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Miscibility criteria of blends of polystyrene/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 polystyrene (PS) was investigated at 25 ^oC in dilute solutions by viscometric analysis. The intrinsic viscosity and viscometric parameters of this blend system were determined for several PAr/PS mixtures in compositions such as 80/20, 60/40, 40/60, 20/80 in chloroform solutions at several concentrations. The miscibility criteria on the basis of the sign of Δb, $\Delta b'$ and $\Delta[\eta]$ which are the difference between their experimental and ideal values were calculated by applying theoretical equations proposed by Krigbaum–Wall, Catsiff–Hewett and Garcia et al. The parameters α and β were also evaluated. The data obtained from the viscometry studies showed that the prepared blends were immiscible in all the studied composition range.

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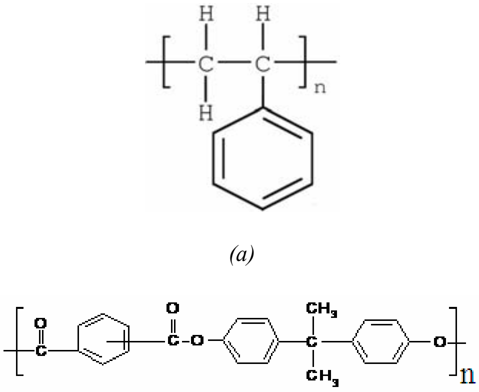
1. Introduction

Polystyrene (PS) is an inexpensive and aromatic polymer made from the aromatic monomer styrene, a liquid hydrocarbon that is commercially manufactured from petroleum by the chemical industry. PS is a thermoplastic substance, normally existing in solid state at room temperature, but melting if heated (for molding or extrusion), and becoming solid again when cooling off. Pure solid PS is a colorless, hard plastic with limited flexibility. Solid PS is used, for example, in disposable cutlery, plastic models, CD and DVD cases, and smoke detector housings. PAr being an amorphous aromatic polyester of bisphenol-A with terephthalic and isophthalic acid (50/50) offers outstanding performance, i.e. 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, 190 °C [1,2]. There is no any research in the literature on the miscibility of PAr and PS. However, their blends have some potential use in preparing cheap, ultraviolet- and high heat-resistant composites. Meanwhile, PAr will be effect on the mechanical properties of PS. Chemical structures of PS and PAr were given in Scheme 1.



(a)

(b)

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

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 [3]. 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 [4-6].

In this study, the miscibility criteria of PS and PAr 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 25 ^{o}C.

2. Experimental

2.1 Materials and Instrumentation

PAr and PS were supplied by Amoco and Scientific Polymer Products, respectively. The molecular weights of PAr and PS were determined as 14500 gmol^{-1} and 250000 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 precipitated in a large amount of methanol.

All viscosity measurements were performed at 25 ^{o}C using a home-made modified Ubbelohde-type capillary viscometer in a constant temperature bath controlled with ± 0.02 ^{o}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 four lower concentrations. The elution time of each solution was taken as the average of four readings agreed to within ±0.5%.

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 [7]

$$(\eta_{\mathrm{sp}})_{\mathrm{m}} / c_{\mathrm{m}} = [\eta]_{\mathrm{m}} + b_{\mathrm{m}} c_{\mathrm{m}} \tag{1}$$

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 $[\eta]_{\mathrm{m}}$.

Krigbaum and Wall [8] have defined the ideal value of the interaction parameter $b_{\mathrm{m}}^{\mathrm{id}}$ as

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

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

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

Catsiff and Hewett [9] have defined the ideal value of the interaction parameter b_{12}^{id} as an arithmetic mean

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

Garcia et al. have also proposed another miscibility criterion based on the difference between the experimental and ideal values of $[\eta]_{\mathrm{m}}$ assuming that the intrinsic viscosity can be treated as an excess property. The value of $[\eta]_{\mathrm{m}}^{\mathrm{id}}$ has defined as [10]

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

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

Sun et al. [11] have proposed another miscibility criterion, α for polymer-polymer miscibility defined as

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

where

$$k_1 = b_1 / [\eta]_1^2 ; \; k_2 = b_2 / [\eta]_2^2 ; \; k_{\mathrm{m}} = b_{\mathrm{m}} / [\eta]_{\mathrm{m}}^2 , \; k_{12} = b_{12} / [\eta]_1 [\eta]_2 \tag{7}$$

With the weighted additive rule as shown in Eq. (5) exhibited, an expression of k_{m} can be concluded from Eqs. (7) as

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

Jiang and Han [12] derived an improved criterion by substituting Eq.(8) to (6), and parameter α was replaced with β

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

Where

$$\Delta k = k_{12} - \sqrt{k_1 k_2} \tag{10}$$

3. Results and discussion

The intrinsic viscosity and viscometric parameters of this system have been determined at 25 °C in chloroform. Fig. 1 shows 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/PS: 0/100, 20/80, 40/60, 60/40, 80/20 and 100/0 by weight.

