Studies on the Compatibility of Pullulan – Carboxymethyl Cellulose Blend Using Simple Techniques

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ABSTRACT: Miscibility studies of Pullulan – Carboxymethyl cellulose in common solvent water were carried out at 100/0, 80/20, 60/40, 50/50, 40/60, 20/80 and 0/100 (v/v%) blend compositions. Using Ubbelohde viscometer, Ultrasonic Interferometer and Specific gravity bottle, viscosity, ultrasonic velocity and density were measured at 30 and 40°C respectively. Chee’s and Sun’s interaction parameters (µ and α) were calculated by using the viscosity data. These values revealed that, the blend was semi-compatible. The obtained results were confirmed by ultrasonic velocity and density studies. Further, blend films were prepared by using 1% blend solutions. Solid state compatibility of the blend was then confirmed by Scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) techniques. The SEM and FTIR results revealed that blend was miscible only when Pullulan content is 60% and above. Change in temperature had no effect on the miscibility of Pullulan– Carboxymethyl cellulose blend.

Key words: blends, Pullulan, Carboxymethyl cellulose, viscosity, ultrasonic, SEM., FTIR.

1.0 INTRODUCTION

Polymers are playing an important role in all branches of industry today. Many notable advances in technology have followed exploitation of the properties offered by new polymeric materials like blends, composites, etc. Polymer blends are prepared by physical mixing of two or more polymers. The resulting blends system often exhibits properties that are superior to any one of the component polymers [1-5]. However, the manifestation of superior properties depends upon the miscibility of homo-polymers at the molecular scale. The miscibility results in different morphology of the blends ranging from single phase system to two phase or multiphase systems [2]. The basis of polymer-polymer miscibility may arise from any specific interaction, such as hydrogen bonding, dipole-dipole forces, and charge transfer complexes for homo-polymer mixtures [1].

There have been various techniques of studying the polymer-polymer miscibility. Chee [4] and Sun et al. [5] have suggested the viscometric method for the study of polymer – polymer miscibility. Singh et al. [6,7] have suggested the ultrasonic velocity and viscosity measurements for investigating the polymer miscibility. Paladhi et al.[6], Singh et al. [7] and Varada Rajulu et al. [8] have shown that the variation of ultrasonic velocity and viscosity with blend compositions were linear for miscible blends and non-linear for immiscible blends. Changhua Liu et al. [9] and Manisara Peesan et al. [10] have suggested the SEM and FTIR techniques to determine the miscibility of polymers.

In the present work the authors have carried out the miscibility studies of Pullulan-CMC blend in water by using viscosity, ultrasonic velocity and density techniques at 30 and 40 °C. Solid state compatibility of the blend was studied by scanning electron microscopy and FTIR techniques. The miscibility studies of Pullulan-CMC blend might be important to enhance some of their properties.
Pullulan is a natural water-soluble polysaccharide, produced from starch by fermentation. Pullulan consist of three glucose units linked through α-1, 4- glycosidic bond as in maltotriose units which are linked by α-1, 6-glycosidic bonds. Pullulan is a non-hygrosopic polymer used in food industry and in pharmaceuticals. It has several useful properties, including very low toxicity, forming good films, adhesive properties and soluble in a broad range of solvents [3]. In addition, Carboxymethyl cellulose is a derivative of cellulose formed by its reaction with alkali and chloroacetic acid. Carboxymethyl cellulose (CMC) is important industrial polymer with a wide range of applications in detergents, textiles, paper, food, drugs and oil well drilling operations. Most properties of CMC in specific applications depends on a three key parameters, namely the molecular weight of the polymer, the average number of carboxymethyl substituents per anhydroglucose unit (degree of substitution, DS) and the distribution of the carboxymethyl substituents along the polymer chain [16,17].

2.0 MATERIALS AND METHODS

Carboxymethyl cellulose and Pullulan (Nutriscience Innovations LLC, USA) have been employed in the present study. A dilute polymer solution of 0.1% w/v was prepared for viscometric studies. Stock solutions of homo-polymers and the different blend compositions of Pullulan – Carboxymethyl cellulose (100/0, 80/20, 60/40, 50/50, 40/60, 20/80 and 0/100) were prepared in water. Viscosity measurements were made at 30 and 40 °C using an Ubbelohde suspended level viscometer (USLV). Different temperatures were maintained in a thermostat bath with a thermal stability of ± 0.05 °C. Ultrasonic velocity of the blend solution for different compositions of 0.5% w/v was performed by an ultrasonic interferometer technique at 30 and 40 °C [8]. During the experiment, temperature was maintained by circulating water from a thermostat, with a thermal stability of ± 0.05 °C. The experimental frequency was 2MHz. Density of the blend solution for different compositions of 0.5% w/v was measured at 30 and 40 °C using specific gravity bottle [11]. For FTIR and SEM studies, the thin films of Pullulan, Carboxymethyl cellulose and their different blend compositions were prepared by solution casting method. Films were dried by using IR lamp. FTIR spectra were measured using NICOLET AVATAR 530 spectrophotometer. Scanning electron microscopic analysis were recorded using a JOEL (JSM 6380LA) analyzer.

