# Studies on the miscibility of poly(isobutylene) with poly(ether imide) blends in dilute solutions

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The miscibility criteria of poly(isobutylene) (PIB) and poly(ether imide) (Ultem) were investigated at 30 °C in chloroform in dilute solutions by viscometric analysis. The intrinsic viscosity and viscometric parameters of this blend system were determined for several PIB/Ultem mixtures in compositions such as 80/20, 70/30, 60/40, 40/60, 20/80 in chloroform solutions. The miscibility criteria on the basis of the sign of $\Delta b$, $\Delta b'$, $\Delta[\eta]$, $\alpha$ and $\beta$ which are the difference between their experimental and ideal values were calculated by applying theoretical equations. The data obtained from the viscometry studies showed that the prepared blends were immiscible in all the studied composition ranges at 30 °C. The miscibility of the mixtures was also studied by fourier transform infrared spectroscopy.

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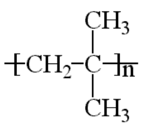
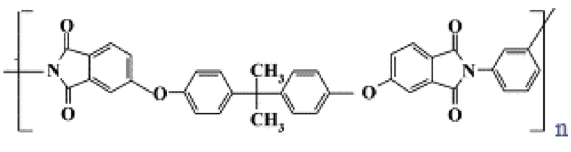
## 1. Introduction

Aromatic polyimides have useful physical properties such as superior thermal stability, high modulus and toughness. They are used in a variety of applications such as coatings, adhesives, composites and molded components needed ultraviolet radiation resistance. Poly(ether imide) (Ultem) is a high performance amorphous engineering thermoplastic possessing excellent mechanical properties even at elevated temperatures due to its high glass transition temperature and also possesses excellent electrical properties [1-5]. Poly(isobutylene) (PIB) is a fully saturated hydrocarbon elastomer with outstanding oxidative and chemical resistance, superior gas-barrier and mechanical damping characteristics, and excellent biocompatibility. Because of these characteristics, block copolymers based on PIB elastomeric segments are currently of great interest as self-assembling materials with unique properties [6]. Chemical structures of PIB and Ultem were given in Scheme 1.



*(a)*



*(b)*

*Scheme 1. Chemical structure of (a) PIB and (b)Ultem*

Polymer blending offers an attractive alternative in the development of new polymeric materials. Due to the high cost and the toxicologic uncertainty associated with the development of new monomers, most new polymeric materials are now being developed through blending or modifying the architecture of the polymer chains (graft, block and star polymers, etc.). Most of the blend components are also highly incompatible with each other. There have been various techniques of studying the polymer-polymer miscibility. Some of these techniques are quite complicated, costly and time consuming. Viscosity is simple, low cost and rapid technique and provides valuable information to determine polymer-polymer miscibility [7-11].

In this study, the miscibility criteria of PIB and Ultem were found by viscosity measurements as suggested by several research groups such as Krigbaum and Wall, Garcia et al., Sun et al., Jiang and Han at 30 °C. And then, specific interactions between the components of the blend have been investigated by fourier transform infrared spectroscopy (FT-IR).

## 2. Experimental

### 2.1 Materials and instrumentation

All viscosity measurements were performed at 30 °C using a home-made modified Ubbelohde-type capillary viscometer in a constant temperature bath controlled with ± 0.02 °C by a Huber type electronically controlled thermostat. Stock solutions of the binary and ternary systems were freshly prepared by dissolving appropriate amount of polymers in chloroform into a concentration of 0.5 g /100 cm$^3$ solutions. For each measurement, 7 cm$^3$ stock solution was loaded into the viscosimeter and diluted by adding 2 $cm^3$ chloroform to yield several lower concentrations. The elution time of each solution was taken as the average of four readings agreed to within ±0.5%.

FT-IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR Spectrometer at 2 $cm^{-1}$ resolution from Fourier transforms of 60 scans. The samples were prepared as a film on KBr pellets *via* dropped polymer solutions and evaporated solvent.

### 2.3 Theoretical background on IGC

For the ternary mixture of polymer (1), polymer (2) and a common solvent, at constant weight ratio of polymer 1 to 2 for a given composition, the well-known Huggins' equation is written as [12]

$$(\eta_{sp})_m / c_m = [\eta]_m + b_m c_m \tag{1}$$

where $c$, $(\eta_{sp})/c$, $[\eta]$, and $b$ are concentration, reduced viscosity, intrinsic viscosity and viscometric interaction parameter of the polymer in the solution, respectively, while subscript "m" denotes "mixture". The miscibility of the polymer (1) and (2) is estimated by comparison of the experimental and ideal values of $b_m$ and $[\eta]_m$.

