Miscibility criteria of blends of poly(2,6-di methyl-1,4-phenylene oxide)/A copolyester of bisphenol-A with terephthalic and isophthalic acids by viscometric analysis

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The miscibility criteria of a copolyester of bisphenol-A with terephthalic and isophthalic acids (50/50) (PAr) and poly (2,6-di methyl-1,4-phenylene oxide) (PPO) was investigated at 30 ^{o}C in chloroform and 70 ^{o}C in dioxane dilute solutions by viscometric analysis. The intrinsic viscosity and viscometric parameters of this blend system were determined for several PAr/PPO mixtures in compositions such as 80/20, 60/40, 50/50, 40/60, 20/80 in chloroform and 75/25, 50/50 and 25/75 in dioxane solutions. The miscibility criteria on the basis of the sign of Δb, $\Delta b'$, $\Delta[\eta]$, α and β which are the difference between their experimental and ideal values were calculated by applying equations proposed by Krigbaum–Wall, Catsiff–Hewett, Garcia et al., Sun et al. and Jiang-Han. The data showed that the prepared blends were immiscible in the studied compositions at 30 and 70 ^{o}C. However, variation of the values of miscibility criteria indicates that the blend tends to be miscible by increasing temperature and PPO content in blend.

1. Introduction

Polymer blending is one of the most important ways to develop new polymeric materials with a desirable combination of properties. The study of miscibility of binary mixtures is important because miscible polymer blends often exhibit more desirable characteristics than individual homopolymers. Most of the blend components are also highly incompatible with each other [1]. 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 [2-5].

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is one of the most important engineering plastics exhibiting a high strength, excellent heat resistance, high glass transition temperature (T$_g$) and good dimensional stability with low moisture absorption. PPO has excellent compatibility with other polymers for blending [6]. PAr being the trademark of an amorphous aromatic polyester of bisphenol-A with terephthalic and isophthalic acids (50/50) offers outstanding performance such as retention of gloss, transparency and lower haze when it is exposed to ultraviolet lighting and accelerated aging tests as well as it posses excellent mechanical properties with a high glass transition temperature[7]. PAr and PPO blends have some potential use in preparing ultraviolet-resistant and high heat-resistant composites.

Chemical structures of PPO and PAr were given in Scheme 1.

(a)

(b)
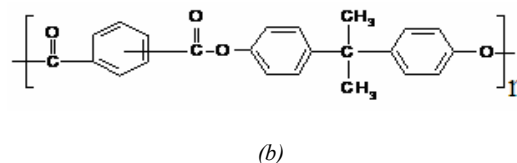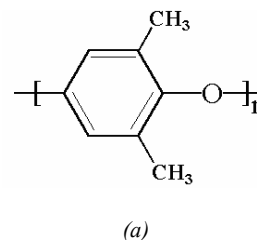
Scheme 1. Chemical structure of (a) PPO and (b) Par.

In our previous paper, we investigated miscibility of PAr and PPO blends by inverse gas chromatography at high temperatures. It was seen that PAr and PPO blends are miscible all studied proportions between 220 and 260 ^{o}C. [8]. No data is available in the literature related to the miscibility of PPO and PAr at low temperature.

In this study, the miscibility of PPO and PAr were studied 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 ^{o}C and 70 ^{o}C.

2. Experimental

2.1 Materials and instrumentation

PAr and PPO were supplied by Amoco and Scientific Polymer Products, respectively. The molecular weights of PAr and PPO were determined as 14500 gmol[-1] and 20200 gmol[-1], respectively, by gel permeation chromatography which is an Agilent model 1100 instrument consisting of pump and refractive-index and UV detectors and three Waters Styragel columns (HR4, HR3, and HR2). Both of the polymers were purified by dissolving in chloroform as a dilute solution and precipitating in a large amount of methanol.

All viscosity measurements were performed at 30 °C and 70 °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 in a concentration of 0,5 g /100 cm^3. 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 within ± 0.5%.

2.3 Theoretical background on viscosity

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 [9].

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

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 [10] have defined the ideal value of the interaction parameter b_m^{id} as

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

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

$$b_{12}^{id} = b_{11}^{1/2} b_{22}^{1/2} \qquad (3)$$

Catsiff and Hewett [11] have defined the ideal value of the interaction parameter b_{12}^{id} as an arithmetic mean

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

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 been defined as [12].

