\pm 0.05^\circ\text{C}$. The refractive indices of blends solutions with different compositions 10/90, 30/70, 50/50, 70/30, and 90/10 were measured directly with an Abbe's refractometer. The accuracy of the refractive index measurements is $\pm 0.02\%$.

2.1. Preparation of Na Salt of CMC Solution

Weighed 1.5 g of Na salt of CMC in 100 ml of deionized water. It was stirred continuously for about 24 h. This highly viscous solution of 1 ml was diluted to 100 ml volumetric flask. The obtained solution was 0.015%, used for miscibility studies.

2.2. Preparation of PVA Solution

Weighed 1.5 g of PVA and poured in 100 ml of boiled distilled water. It was stirred well continuously using a magnetic stirrer until a homogeneous solution was obtained. The solution was diluted as in the Na salt of CMC the identical volume and concentration for calculation purpose.

2.3. Preparation CMC/PVA Blend Films

A homogeneous solution of Na salt of CMC and PVA of higher concentration than experimental and different compositions (0/100, 10/90, 30/70, 50/50, 70/30, 90/10, and 100/0) was prepared by continuous stirring. The solutions were then transferred into a ceramic plate at ambient temperature for the complete

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evaporation of water. After 24 h (complete evaporation of water), the films were peeled off from the ceramic plate. Finally, the blend films of appropriate thickness were obtained.

2.4. Synthesis of ZnO Nanoparticle by Precipitation Method

The aqueous solution of zinc nitrate and potassium hydroxide solution were prepared with de-ionized water. The KOH solution was slowly added into zinc nitrate solution at room temperature under vigorous stirring. This results the formation of the white suspension. The white product was centrifuged at 5000 rpm for 20 min and washed with absolute alcohol, at last, it was washed with acetone and dried.

2.4. CMC/PVA ZnO Nanocomposite Films

CMC/PVA ZnO nanocomposite films were prepared by the solution casting technique. A homogeneous solution of 2% (w/v) CMC/PVA solution of different composition (30/70, and 50/50) was prepared with continuous stirring. A series of ZnO aqueous suspensions (0.5, 1.5, and 2%) were prepared using ultra sonication for 1 h. To fabricate the nanocomposite films, the solutions were then transferred into a ceramic plate at ambient temperature for the complete evaporation of water. After 24 h (complete evaporation of water), the films were peeled off from the ceramic plate. Finally, the nanocomposite films of appropriate thickness were obtained.

3. RESULT AND DISCUSSIONS

The Huggins plots for the pure components and their blends at room temperature are shown in Figure 1. Figure 1 indicates that the considerable higher slope variation. Hence, CMC/PVA blend is found to be miscible, when the PVA concentration is above the 50%. The miscibility of the polymer blends is predicted by the Chee's[5] and Sun *et al.*[6] interactions parameters, ΔB and μ using the formulae as follows in Table 1.

$$\Delta B = b - b^* \div 2w_1w_2 \tag{1}$$

Where, $b^* = w_1b_{11} + w_2b_{22}$, where, b_{11} and b_{22} are the slopes of the viscosity curves for the pure components before mixing,

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

Where, b_{12} is the slopes of the viscosity curves for the blend solutions.

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

Where, $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities for the pure component solutions. The polymer blend is miscible if $\mu \geq 0$ and immiscible when $\mu < 0$. Recently,

Sun *et al.* suggested a most satisfactory new equation for the determination of polymer miscibility as,

$$\alpha = K_m \frac{K_1[\eta]_1^2 w_1^2 + K_2[\eta]_2^2 + 2\sqrt{K_1K_2}[\eta]_1[\eta]_2 w_1w_2}{\{[\eta]_1 w_1 + [\eta]_2 w_2\}^2} \tag{3}$$

Where, K_1 , K_2 , and K_m are the Huggins constants for individual components 1, 2, and blends, respectively. The long-range hydrodynamic interactions are considered while deriving the equation. The polymer blend is miscible, if $\alpha \geq 0$ and immiscible when $\alpha < 0$. As the secondary interactions are considered in the equation for a equation (3) is more accurate than equation (2). Hence, it can be stated that the blend of CMC/PVA is miscible when PVA content is higher than 50%. The graph shows linear regions. It was already established that the variation is linear for miscible and nonlinear for immiscible blends. In this case, the variation is found to be linear, when the PVA content is higher than 50%. This observation is in the conformity with the μ and α value. Hence, the present study indicates the miscibility windows when PVA is higher than 50%. It may be due to specific interaction like hydrogen bonding to some extend between CMC and PVA (Figure 2).