Krigbaum and Wall [13] have defined the ideal value of the interaction parameter $b_m^{id}$ as

$$b_m^{id} = b_{11} w_1^2 + b_{22} w_2^2 + 2 b_{12}^{id} w_1 w_2 \tag{2}$$

and the $b_{12}^{id}$ as a geometric mean;

$$b_{12}^{id} = b_{11}^{1/2} b_{22}^{1/2} \tag{3}$$

Catsiff and Hewett [14] have defined the ideal value of the interaction parameter $b_{12}^{id'}$ as an arithmetic mean

$$b_{12}^{id'} = (b_{11} + b_{22}) / 2 \tag{4}$$

Garcia et al. have also proposed another miscibility criterion based on the difference between the experimental and ideal values of $[\eta]_m$ assuming that the intrinsic viscosity can be treated as an excess property. The value of $[\eta]_m^{id}$ has defined as [15]

$$[\eta]_m^{id} = [\eta]_1 w_1 + [\eta]_2 w_2 \tag{5}$$

where $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities of corresponding polymers.

Sun et al. [16] have proposed another miscibility criterion, $\alpha$ for polymer-polymer miscibility defined as;

$$\alpha = k_m - \frac{k_1 w_1^2 [\eta]_1^2 + 2(k_1 k_2)^{1/2} w_1 w_2 [\eta]_1 [\eta]_2 + k_2 w_2^2 [\eta]_2^2}{(w_1[\eta]_1 + w_2[\eta]_2)^2} \tag{6}$$

where

$$k_1 = b_1 / [\eta]_1^2 ;\ k_2 = b_2 / [\eta]_2^2 ;\ k_m = b_m / [\eta]_m^2 ,\quad k_{12} = b_{12} / [\eta]_1 [\eta]_2 \tag{7}$$

With the weighted additive rule as shown in Eq. (5) exhibited, an expression of $k_m$ can be concluded as

$$k_m = \frac{k_1 w_1^2 [\eta]_1^2 + 2 k_{12} w_1 w_2 [\eta]_1 [\eta]_2 + k_2 w_2^2 [\eta]_2^2}{(w_1[\eta]_1 + w_2[\eta]_2)^2} \tag{8}$$

Jiang and Han [17] derived an improved criterion by substituting Eq.(8) to (6) and parameter $\alpha$ was replaced with $\beta$

$$\beta = \frac{2 w_1 w_2 [\eta]_1 [\eta]_2}{(w_1[\eta]_1 + w_2[\eta]_2)^2} \Delta k \tag{9}$$

where $\Delta k = k_{12} - \sqrt{k_1 k_2}$

## 3. Results and discussion

The intrinsic viscosity and viscometric parameters of this system have been determined at 30°C in chloroform. Fig. 1 shows the plots of variation of reduced viscosity ($\eta_{sp}/c$) with total polymer concentration, $c$ in the solution for the blends in the compositions of PIB/Ultem: 100/0, 80/20, 70/30, 60/40, 40/60, 20/80 and 0/100 in chloroform by weight, respectively. The linear relationships are observed for pure polymers and all of the compositions studied.

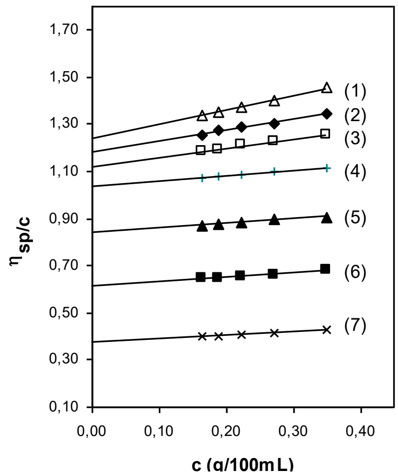



*Fig. 1. Reduced viscosity values ($\eta_{sp}/c$) against total concentrations of the pure polymers of PIB, Ultem and their mixtures at 30 °C in chloroform the following compositions of PIB/Ultem: 100/0 (1), 80/20 (2), 70/30 (3), 60/40 (4), 40/60 (5), 20/80 (6), 0/100 (7) by weight.*

The values of $b_m^{\exp}$ and $[\eta]_m^{\exp}$ are determined from the slope and intercept of the linear straight line plotted according to Eq.1 for solutions containing one of the polymer in binary mixtures or both of them at a given ratio in ternary mixtures. The data were collected in Table 1.

*Table 1. Experimental dilute solution viscosity data of the blends and constituent polymers at 30 °C in chloroform .*

| PIB/Ultem 30°C in chloroform | $b^{\exp}$ ($cm^6/g^2$) | $[\eta]^{\exp}$ ($cm^3/g$) | $r^2$ |
|---|---|---|---|
| 100/0 | 0,6025 | 1,2408 | 0,9973 |
| 80/20 | 0,4662 | 1,1814 | 0,9855 |
| 70/30 | 0,3869 | 1,1204 | 0,9782 |
| 60/40 | 0,2219 | 1,0384 | 0,9847 |
| 40/60 | 0,1981 | 0,8395 | 0,9199 |
| 20/80 | 0,1882 | 0,6131 | 0,9038 |
| 0/100 | 0,1483 | 0,3753 | 0,9669 |

