Determination of Compatibility nature of blends of PMMA 350000 in Toluene by Physical methods

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ABSTRACT
Polymer blends are capable of providing materials with extended useful properties beyond the range that can be obtained from single polymer equivalents. From the beginning of the plastic industry it has been recognized that blending yields materials with properties superior to the feature of the individual components. There has been progress in the understanding of the behaviour of polymer blends especially its rheology properties. In the present study, Poly(methyl methacrylate) (molar volume 350000) is blended with Polyethylene Glycol (molar volume 4000) in toluene at 303K. The miscibility nature of PMMA 350000 with PEG 4000 is analysed for various blend compositions using ultrasonic velocity, density, viscosity, refractive index technique and α studies. The results obtained reveal that PMMA forms an immiscible blend with PEG in the entire composition range.

Key words: Blend, Compatibility, Refractive index, Ultrasonic velocity.

1. INTRODUCTION
Polymer blending is one of the most important contemporary ways for the development of new polymeric materials [1]. Polymer blends often exhibit properties that are superior to any one of the component polymers alone. However, the manifestation of superior properties depends upon the miscibility of homopolymers on the molecular scale. Methods for the experimental study of polymer miscibility are numerous and very diverse, and may be divided into several main groups:

- Methods based on the determination of optical homogeneity of the mixture.
- Methods for the determination of glass transition temperatures.
- Methods for the direct determination of interactions on molecular levels.
- Indirect methods for the miscibility.
Some of these techniques may be complicated, costly and time consuming. Hence, it is desirable to identify simple, low-cost and rapid techniques to study the miscibility of polymer blends. The main method to find the number of amorphous phases in polymer blends is the determination of ultrasonic velocity [2]. The determination of density and refractive index of the different compositions of the blend is an additional method to assess its phase behaviour and miscibility state. It is more in expensive method. Viscometry is also a simple, quick and inexpensive method to determine the miscibility [3–4]. Polymers containing proton donor groups are found to be miscible with those containing proton acceptor groups due to a specific interaction like hydrogen bonding. PMMA is miscible with many polymers like PVC, PEO, PVDF, SAN, etc [5–8]. In PMMA–PVC blend, Schurer et al [9] has reported that ester group in PMMA is a proton acceptor, and PVC is a weak proton donor via hydrogen, and the interaction involved is hydrogen bonding. There are few reports on the studies of interactions of PMMA with other polymers. Hence, in this paper we report a new blend system of PMMA and PEG, and make an attempt to study the interactions involved in blending PMMA with a proton donor polymer. PMMA 350000 and PEG 4000 are chosen for the present study because of their industrial applications.

2. METHODS AND MATERIALS
Polyethylene Glycol and Poly(methyl methacrylate) was obtained from KAVIN SCIENTIFIC, Chennai, India. In the present study, PMMA 350000 is blended with PEG 4000 in Toluene. 1% concentration of PMMA 350000 and PEG 4000 were separately prepared by dissolving 2.5 gms of each polymer in 250 ml Toluene. Then various compositions of the blend PMMA 350000 / PEG 4000 in the following ratio (0/100, 20/80, 40/60, 50/50, 60/40, 80/20, 100/0) were prepared by proper mixing at 30º C (accuracy ± 0.5 º C). The relative viscosity of the polymer solutions is studied at all the composition ranges at 303K using Brookfield Viscometer (USA) (accuracy ±0.01cP). The temperature is maintained using a thermostat with a thermal stability of ± 0.05° C. The density values are measured using specific gravity method. The mass of the liquid was measured using a K-ROY make Electronic balance, with an accuracy of ±0.001gm. Refractive index studies are performed at 303K using Mittal make Abbe Refractometer (uncertainty ± 0.5%). The ultrasonic velocity measurements are performed using Mittal make single frequency Ultrasonic interferometer at 2 MHz (F-81 model) (uncertainty ± 0.1m/s). The temperature is maintained at 303K by circulating water from a thermostat with a thermal stability of ± 0.05° C through the double wall jacket of the cell.