Using viscosity, refractive index, density, and ultrasonic velocity method, it is concluded that the polymer blend

Table 1: Chee and Sun's interaction parameters of different composition of CMC/PVA blends at room temperature.

CMC/ PVA blend composition	Chee's differential interaction parameters		Sun's miscibility parameter
	ΔB	μ	α
10/90	-122.59	-1.961 × 10 ⁻³	3.8400 × 10 ⁻⁴
30/70	-53.2071	-8.513 × 10 ⁻⁴	1.134 × 10 ⁻⁴
50/50	-43.17	-6.9072 × 10 ⁻⁴	-6.933 × 10 ⁻³
70/30	-50.840	-8.1377 × 10 ⁻⁴	-6.737 × 10 ⁻⁵
90/10	-119.583	-1.913 × 10 ⁻³	-2.7752 × 10 ⁻⁶

CMC/PVA=Carboxymethylcellulose/poly (vinyl alcohol)

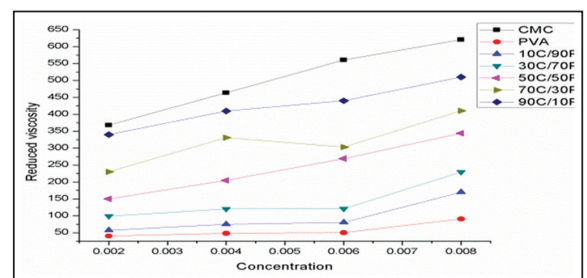


Figure 1: Huggins plots for carboxymethylcellulose/poly (vinyl alcohol) polymer blends in room temperature.

of CMC/PVA blend is found to be miscible when the PVA content is higher than 50%. Below this critical concentration, the blends were found to be immiscible. Thus, the above-mentioned techniques are simple, low cost, rapid, and efficient methods in exploring the miscibility windows of CMC/PVA blend (Figure 3).

The Fourier-transform infrared (FTIR) spectra of Na salt of CMC (Figure 1) shows absorption peak at $1606-1632\text{ cm}^{-1}$ for C-O group. According to Pecsok shield and McWilliams (1976) carboxyl group and its salt show, two peaks at wave number about $1595-1620\text{ cm}^{-1}$ and $1395-1430\text{ cm}^{-1}$, which indicate the presence of carboxymethyl substituent the bonds around 1425 and 1317 cm^{-1} is assigned to CH_2

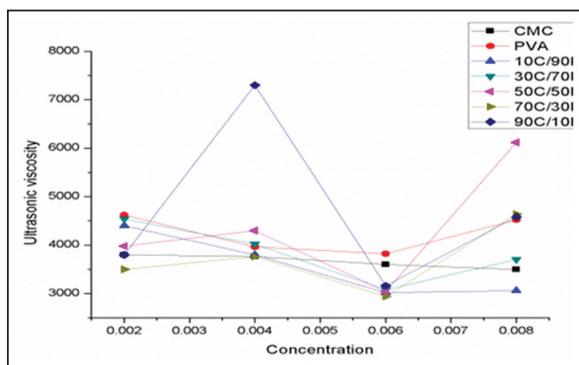


Figure 2: Ultrasonic velocity plot for carboxymethylcellulose/poly (vinyl alcohol) polymer blends in room temperature.

