Solution and Solid-State Blend Compatibility of Poly(vinyl alcohol) and Poly(methyl methacrylate)

ABSTRACT

In this chapter, the blend miscibility of poly(vinyl alcohol) and poly(methyl methacrylate) in N,N'-dimethylformamide solution was investigated by viscosity, density, ultrasonic velocity, refractive index and UV and fluorescence spectra studies. Differential scanning calorimetry and scanning electron microscopy were used to confirm the blend miscibility in the solid state. Blends were compatible when the concentration of poly(vinyl alcohol) was greater than 60 wt. %.

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III.1. INTRODUCTION

Polymer-polymer miscibility has been widely studied in the polymer literature [1]. Such studies have great significance for engineering applications of polymers. Polymer blends can be incompatible due to unfavorable entropies of mixing [2,3], but for blends to be compatible, covalent, H-bond, or charge-transfer interactions are important [4,5]. Polymer blend compatibility has been studied widely with a large number of techniques [6-13]. Poly(vinyl alcohol) (PVA) and poly(methyl methacrylate) (PMMA) are widely used polymers in many engineering areas [14-17]. A literature search suggested that no previous studies have been made on the blend compatibility of PVA and PMMA. This prompted us to investigate the compatibility of PVA and PMMA in N,N'-dimethylformamide (DMF) solution by the measurement of viscosity (\(\eta\)), density (\(\rho\)), ultrasonic velocity (\(u\)), refractive index (\(n_0\)), and UV and fluorescence spectra. Blend compatibility in the solid state was confirmed by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) techniques.

III.2. RESULTS AND DISCUSSION

III.2.1. Solution Property Studies

Viscosity, density, and refractive index of the blend solutions were measured at 30\(^\circ\), 40\(^\circ\) and 50\(^\circ\)C, whereas ultrasonic velocity was measured at 30\(^\circ\)C for six concentrations namely, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0 % (v/v), of the blends. The results of absolute viscosity vs wt % of PVA in PVA/PMMA blend displayed in Fig.III.1 exhibited curvature (nonlinear) trends up to 50 wt. % of PVA in the blend. However, at 60, 80 and 90 wt. % of PVA in the PVA/PMMA blends, linear trends were observed, indicating the blend compatibility at these compositions. The nonlinear (curvature) trends indicate the incompatibility of PVA and PMMA.
Fig. III.1. Absolute viscosity vs composition of blends of PVA/PMMA at 30, 40 and 50°C for different concentrations of blend. Symbols: (Δ) 0.2%; (▲) 0.4%; (+) 0.5%; (○) 0.6%; (■) 0.8% and (○) 1%

Similar trends are observed for density, ultrasonic velocity and refractive index results displayed in Figs. III.2, III.3 and III.4, respectively.
Fig. III.2. Density vs composition of blends of PVA/PMMA at 30, 40 and 50°C for different concentration of blend. Symbols: (△) 0.2 %; (▲) 0.4 %; (●) 0.5 %; (□) 0.6 %; (■) 0.8 % and (○) 1 %
Fig. III.3. Ultrasonic velocity vs compositions of PVA/PMMA blends at 30°C for different concentration of blend. Symbols: (△) 0.2 %; (▲) 0.4 %; (●) 0.5 %; (□) 0.6 %; (■) 0.8 % and (○) 1 %

Fig. III.4. Refractive index vs compositions of PVA/PMMA blends at 30, 40 and 50°C for different concentration of blend. Symbols: (△) 0.2 %; (▲) 0.4 %; (●) 0.5 %; (□) 0.6 %; (■) 0.8 % and (○) 1 %

CHAPTER-III
In the earlier literature [18], ultrasonic velocity was used in predicting miscibility of cellulose acetate-PMMA blends, wherein nonlinear dependence was attributed to the incompatible nature of the blend. The linear variation in case of PMMA and poly(vinyl acetate) blend was the result of their miscibility [19,20]. From the viscosity data, blend miscibility in solution was studied [21] with the relationship:

\[ b_n = x_1^2b_{11} + 2x_1x_2b_{12} + x_2^2b_{22} \]  