The linear relationships are observed for pure polymers and all of the compositions studied.

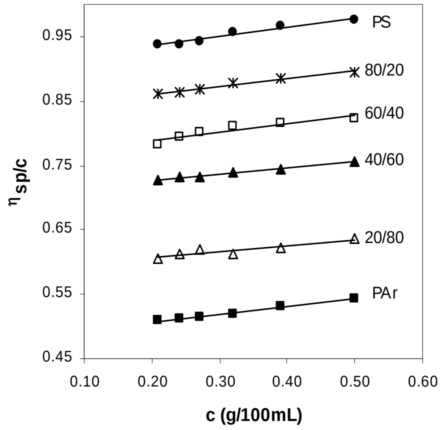


Fig. 1. Reduced viscosity values ($\eta_{\rm sp}/c$) against total concentrations of the pure polymers of PAr, PS and their mixtures in the following compositions of PAr/PS: 0/100, 20/80, 40/60, 60/40, 80/20 and 100/0 by weight.

The values of $b_{\rm m}^{\rm exp}$ and $[\eta]_{\rm m}^{\rm exp}$ 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 25 ^{o}C.

PAr/PS	$b^{\rm exp}$ (cm^6/g^2)	$[\eta_{\rm exp}]$ (cm^3/g)	r^2
100/0	0.118	0.484	0.985
80/20	0.089	0.590	0.859
60/40	0.097	0.707	0.991
40/60	0.127	0.763	0.855
20/80	0.126	0.835	0.980
0/100	0.144	0.907	0.945

The miscibility criteria Δb was described by Krigbaum and Wall. The polymer blend is miscible if $\Delta b_{\rm m} = b_{\rm m}^{\rm exp} - b_{\rm m}^{\rm id} > 0$ nd attractive molecular interactions are present or immiscible if $\Delta b_{\rm m} = b_{\rm m}^{\rm exp} - b_{\rm m}^{\rm id} < 0$ nd repulsive molecular interactions are considered. In the case of $\Delta b_{\rm m} = 0$, neither attractive nor repulsive molecular interactions are present between polymers. The other miscibility criteria 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 criteria of $\Delta[\eta]$ was described by Garcia et al. and found from Eq. (5). According to Garcia et. al, if $\Delta[\eta]_{\rm m} = ([\eta]_{\rm m}^{\rm exp} - [\eta]_{\rm m}^{\rm id}) < 0$, the system is miscible, and if $\Delta[\eta]_{\rm m} = ([\eta]_{\rm m}^{\rm exp} - [\eta]_{\rm m}^{\rm id}) > 0$, 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 miscible, and $\beta < 0$ indicates immiscibility of the system.

The all miscibility criteria of PAr/PS blends obtained using viscosity measurements were given in Table 2. According to the values of miscibility criteria of PAr/PS blends, $\Delta b < 0$, $\Delta b' < 0$, $\Delta[\eta]_{\rm m} > 0$, $\alpha < 0$, $\beta < 0$ shows that PAr/PS blends are immiscible in all prepared compositions.

Table 2. Numerical values of polymer-polymer interaction coefficient for PAr/PS blends.

PAr/PS	$-\Delta b$ (cm^6/g^2)	$-\Delta b'$ (cm^6/g^2)	$\Delta[\eta]$ (cm^3/g)	$-\alpha$	$-\beta$
80/20	0.034	0.034	0.021	0.375	0.018
60/40	0.031	0.031	0.054	0.214	0.051
40/60	0.006	0.006	0.026	0.018	0.031
20/80	0.013	0.013	0.013	0.032	0.024

4. Conclusions

The miscibility of PAr/PS blends was investigated by viscosity. The results obtained by viscosity that blends are immiscible in the whole composition range in chloroform solution. 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 in determination of the miscibility of polymers.

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