3. RESULTS AND DISCUSSION
Density studies have been performed for the blend composition of PMMA 350000 / PEG 4000 in toluene. Fig. 1 shows the variation of density against blend composition of the PMMA 350000. Density studies show (Fig. 1) that the variation is non linear (S-type) with the increase in composition and it confirmed that the blend is immiscible. For further confirmation Relative Viscosity study was done. Viscosity method is simple and it offers very useful information about the relationship between dilute solution properties and bulk structure of the polymer blend. Viscosity studies are done for various blend compositions [0/100, 20/80, 40/60, 50/50, 60/40, 80/20, 100/0] of PMMA 350000 / PEG 4000 in Toluene at 303 K. Fig. 2 shows the variation of relative viscosity against blend composition of PMMA 350000 / PEG 4000 in toluene at 303 K. Here the variation is linear which confirmed the blend is miscible. For further confirmation additive rule is applied. Sun et al [10] have suggested viscometric method to study polymer-polymer miscibility. The basic idea of using viscosity as a parameter for compatibility determination of polymer blends lies in the fact that in solution the repulsive interaction may cause shrinkage of polymer coils resulting in the viscosity of the polymer mixture that is lower than the value calculated from viscosities of the pure components on the assumption of additive law.

![Figure 1](image-url)
Venkatramanan et al [3] have used a few empirical and semi-empirical equations for predicting the miscibility of polymer blends based on viscosity viz., the additive rule, log additive rule, and free volume additive rule given by Eq. 1, Eq. 2 and Eq. 3.

\[ \eta_b = W_1 \eta_1 + W_2 \eta_2 \] (1)
\[ \log \eta_b = W_1 \log \eta_1 + W_2 \log \eta_2 \] (2)
\[ \frac{1}{\log \eta_b} = W_1 \left( \frac{1}{\log \eta_1} \right) + W_2 \left( \frac{1}{\log \eta_2} \right) \] (3)

In the case of completely miscible blends, that is 100% miscible blends, the experimental values will be the same as the values calculated from the additive rule of the mixture. When the blend is less than 100% miscible or partially miscible, the values predicted from log additive rule of the mixture will be close to the experimental value. Utrachi and Kamal [11] have described the complexity of the viscosity composition behaviour of polymer blends. Using rheological data, they are divided into three categories depending on the deviation from log additive rule. They are a) positively deviating, b) negatively deviating and c) positively-negatively deviating. The negative deviation of the log additive rule in the case of immiscible blends was reported by Venkatramanan et al [12].
From (Fig. 3), we could observe that the experimental values are negatively deviated to additive rule. This shows that the blend may be immiscible. For further confirmation, alpha (α) studies were carried out. It is possible to use the intrinsic viscosity of dilute polymer solutions as a measure of the solvent power of the liquid for the polymer. When a polymer is dissolved in a strong solvent it tends to stretch out, while it tends to coil up in a poor solvent. Since viscosity is a measure of resistance to flow, a polymer dissolved in a strong solvent being stretched would give a higher quantity, which is independent of the concentration of the solution. The intrinsic viscosity is such a quantity, whose measurement is discussed earlier.

According to Sabu thomas [13] the basis for using dilute solution viscosity as a parameter for compatibility determination of polymer blends lies in the fact that while in solution the repulsive interaction may cause shrinkage of polymer coils resulting in a viscosity of the polymer mixture that is lower than the value calculated from the viscosities of the pure components on the assumption of additive law. On the other hand, attractive interaction increases the viscosity of the system. Basically the dilute solution viscometry hinges on the classical Huggin's equation [14]. Huggin's equation expresses the specific viscosity [ŋ]_m of the polymer as a function of the concentration C, when one of the components is alone in solution.

\[ \frac{\eta_{sp}}{c} = [\eta] + K [\eta]^2 c \]

Where \([\eta]\) is the intrinsic viscosity. Let us put \(b = K [\eta]^2\)

\[ \frac{\eta_{sp}}{c} = [\eta] + bc \]  \hspace{1cm} (4)

Where 'b' is the interaction term.