(III.1)

where, \( x_1 \) and \( x_2 \) are mass fractions of polymer 1 and 2, \( b_{11} \) and \( b_{22} \) are the respective interaction parameters, \( b_{12} \) is interaction parameter of the blend system and \( b_m \) represents the global interaction parameter between the individual polymers. Interaction parameters, \( b_{11}, b_{22} \) and \( b_m \) were calculated from the slopes of the plot of reduced viscosity vs concentration (see Fig.III.5). Interaction parameter, \( b_{12}^* \) was then calculated theoretically with:

\[ b_{12}^* = (b_{11} b_{22})^{1/2} \]  

(III.2)

The values of \( b_{11} \) and \( b_{22} \) are slopes of the plots of reduced viscosity vs concentration of individual polymers calculated from the Huggins equation [22]:

\[ \frac{[\eta]_p}{c} = [\eta]_o + bc \]  

(III.3)

where \( [\eta]_p \) is the specific viscosity, \( c \) is the concentration, \([\eta] \) is the intrinsic viscosity, and \( b \) is the Huggins constant.

The difference, \( \Delta b \), calculated from theoretical \( b_{12}^* \) from Eq. (III.2) and experimental \( b_{12} \) using Eq. (III.1) is given as:

\[ \Delta b = (b_{12} - b_{12}^*) \]  

(III.4)
Fig. III.5. Reduced viscosity vs concentration of PVA/PMMA blends at 30, 40 and 50°C for different compositions of blend. Symbols: (Δ) 20 %; (▲) 40 %; (+) 50 %; (○) 60 %; (■) 80 %; (○) 90 %; (♦) pure PMMA; (●) pure PVA
If $\Delta b > 0$, then blends are compatible; if $\Delta b < 0$, then phase separation occurs. The calculated values of $\Delta b$ for all of the blends at different temperatures are given in Table III.1. Positive $\Delta b$ values at 60, 80 and 90 % of PVA in the blend at all the temperatures indicate the compatible nature of the blends, whereas the negative $\Delta b$ values at other compositions (i.e., 20-50% of PVA) indicate the blend immiscibility.

Table III.1. The $\Delta b$ Values for PVA/PMMA Blends at Different Temperatures

<table>
<thead>
<tr>
<th>Wt % of PVA in PVA/PMMA</th>
<th>30°C</th>
<th>40°C</th>
<th>50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>20/80</td>
<td>-0.4162</td>
<td>-0.7708</td>
<td>-0.4056</td>
</tr>
<tr>
<td>40/60</td>
<td>-0.0753</td>
<td>-0.1857</td>
<td>-0.4062</td>
</tr>
<tr>
<td>50/50</td>
<td>-0.0743</td>
<td>-0.1222</td>
<td>0.1335</td>
</tr>
<tr>
<td>60/40</td>
<td>0.6328</td>
<td>0.4346</td>
<td>0.0914</td>
</tr>
<tr>
<td>80/20</td>
<td>1.2576</td>
<td>1.1561</td>
<td>1.2629</td>
</tr>
<tr>
<td>90/10</td>
<td>1.3715</td>
<td>1.4452</td>
<td>1.6861</td>
</tr>
</tbody>
</table>

Isentropic compressibility ($K_s$) was also used to study the miscibility of blends [23]. It was calculated from the density, $\rho$ and ultrasonic velocity, $u$ of the solutions using:

$$K_s = \frac{1}{u^2 \rho} \quad \text{(III.5)}$$

Plots of $K_s$ versus composition of the blend are displayed in Fig.III.6 at 30°C. Linear variation of $K_s$ with 60–90 wt % PVA suggested their miscibility, whereas the nonlinear trends in the composition range 20–50% PVA indicated their incompatible nature. These results are in conjunction with those of the $\rho$, viscosity, and $n_D$ data discussed previously.
The heat of mixing ($\Delta H_m$) was also used as a measure to study the blend compatibility [24–26]. According to Schneier [26], $\Delta H_m$ of the polymer blends is given by:

$$
\Delta H_m = \left[ w_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 \left[ w_2 / (1 - w_2) M_2 \rho_2 + (1 - w_1) M_1 \rho_1 \right] \right]^{1/2}
$$