3.0 RESULTS AND DISCUSSION

3.1 Viscometric studies

From viscometric measurements, reduced viscosities of homo-polymers and their blend compositions (100/0, 80/20, 60/40, 50/50, 40/60, 20/80 and 0/100) were measured at 30 and 40 °C. Reduced viscosities of the pure polymers and their blend compositions were plotted against concentrations at 30 and 40 °C are shown in Figures 1 and 2 respectively. Huggin’s plot of 80/20 and 60/40 Pullulan-CMC blend compositions gave higher slope values, indicating strong interactions at those compositions (Tables 1 & 2). On the other hand, at a composition less than 60 % pullulan in the Pullulan-CMC blend, the slope decreases indicating phase separation [11,14].
Pullulan-CMC blends were found to be miscible only when Pullulan content is 60% and above, below this critical concentration, smaller slope value was observed in the Huggin’s plot, due to the phase separation.
In order to quantify the miscibility of polymer blends, Chee [4] suggested the general expression for interaction parameter when the polymers are mixed in weight fractions \( w_1 \) and \( w_2 \) as

\[
\Delta B = \frac{b - \bar{b}}{2w_1w_2}
\]  

(1)

where \( \bar{b} = w_1b_{11} + w_2b_{22} \) where \( b_{11} \) and \( b_{22} \) are the slopes of the viscosity curves for the components and \( b \) is related to Huggin’s coefficient \( K_H \) as,

\[
b = K_H \eta^2
\]  

(2)

where \( \eta \) is the intrinsic viscosities of blend solution.

For ternary system, it is also given by

\[
b = w_1^2b_{11} + w_2^2b_{22} + 2w_1w_2b_{12}
\]  

(3)

where \( b_{12} \) is the slope for blend solution.

However, Chee’s theory fails to account for the experimental data when intrinsic viscosities of pure components are far apart. In such cases he defined a more efficient parameter (\( \mu \)) to predict compatibility,

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

(4)

where \( \mu \) is Chee’s interaction parameter, \( [\eta]_1 \) and \( [\eta]_2 \) are intrinsic viscosities of pure component solutions. The polymer blend is miscible if \( \mu \geq 0 \) and immiscible when \( \mu < 0 \).

Later Sun et al. [5] have suggested a most satisfactory new equation for the determination of polymer miscibility as

\[
\alpha = K_m - \frac{K_1[\eta]_1^2w_1^2 + K_2[\eta]_2^2w_2^2 + 2\sqrt{K_1K_2}[\eta]_1[\eta]_2w_1w_2}{([\eta]_1w_1 + [\eta]_2w_2)^2}
\]  

(5)

where \( \alpha \) is Sun’s interaction parameter; \( K_1, K_2 \) and \( K_m \) are the Huggins constants for individual components 1, 2 and blend respectively. The long-range hydrodynamic interactions are considered while deriving the equation. The polymer blend is miscible if \( \alpha \geq 0 \) and immiscible when \( \alpha < 0 \).

The computed values of \( \mu \) and \( \alpha \) were found to be positive when Pullulan content is more than 50 % in the blend composition, and beyond this percentage \( \mu \) and \( \alpha \) were negative, this values at 30 and 40 °C are presented in the Tables 1 and 2 respectively. As the long ranges of interactions are considered in the equation for \( \alpha \), equation (5) is more accurate than equation (4).
Table 1: Interaction parameters $\mu$ and $\alpha$ of 0.1% w/v Pullulan-CMC blend at 30 °C

<table>
<thead>
<tr>
<th>Composition</th>
<th>Slope of the reduced viscosity vs. concentration curve</th>
<th>$\mu$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pullulan</td>
<td>0.200</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>80/20</td>
<td>3.021</td>
<td>0.000612</td>
<td>0.027779</td>
</tr>
<tr>
<td>60/40</td>
<td>2.325</td>
<td>0.000140</td>
<td>0.002462</td>
</tr>
<tr>
<td>50/50</td>
<td>1.000</td>
<td>-0.000228</td>
<td>-0.000295</td>
</tr>
<tr>
<td>40/60</td>
<td>0.778</td>
<td>-0.000290</td>
<td>-0.000635</td>
</tr>
<tr>
<td>20/80</td>
<td>0.667</td>
<td>-0.000321</td>
<td>-0.000751</td>
</tr>
<tr>
<td>CMC</td>
<td>3.444</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2: Interaction parameters $\mu$ and $\alpha$ of 0.1% w/v Pullulan-CMC blend at 40 °C