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

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

Sun et al. [13] have proposed another miscibility criterion, α for polymer-polymer miscibility defined as;

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

where

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

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

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

Jiang and Han [14] derived an improved criterion by substituting Eq.(8) to (6) and parameter α was replaced with β

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

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 and 70 °C in dioxane. Fig. 1 and Fig. 2 show the plots of variation of reduced viscosity (η_{sp} / c) with total polymer concentration, c in the solution for the blends in the compositions of PAr/PPO: 100/0, 80/20, 60/40, 50/50, 40/60, 20/80 and 0/100 in chloroform and PAr/PPO: 100/0, 75/25, 50/50, 25/75 and 0/100 in dioxane by weight. The linear relationships are observed for pure polymers and blends in studied compositions as expected from Eq. 1. The solutions contain one of the constituent polymers in the solvent, i.e. in binary mixture or both of them at a given ratio in the solvent, i.e. in ternary mixtures. The data were collected in Table 1.
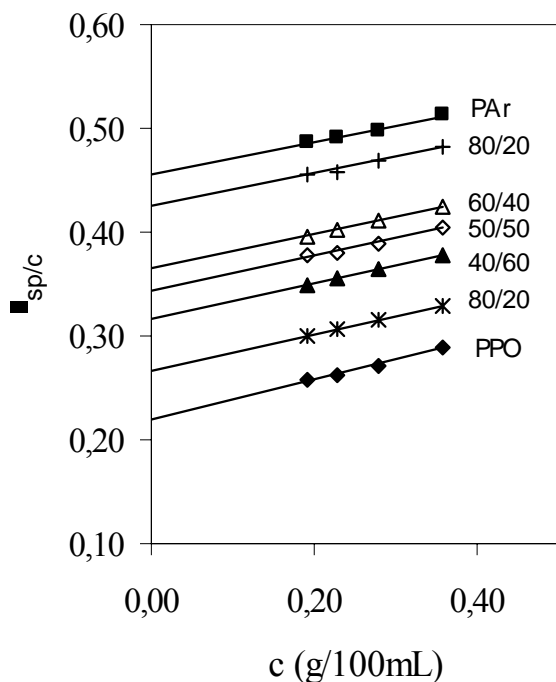
Fig. 1. Reduced viscosity (η_{sp}/c) against to total concentration of the constituent p olymers and their mixtures in the following compositions, PAr/PPO: 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, 0/100 by weight in chloroform at 30 ^{o}C.

The values of b_m^{exp} and $[\eta]_m^{exp}$ are determined from the slope and intercept of the linear straight lines given in the Figs. 1 and 2.
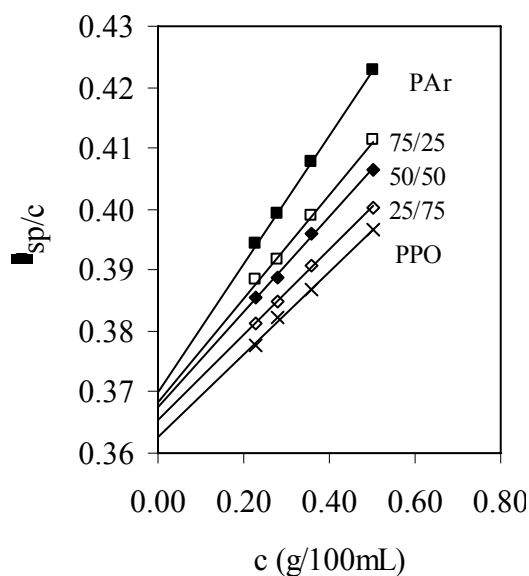

Fig. 2. Reduced viscosity (η_{sp}/c) against to total concentration of the constituent polymers and their mixtures in the following compositions, PAr/PPO:100/0, 75/25, 50/50, 25/75, 0/100 by weight in dioxane at 70 ^{o}C.

Table 1. Experimental dilute solution viscosity data of the blends and constituent polymers in chloroform at 30 ^{o}C and in dioxane at 70 ^{o}C.