(III.6)

where $w$, $M$, and $\rho$ are the weight fraction of the polymer, the monomer molecular weight, and the polymer density, respectively, and $\delta$ represents the solubility parameter of the polymer. The $\delta$ values of PVA [12.6 (cal/cm$^3$)$^{1/2}$] and PMMA [9.1 (cal/cm$^3$)$^{1/2}$] were taken from the literature [27] and these values were used to calculate $\Delta H_m$ with Eq. (III.6). Figure III.7 shows the variation of $\Delta H_m$ versus blend composition. Here also, linear trends are observed over the range of 60–90 mass % of PVA in the blend, thus confirming the blend compatibility in the studied region.
Heat of mixing vs composition of PVA/PMMA blends. Symbols: (♦) 30°C; (x) 40°C; (0) 50°C

III.2.2. Interaction Parameter

The polymer-solvent interaction parameter ($\chi$) was computed from Flory-Huggins theory [25] with

$$\chi_i = \left(\frac{V_i}{RT}\right)(\delta_2 - \delta_1)^2$$  \hspace{1cm} (III.7)

where $\delta_1$ and $\delta_2$ are the solubility parameters of solvent and polymer, respectively and $V_i$, $R$ and $T$ are the molar volume of the solvent, universal gas constant, and temperature (K), respectively. Eq. (III.7) was also used by others [28,29] to calculate $\chi$ of the blends. The blend $\delta$ was calculated from the additivity relationship:

$$\delta = x_1\delta_1 + x_2\delta_2$$  \hspace{1cm} (III.8)

where $x_1$ and $x_2$ are the mass fractions and $\delta_1$ and $\delta_2$ are the solubility parameters of the component polymers in the blend system. The interaction parameters of the polymer-polymer blend systems are presented in Table III.2, whereas the blend-solvent interaction parameters are given in Table III.3.
Table III.2. Polymer–Polymer Interaction Parameters of the PVA and PMMA in the Blend

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Polymers</th>
<th>( \chi ) calculated from Eq. (III.7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>PVA</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>PMMA</td>
<td>1.75</td>
</tr>
<tr>
<td>40</td>
<td>PVA</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>PMMA</td>
<td>1.75</td>
</tr>
<tr>
<td>50</td>
<td>PVA</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>PMMA</td>
<td>1.74</td>
</tr>
</tbody>
</table>

Table III.3. Blend–Solvent Interaction Parameters at Different Temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>PVA/PMMA (w/w)</th>
<th>( \delta ) calculated from Eq. (III.8)</th>
<th>( \chi ) calculated from Eq. (III.7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>20/80</td>
<td>9.8</td>
<td>0.698</td>
</tr>
<tr>
<td></td>
<td>40/60</td>
<td>10.5</td>
<td>0.340</td>
</tr>
<tr>
<td></td>
<td>50/50</td>
<td>10.9</td>
<td>0.209</td>
</tr>
<tr>
<td></td>
<td>60/40</td>
<td>11.2</td>
<td>0.200</td>
</tr>
<tr>
<td></td>
<td>80/20</td>
<td>11.9</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>90/10</td>
<td>12.3</td>
<td>0.002</td>
</tr>
<tr>
<td>40</td>
<td>20/80</td>
<td>9.8</td>
<td>0.683</td>
</tr>
<tr>
<td></td>
<td>40/60</td>
<td>10.5</td>
<td>0.333</td>
</tr>
<tr>
<td></td>
<td>50/50</td>
<td>10.9</td>
<td>0.205</td>
</tr>
<tr>
<td></td>
<td>60/40</td>
<td>11.2</td>
<td>0.107</td>
</tr>
<tr>
<td></td>
<td>80/20</td>
<td>11.9</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>90/10</td>
<td>12.3</td>
<td>0.002</td>
</tr>
<tr>
<td>50</td>
<td>20/80</td>
<td>9.8</td>
<td>0.668</td>
</tr>
<tr>
<td></td>
<td>40/60</td>
<td>10.5</td>
<td>0.326</td>
</tr>
<tr>
<td></td>
<td>50/50</td>
<td>10.9</td>
<td>0.200</td>
</tr>
<tr>
<td></td>
<td>60/40</td>
<td>11.2</td>
<td>0.105</td>
</tr>
<tr>
<td></td>
<td>80/20</td>
<td>11.9</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>90/10</td>
<td>12.3</td>
<td>0.002</td>
</tr>
</tbody>
</table>
From these data, we observed that polymer–polymer interactions were quite higher than those observed for blend–solvent interactions for blend compositions containing 80–90% PVA at all of the temperatures. Such a large difference between polymer–polymer interactions and blend–solvent interactions suggested the compatible nature of the blends in the range 80–90% PVA.