Sun et al [15] proposed another parameter \(\alpha\) for the miscibility studies and they reasoned out the failure of Chee's theory in case of PVC/PMMA blend. The reason is the parameter \(b\) (in eqn 2) or \(K\) [Huggin’s const] originates from a superposition of several types of interactions viz, the hydrodynamic and thermodynamic contributions. The thermodynamic contributions include the intra and inter molecular excluded volume effect. The proposed interaction parameter \(\alpha\), is based on the long range hydrodynamic interactions for pairs of single molecules, the interaction due to double molecules and their inter molecular attraction, viscosities of double and single molecule species at molecular level, indicating miscibility, depending on attractive or repulsive forces in dilute solution. Sun et al [15] have modified Chee’s theory and suggested that Huggin’s coefficient \(K_m\) can be defined by three types of interaction,

A long range hydrodynamic interaction of pairs of single molecules \(K_{m1}\) as in the equation given below,

\[ K_{m1} = \frac{K_a \left( [\eta_1]^2 c_1 + K_b [\eta_2]^2 c_2 + 2 \left( K_a K_b \right)^{0.5} [\eta_1] [\eta_2] c_1 c_2 \right)}{( [\eta_1] c_1 + [\eta_2] c_2)^2} \]

Where \(c_1\) and \(c_2\) correspond to the weight fraction of the components 1 and 2.

\(K_a\) and \(K_b\) are the Huggin’s coefficient for the pure components.

The formation of double molecules can be neglected because of the absence of strong specific forces of attraction between the molecules and sufficiently low concentration.

The intermolecular attraction or repulsion represented by \(K_{m3} = \alpha\).

In this condition \(K_m\) can be defined by \(K_m = K_{m1} + K_{m3}\)

\[ K_m = \frac{K_a \left( [\eta_1]^2 c_1 + K_b [\eta_2]^2 c_2 + 2 \left( K_a K_b \right)^{0.5} [\eta_1] [\eta_2] c_1 c_2 \right)}{( [\eta_1] c_1 + [\eta_2] c_2)^2} + \alpha. \]

Thus, \(\alpha = K_m - K_{m1}\)

Here, \(K_m\) is Huggin’s constant for the blend, whereas \(K_a, K_b\) are that of pure components and were determined by

\[ \frac{\eta_{sp}}{c} = [\eta] + K [\eta]^2 c \]

If \(\alpha > 0\) then the system is miscible and immiscible when \(\alpha < 0\)
Table 1
α- Values for PMMA 350000 / PEG 4000 in Toluene

<table>
<thead>
<tr>
<th>Blend system</th>
<th>Composition</th>
<th>α value</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA 350000 / PEG 4000</td>
<td>0/100</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>20/80</td>
<td>-0.4409</td>
</tr>
<tr>
<td></td>
<td>40/60</td>
<td>-0.6392</td>
</tr>
<tr>
<td></td>
<td>50/50</td>
<td>-0.58696</td>
</tr>
<tr>
<td></td>
<td>60/40</td>
<td>-0.65013</td>
</tr>
<tr>
<td></td>
<td>80/20</td>
<td>-0.31415</td>
</tr>
<tr>
<td></td>
<td>100/0</td>
<td>0</td>
</tr>
</tbody>
</table>

In the present study, α < 0 for all the blend compositions. Hence the blend system is immiscible. For further confirmation, ultrasonic velocity and refractive index studies are performed.

Figure 4 Variation of Ultrasonic Velocity against Blend composition of PMMA

Figure 5 Variation of refractive Index against Blend composition of PMMA
Fig. 4 and Fig. 5 show the variation of Ultrasonic velocity and refractive index against blend composition of PMMA in toluene. Both cases show the S-type variation which confirm that blend taken for study is immiscible in nature.

4. CONCLUSION

PMMA 350000 is blended with PEG 4000 in Toluene at 303K and the compatibility nature of the blend has been analysed using various physical methods like viscosity, density, refractive index and ultrasonic techniques. The blend showed immiscible in nature.

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