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Viscometric study on the miscibility of polystyrene/brominated polystyrene blends

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Abstract

The miscibility of polystyrene/brominated polystyrene blends (PS/PBrS) was investigated by using dilute-solution viscometry (DSV) method. The intrinsic viscosity and the viscometric parameters of this system have been determined at $20 \pm 0.1\ ^\circ C$ for prepared several PS/PBrS compositions (85/15, 75/25, 50/50, 25/75, 10/90). The binary systems were prepared in chloroform at five different concentrations; 0.15, 0.30, 0.60, 0.90, 1.20 g 100 ml^{-1}. The miscibility criteria on the basis of the sign of $\Delta[\eta]_m$, Δb and $\Delta b'$, which are based on the difference between experimental and ideal values of $[\eta]_m$, and b_m were calculated by applying the Garcia et al., Catsiff–Hewett and Krigbaum–Wall theoretical equations. The thermodynamic parameter, α, modified thermodynamic parameter, β, and interaction parameter, μ, were also estimated. The data obtained from the viscometry studies showed that the examined blends were immiscible in all the compositions range besides the composition (10/90). The results from the DSV method are correlated with the miscibility data obtained for the same blend by differential scanning calorimetry (DSC) find.
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1. Introduction

Polymer blends are currently receiving great attention because they offer low-cost alternatives to the development of entirely new materials with improved properties [1]. The miscibility of polymer mixtures is an important factor in the preparing of polymer blends. The most commonly used techniques for examining the miscibility of the polymers are morphological analysis [2], thermal analysis [3–5],

spectroscopy [6], and inverse gas chromatography [7]. The viscometric method is a simple, inexpensive and sensitive analytical technique and also alternative to other methods [8–12]. The application of the dilute-solution viscosity (DSV) method for the study of interactions and miscibility of the polymeric system has been described in more details elsewhere [8–17].

In DSV method, the viscometric interaction parameters of pure polymer solutions are compared with the interaction parameters of solution of polymer blends. Beside viscometric interaction parameters there are many other criteria, such as the thermodynamic parameter, α, the modified

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thermodynamic parameter, β, and interaction parameter, μ, for determining polymer–polymer miscibility using the DSV method [14–21]. Positive deviation between experimental and ideal values obtained by experimental and theoretical studies indicates the miscible systems and negative deviation shows the immiscible systems.

In the present study, the viscosity measurements of dilute solution of blends of PS/PBrS of different concentrations have been performed based on DSV method. The miscibility of the investigated polymer blends, PS/PBrS in different compositions has been confirmed by the DSC technique and morphological studies in literature [5].

2. Theoretical background

The concentration of viscosity of the dilute solution is given by the classical Huggins equation [22].

$$\eta_{sp} = [\eta]c + bc^2 \tag{1}$$

where $[\eta]$ is intrinsic viscosity (limiting viscosity number, LVN), c is a concentration and b is related to the Huggins coefficient, k reflects binary interactions between polymer segments.

$$b = k[\eta]^2 \tag{2}$$

Eq. (1) extended by Krigbaum and Wall can be applied to polymer mixtures in a common solvent [17]. The total concentration ($c = c_1 + c_2$) is introduced as,

$$\eta_{spm} = [\eta]_m(c_1 + c_2) + b_m(c_1 + c_2)^2 \tag{3}$$

Subscripts 1, 2 and m represent polymer 1, polymer 2, and polymer blends, respectively. b_m is related to the Huggins parameter, k_m of the polymer blend as

$$b_m = k_m[\eta]_m^2 \tag{4}$$

$[\eta]_m$ is the weight average of intrinsic viscosity of the two-component polymer mixture. The experimental values of $[\eta]_m^{exp}$ were determined by extrapolation to infinite dilution of the plots and the values of b_m^{exp} were obtained from the slopes of the plots according to Eq. (3). The criterion $\Delta[\eta]_m$ based on the difference between the experimental and ideal values of $[\eta]_m$ have proposed by Garcia et al. [18] as follows

$$\Delta[\eta]_m = [\eta]_m^{exp} - [\eta]_m^{id} \tag{5}$$

$\Delta[\eta]_m < 0$ and $\Delta[\eta]_m > 0$ values show miscibility and immiscibility, respectively. $[\eta]_m^{id}$ is the intrinsic viscosity of the ideal solution introduced as follows:

$$[\eta]_m^{id} = w_1[\eta]_1 + w_2[\eta]_2 \tag{6}$$

where, w_1 and w_2 are the weight fractions of polymer 1 and 2, respectively. $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities of the pure polymer solutions.

Depending on the comparison of the experimental and theoretical value, the compatibility criterion, Δb is proposed as [16,17]

$$\Delta b = b_{12}^{exp} - b_{12}^{id} \tag{7}$$

Some authors defined the ideal value of specific interaction parameter b_{12}^{id}, as geometric mean value of b_{11} and b_{22} parameters [17,19]. b_{12}^{id} corresponds to the interaction between like chain polymers,

$$b_{12}^{id} = (b_{11}b_{22})^{1/2} \tag{8}$$

b_{11} and b_{22} are easily determined from pure polymer/solvent systems formed by polymer 1 and polymer 2 in the solvent, respectively.

Catsiff and Hewett defined the compatibility criterion $\Delta b'$ based on the arithmetical mean value [20].

$$\Delta b' = b_{12}^{exp} - b_{12}^{id'} \tag{9}$$

where

$$b_{12}^{id'} = (b_{11} + b_{22})/2 \tag{10}$$

Positive values of Δb and $\Delta b'$ show the presence of attractive molecular interaction and miscibility whereas negative values of these parameters indicate immiscibility and phase separation in the binary systems.

The experimental value b_{12}^{exp} is obtained from the following equation

$$b_m^{exp} = b_{11}w_1^2 + b_{22}w_2^2 + 2b_{12}^{exp}w_1w_2 \tag{11}$$

The ideal value of interaction parameter, b_m^{id} has been defined by Krigbaum and Wall [17] as;

$$b_m^{id} = b_{11}w_1^2 + b_{22}w_2^2 + 2b_{12}^{id}w_1w_2 \tag{12}$$

Garcia et al. have proposed the ideal value of the interaction parameter b_m^{id} to eliminate the uncertainity of defining b_m^{id} parameter [18].

$$b_m^{id} = b_{11}w_1^2 + b_{22}w_2^2 \tag{13}$$

Sun et al. [15] suggested a new parameter, α in the absence of strong specific interaction forces between macromolecules.

$$\alpha = K_m - \frac{k_1 w_1^2[\eta]_1^2 + 2(k_1 k_2)^{1/2} w_1 w_2[\eta]_1[\eta]_2 + k_2 w_2^2[\eta]_2^2}{(w_1[\eta]_1 + w_2[\eta]_2)^2} \tag{14}$$