Par/PPO	b_m^{exp} (cm^6/g^2)	$[\eta]_m^{exp}$ (cm^3/g)	r^2
in chloroform at 30°C			
100/0	0.1558	0.4561	0.9779
80/20	0.1590	0.4246	0.9774
60/40	0.1654	0.3647	0.9978
50/50	0.1709	0.3427	0,9847
40/60	0.1722	0.3162	0.9978
20/80	0.1754	0.2669	0.9941
0/100	0.1941	0.2188	0.9830
in dioxane at 70°C			
100/0	0.1052	0.3652	0.9999
75/25	0.0851	0.3636	0.9998
50/50	0.0781	0.3626	0.9981
25/75	0.0699	0.3605	0.9996
0/100	0.0678	0.3578	0.9959

The miscibility criterion Δb was described by Krigbaum and Wall. The polymer blend is miscible if $\Delta b = b_m^{exp} - b_m^{id} > 0$ and attractive molecular interactions are present or immiscible if $\Delta b = b_m^{exp} - b_m^{id} < 0$ and repulsive molecular interactions are considered. In the case of $\Delta b = 0$, neither attractive nor repulsive molecular interactions are present between polymers. The other miscibility criterion $\Delta b'$ defined by Catsiff and Hewett proposes that $\Delta b' > 0$ shows miscibility and $\Delta b' < 0$ shows immiscibility. The miscibility criterion $\Delta[\eta]$ was described by Garcia et al. and found from Eq. (5). According to Garcia et. al, if $\Delta[\eta] = ([\eta]_m^{exp} - [\eta]_m^{id}) < 0$, the system is miscible, and if $\Delta[\eta] = ([\eta]_m^{exp} - [\eta]_m^{id}) > 0$, the system is immiscible. Sun et al. and Jiang et al. were described the parameter, α and β, respectively. The sign of α 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 miscibility, and $\beta < 0$ immiscibility of the system.

The miscibility criteria of PAr/PPO blends obtained using viscosity measurements at 30 and 70 ^{o}C were given in Table 2.

Table 2. Numerical values of polymer-polymer interaction coefficient for PAr/PPO blends in chloroform at30^{o}C in CHCl$_3$ and in dioxane at 70°C .

PAr/PPO	$-\Delta b$ (cm^6/g^2)	$-\Delta b'$ (cm^6/g^2)	$\Delta[\eta]$ (cm^3/g)	$-\alpha$	$-\beta$
in chloroform at 30°C					
80/20	0.0041	0.0045	0.0160	0.0949	0.1646
60/40	0.0052	0.0057	0.0035	0.0643	0.1832
50/50	0.0035	0.0041	0.0053	0.0766	0.1259
40/60	0.0061	0.0066	0.0025	0.0891	0.0097
20/80	0.0107	0.0111	0.0006	0.1628	-0,3242
in dioxane at 70°C					
75/25	0.0100	0.0108	0.0003	0.0765	0.0010
50/50	0.0074	0.0084	0.0011	0.0601	0.0262
25/75	0.0065	0.0073	0.0009	0.0527	0.0411

According to the signs of miscibility criteria which are $\Delta b < 0$, $\Delta b' < 0$, $\Delta[\eta] > 0$, $\alpha < 0$, $\beta < 0$, PAr/PPO blends are immiscible in studied compositions in solid state at 30 and 70 ^{o}C**.** However, it can be seen from the Table 2 that magnitudes of the criteria are somewhat higher at 70°C than 30°C. This implies that the blends tend to be miscible by increasing temperature. In our previous paper, we determined that these blends were miscible at temperature region between 220°C and 260 ^{o}C by inverse gas chromatography measurements [8]. Therefore, it can be stated that viscometric miscibility criteria in this study support the results given in our previous work.

4. Conclusions

The miscibility of PAr/PPO blends was investigated by viscosity measurements. The results suggest that studied blends are immiscible in the whole composition range in the solid state at 30°C and 70°C. Increasing of temperature and PPO content increase miscibility of PAr/PPO blends. According to the results in this study, the miscibility criteria proposed by Krigbaum and Wall (Δb), Catsiff and Hewett ($\Delta b'$), Garcia et al. ($\Delta[\eta]$), Sun et al. (α), Jiang and Han (β) are in agreement and they can be used reliably in determination of miscibility of polymers.

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