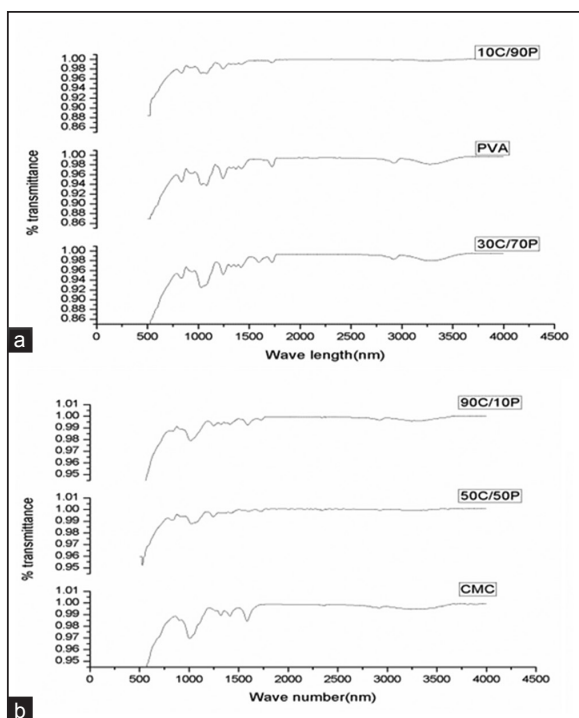


Figure 3: (a and b) Fourier-transform infrared spectra of pure carboxymethylcellulose/poly (vinyl alcohol) and their blend films.

scissoring and OH bending vibration, respectively. The FTIR spectra of PVA (Figure 3a) show characteristic absorption peak at 3274 cm^{-1} is for hydroxyl groups. The peak at 2937 cm^{-1} represents for C-H alkyl stretching bond and peak at 1422 cm^{-1} is for CH_2 group. The sharp absorption peak at $1081-1027\text{ cm}^{-1}$ is used for indication of PVA (Figure 4).

In the FTIR spectra of CMC/PVA [50:50], nanocomposite film the peaks are shifted from higher to lower wave length. Comparing the IR spectra of pure immiscible blend [50:50] as well as the CMC/PVA/ZnO nanocomposite containing a different concentration of ZnO-NPs (0.5% and 1.5%), the peaks of nanocomposites films are shifted to a higher range, $3288-3333\text{ cm}^{-1}$, respectively (Figures 5 and 6).

In the FTIR spectra of fabricated CMC/PVA/ZnO nanocomposite film (0.5 and 1.5%), the peaks were shifted to lower wave number [3303 and 3308 cm^{-1} , respectively] as compared to without ZnO miscible CMC/PVA blend ($30\text{C}/70\text{P}$) [3322 cm^{-1}] with the addition of nanoparticle. After the addition of ZnO nanoparticles, the immiscible polymer blend [50C/50P] is found to be miscible due to H-bonding.

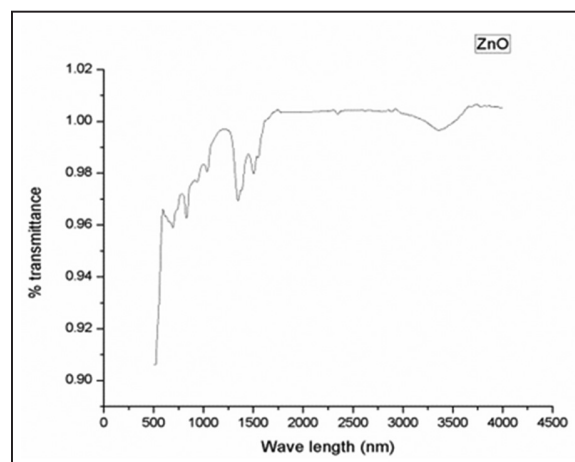


Figure 4: Fourier-transform infrared spectra of ZnO nanoparticles.

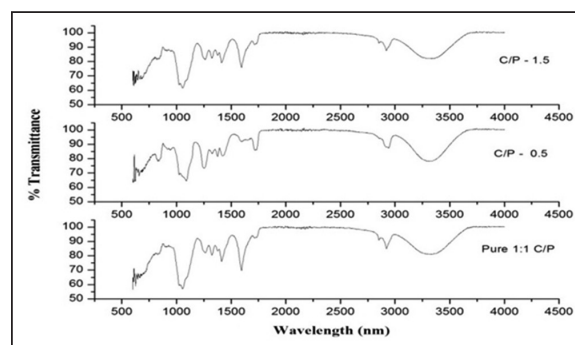


Figure 5: Fourier-transform infrared spectra of carboxymethylcellulose/poly (vinyl alcohol) [50:50] nanocomposite films.