<table>
<thead>
<tr>
<th>Composition</th>
<th>Slope of the reduced viscosity vs. concentration curve</th>
<th>$\mu$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pullulan</td>
<td>0.177</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>80/20</td>
<td>3.656</td>
<td>0.000543</td>
<td>0.028671</td>
</tr>
<tr>
<td>60/40</td>
<td>2.041</td>
<td>0.000003</td>
<td>0.002138</td>
</tr>
<tr>
<td>50/50</td>
<td>1.146</td>
<td>-0.000295</td>
<td>-0.000167</td>
</tr>
<tr>
<td>40/60</td>
<td>0.909</td>
<td>-0.000374</td>
<td>-0.000772</td>
</tr>
<tr>
<td>20/80</td>
<td>0.869</td>
<td>-0.000343</td>
<td>-0.000929</td>
</tr>
<tr>
<td>CMC</td>
<td>3.882</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3.2 Density and Ultrasonic Studies

Density ($\rho$) and ultrasonic velocity ($v$) of blend under consideration at different compositions have been measured at 30 and 40 °C. The variation of these values with percentage composition of CMC is shown in Figures 3, 4 and 5 respectively. The adiabatic compressibility $\beta_{ad}$ of different blend compositions was evaluated by using the equation

$$\beta_{ad} = \frac{1}{V^2 \rho}$$

where ($v$) is the ultrasonic velocity and ($\rho$) is the density of blend solutions. The variation of adiabatic compressibility with composition of Pullulan-CMC blend at 30 and 40 °C is shown in Figure 6. The graph shows both linear and non-linear regions. It has already been established that the variation is linear for miscible blend and non-linear for immiscible blend [8]. In this study, variation was found to be linear when the Pullulan content is 60% and above at 30 and 40 °C. This observation was in confirmation with $\mu$ and $\alpha$ value. When Pullulan is less than 60% in the blend shows non-linearity, it indicates the existence of immiscibility. This is because of intermolecular hydrogen bonding between the hydroxyl groups of the polymer segments are more when Pullulan content is 60 % and above, thus leading to the blend. Below this critical concentration, there will not be much interaction between the polymer segments, which leads to the immiscibility of the blend.
Figure 3: Variation of density with composition of 0.5% w/v, Pullulan-CMC blend at 30 °C

Figure 4: Variation of density with composition of 0.5% w/v, Pullulan-CMC blend at 40 °C
Figure 5: Variation of Ultrasonic velocity with composition 0.5% w/v, of Pullulan-CMC blend at 30 and 40 °C

Figure 6: Variation of Adiabatic compressibility with composition of Pullulan-CMC blend at 30 and 40 °C
3.3 Solid State Studies

3.3.1 Morphology study of Pullulan-CMC blends

Uniformity of the dispersion was examined through SEM of the solution casting films of 100/0, 80/20, 60/40, 50/50 and 0/100 Pullulan-CMC blends. It has been observed that when Pullulan concentration was 60% and above the blend showed uniform dispersion. When Pullulan content was less than 60% the blend showed phase separation (Figure 7). The morphology of Pullulan-CMC revealed that the blend was semi-compatible.

![SEM images of Pullulan-CMC blends](image_url)

Figure 7: Scanning electron micrographs for (a) pure Pullulan (b) pure CMC (c) 80/20 Pullulan-CMC blend, (d) 60/40 Pullulan-CMC blend and (e) 50/50 Pullulan-CMC blend.
3.3.2 FTIR – Spectroscopic study

FTIR spectrometry is a very powerful technique to detect the hydrogen bonding between polymers. Spectra of pure Pullulan, CMC and their blend films (100/0, 80/20, 60/40 and 0/100) are shown in the Figure 8. The IR hydroxyl stretching of Pullulan-CMC blends at 80/20 and 60/40 compositions indicate miscibility. Similar observations were reported by Aminabhavi et al.[18] for blend membranes of sodium alginate and poly (acryl amide)-graft-gaur gum. The -OH frequency of Pullulan is not affected in other blend compositions, showed the absence of intermolecular interaction.

Figure 8: FTIR spectra of (A) pure Pullulan (B) pure CMC (C) 60/40 Pullulan/CMC (D) 80/20 Pullulan/CMC.

4.0 CONCLUSION

Based on viscosity, ultrasonic velocity and density measurements, it was found that polymer blend of Pullulan-CMC is miscible when the Pullulan content is 60% and above. Below this critical concentration the blend was found to be immiscible. Thus, Pullulan-CMC blend is semi-compatible. Variation of temperature did not have any significant effect on the miscibility. FTIR and SEM analysis also confirms semi-compatibility of the Pullulan-CMC blend.
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REFERENCES