**III.2.3. Spectroscopic Studies**

UV and fluorescence studies have been made to analyze the compatibility of blends [8,13]. Because both PVA and PMMA were not suitable for studying the energy transfer processes, they do not emit radiation in the UV region. Therefore, we added a small quantity of POPOP dye, which had a wavelength maximum, $\lambda_{\text{max}}$ value at 360 nm. Absorbance of POPOP in each blend solution was measured at 360 nm, whereas POPOP fluorescence data were collected at 420 nm. Figures III.8 and III.9 display, respectively the variation of dye absorbance and fluorescence versus blend composition. Linear trends observed in the range 60–90% PVA were a further proof of blend compatibility.

**Fig.III.8.** Dye absorbance at 360 nm versus composition of the PVA/PMMA blends for different blend concentrations: (Δ) 0.2, (▲) 0.4, (*) 0.5, (○) 0.6, (■) 0.8, and (○) 1%.
III.2.4 DSC Studies

One of the most commonly used methods for estimating the polymer-polymer compatibility is to determine the glass-transition temperature of the blend and compare it with the glass-transition temperature of the component polymers. If one of the component polymers is crystalline in nature, the depression in the melting temperature ($T_m$) can be used to study the blend compatibility [30-32]. In this study, DSC was used to estimate $T_m$ to investigate the compatibility of PVA and PMMA blends. Figure III.10 displays the DSC thermograms of PVA in the PVA/PMMA blends. The $T_m$ of PVA is observed at 190.55°C. In this study, variations in $T_m$ of PVA in the blend were considered a measure of blend compatibility. $T_m$ did not show any systematic trend between 20 and 50% PVA in the blend, but a systematic depression in $T_m$ for PVA in the blend was observed for 60-90% PVA in the blend. Such a systematic depression in $T_m$ between 60 and 90% of PVA in the blend indicated blend compatibility in the aforementioned range.
Fig. III.10. DSC thermograms of the PVA/PMMA blends: (a) PVA-50, (b) PVA-40, (c) PVA-60, (d) PVA-20, (e) PVA-90, (f) PVA-80, and (g) pure PVA.

III.2.5 SEM Studies

In the earlier literature [33], SEM was used to study blend compatibility. In preparing the blend films of PVA and PMMA, phase separation occurred at less than 50 wt.% PVA, indicating its immiscibility. However, good films were obtained at 60, 80 and 90 wt.% PVA in the blend. A typical SEM photograph of the 80/20 PVA/PMMA blend, shown in Fig. III.11, confirmed the blend compatibility as seen by a single phase. These results were in accordance with those confirmed by the $\rho$, viscosity, $u$, $n_D$, and spectroscopic studies.
Fig. III.11. SEM photograph of the 80/20 PVA/PMMA blend.

III.3. CONCLUSIONS

Binary blend solutions and solid films of PVA and PMMA were prepared in DMF and studied for their physical, spectroscopic, and thermal properties. Judging from the experimental observations, we concluded that PVA and PMMA could form thermodynamically miscible phases at higher contents of PVA (> 60 wt.%) in the blend.
III.4. REFERENCES