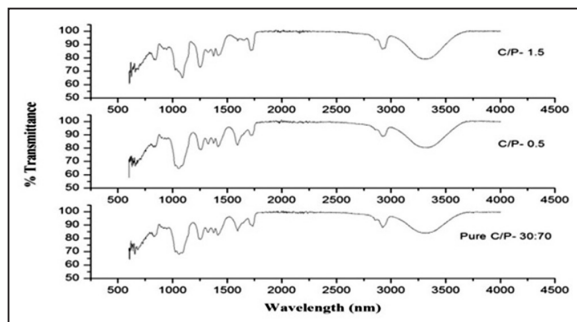


Figure 6: Fourier-transform infrared spectra of carboxymethylcellulose/poly (vinyl alcohol) [30:70] nanocomposite films.

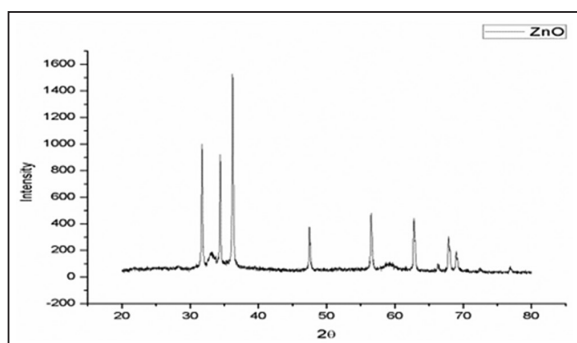


Figure 7: X-ray diffraction peak of ZnO nanoparticles.

The pattern for ZnO nanoparticles (Figure 7) indicated most characteristics peaks that corresponding to $2\theta = 34.2, 48.1, 57.8,$ and 68.6° . The result obtained from X-ray diffraction (XRD) pattern revealed that the fabrication of ZnO nanoparticles very close to the packed hexagonal wurtzite structure and the most of the diffraction peaks agree with the stated JEPDS data (Figure 8).[7]

In the XRD of CMC/PVA [50:50], there is no significant peak except peak at $2\theta=20.3^\circ$ that related to the crystalline cellulosic structure. This peak value is consistent or good agreement with literature value.[1]

4. CONCLUSION

The miscibility of CMC/PVA polymer blends was revealed that the blend is found to be miscible at above 50% PVA. The ZnO nanoparticle was prepared by precipitation technique. The prepared ZnO nanoparticles were incorporated to CMC/PVA polymer blends and characterized by FTIR technique, and ZnO nanoparticles were characterized by FTIR and XRD analysis. FTIR analysis reveals that ZnO nanoparticles incorporated CMC/PVA blend composite films were found to be miscible due to hydrogen bonding, the secondary interactions. ZnO nanoparticles are act as plasticizers.

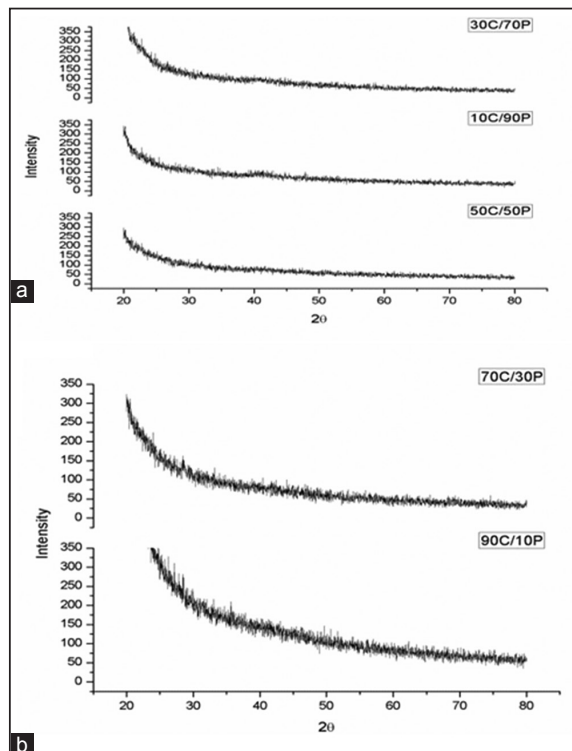


Figure 8: (a and b) XRD peaks of ZnO nanoparticles incorporated carboxymethylcellulose/poly (vinyl alcohol) blend films.

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***Bibliographical Sketch**



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