The miscibility criterion $\Delta b$ was described by Krigbaum and Wall. The polymer blend is miscible if $\Delta b_m = b_m^{\exp} - b_m^{id} > 0$ and attractive molecular interactions are present or immiscible if $\Delta b_m = b_m^{\exp} - b_m^{id} < 0$ and repulsive molecular interactions are considered. In the case of $\Delta b_m = 0$, neither attractive nor repulsive molecular interactions are present between polymers. The other miscibility criterion of a blend, $\Delta b'$ was found from Eq. (4). Catsiff and Hewett were proposed that $\Delta b' > 0$ shows miscibility and $\Delta b' < 0$ shows immicibility. The miscibility criterion on $\Delta[\eta]$ was described by Garcia et al. and found from Eq. (5). According to Garcia et. al, if $\Delta[\eta]_m = ([\eta]_m^{\exp} - [\eta]_m^{id}) < 0$, the system is miscible, and if $\Delta[\eta]_m = ([\eta]_m^{\exp} - [\eta]_m^{id}) > 0$, the system is immiscible. Sun et al. and Jiang et al. were described the parameter, $\alpha$ and $\beta$, respectively. The sign of $\alpha$ indicates miscibility of the blend, i.e. $\alpha > 0$ if attractive intermolecular interactions and miscibility exist whereas $\alpha < 0$ if the repulsive intermolecular interactions and immiscibility exist between polymers in the mixture. Similarly, $\beta > 0$ indicates miscibliity, and $\beta < 0$ indicates immiscibility of the system.

The all miscibility criteria of PIB/Ultem blends obtained using viscosity measurements were given in Table 2. According to the values of miscibility criteria of PIB/Ultem blends, $\Delta b < 0$, $\Delta b' < 0$, $\Delta[\eta]_m > 0$, $\alpha < 0$ and $\beta < 0$ shows that PIB/Ultem blends are immiscible in all prepared compositions.

*Table 2. Numerical values of polymer-polymer interaction coefficient for PIB/Ultem blends.*

| PIB/Ultem at 30 °C in chloroform | $-\Delta b_m$ ($cm^6/g^2$) | $-\Delta b'_m$ ($cm^6/g^2$) | $\Delta[\eta]_m$ ($cm^3/g$) | $-\alpha$ | $-\beta$ |
|---|---|---|---|---|---|
| 80/20 | 0,0209 | 0,0455 | 0,1137 | 0,1630 | 0,0402 |
| 70/30 | 0,0472 | 0,0793 | 0,1393 | 0,1481 | 0,0678 |
| 60/40 | 0,1622 | 0,1989 | 0,1438 | 0,2178 | 0,1218 |
| 40/60 | 0,0952 | 0,1319 | 0,1180 | 0,1011 | 0,1549 |
| 20/80 | 0,0265 | 0,0509 | 0,0647 | -0,1280 | 0,0700 |

The FT-IR spectra of PIB, Ultem and PIB/Ultem:80/20, 70/30, 60/40, 40/60, 20/80 are presented in Fig. 2.

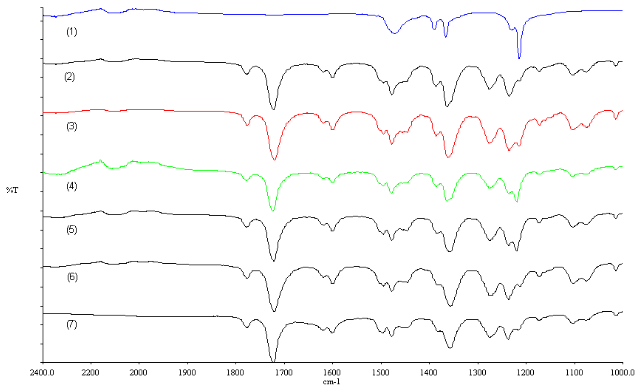



*Fig. 2. FT-IR spectra of PIB (1), PIB/Ultem (80/20) (2), PIB/Ultem (70/30) (3), PIB/Ultem (60/40) (4), PIB/Ultem (40/60) (5), PIB/Ultem (20/80) (6), Ultem (7).*

It was shown in Fig. 2, there is no significant changes in its FT-IR spectra were observed for all compositions of PIB and Ultem blends in comparison with the pure Ultem. It indicate that PIB and Ultem are immiscible.

## 4. Conclusions

The miscibility of PIB/Ultem blends was investigated by viscosity and FT-IR. According to FT-IR and viscosity results, PIB/Ultem blends are immiscible in the whole composition range in chloroform solutions. The agreement on the results of the viscosity measurements for PIB/Ultem system supports the validity of viscometric study. Consequently, this study suggests that miscibility criteria proposed by Krigbaum and Wall, Garcia et al., Sun et al., Jiang and Han can be used accuracy in determination of the miscibility of polymers at least for the polymer pair studied in this paper.

**Acknowledgements**

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