

# Investigation of Poly(vinyl chloride)/Polystyrene Mixture Miscibility: Comparison of Viscometry Criteria with Fourier Transform Infrared Spectroscopy and Refractive Index Measurements

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**ABSTRACT:** The refractive index (RI) and Fourier transform infrared (FTIR) spectrum of a poly(vinyl chloride) (PVC)/polystyrene (PS) mixture were measured. The variation of RI with the mixture composition was found to be nonlinear, which indicated the immiscibility of the PVC/PS mixture. This result agrees with results obtained by the FTIR technique, which indicated negligible intermolecular interactions between the PVC/PS components, and the miscibility of the polymer mixture was limited for the compositions studied. The results obtained by RI and FTIR were compared with the results obtained by the viscosity method with criteria based on interaction parameters proposed by Krigbaum and Wall, Chee, Zhu, and Garcia et al. and the thermodynamic parameter proposed by Jiang and

Han. A criterion based on a simple cluster theory proposed by Pan et al. was also applied to the PVC/PS mixture solutions to study the polymer–polymer interactions. The conclusions about PVC/PS immiscibility made by Pan et al. and Jiang and Han agreed with our conclusions obtained by FTIR and RI measurements. On the other hand, the results obtained by Chee, Zhu, and Krigbaum and Wall showed partial miscibility of the PVC/PS mixture, whereas the polymer mixture was miscible according to the Garcia et al. criterion. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2770–2777, 2011

**Key words:** FTIR; miscibility; poly(vinyl chloride) (PVC); polystyrene; refractive index

## INTRODUCTION

Polymer mixture is an attractive route to the formation of novel materials whose properties may be a useful combination of those of the polymers components. However, most polymers are immiscible and form discrete phases, often with high interfacial tension, which results in a sharp interface between two phases and leads to poor properties of the mixture.<sup>1</sup>

The properties of a polymer mixture are determined mainly by the miscibility of the components and the structure.<sup>1–3</sup> This condition is fulfilled when strong specific intermolecular interactions exist between the components of a mixture. In the case of moderate or weak interactions, the miscibility of polymers pairs is limited; it depends on the temperature, composition of the mixture, and so on.<sup>4</sup>

Polymer–polymer miscibility can be detected by a number of techniques. Fourier transform infrared

(FTIR) spectroscopy has been used extensively to detect and identify the presence of intermolecular interactions occurring between different polymer components in many miscible mixtures.<sup>5</sup> This is because the absorption bands are very sensitive to changes, and some regions of the spectrum can be used to determine the existence of specific interactions. On the other hand, refractometric techniques have been used to study the miscibility of polymers.<sup>6</sup> It was already established that the variation of the refractive index (RI) as function of the mixture composition is linear for a miscible mixture and nonlinear for immiscible systems.

It is well known that determination of the viscometry of a dilute solution is a simple and quick method for determining polymer–polymer miscibility.<sup>7,8</sup> The investigation of the viscometry behavior of a ternary system (polymer–polymer–solvent) also gives useful information about the interactions.<sup>9</sup> The principle of using dilute solution viscosity to measure the miscibility is based on the fact that molecules of both component polymers undergo mutual attraction or repulsion, which influences the solution viscosity. Attraction between two component molecules may cause swelling in macromolecular coils and result in a increase in the viscosity; otherwise, repulsion may cause shrinkage in the

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macromolecular coils and cause a decrease in the viscosity of the solution.<sup>7</sup>

Many criteria have been proposed by researchers to determine the miscibility of a polymer mixture by the viscometric method.<sup>8–17</sup> The viscometric evaluation of miscibility in ternary systems composed of a common low-molecular-weight solvent for the polymer–polymer rely on a comparison of the experimental interaction parameters ( $b^{\text{exp}}$ 's) or equivalent parameters with ideal values. On the bases of many experimental and theoretical studies, the literature data suggest that a positive deviation between the experimental and ideal values indicates a miscible system, whereas a negative deviation indicates an immiscible system.

The purpose of this study was to apply and compare the results of research methods to estimate the polymer–polymer miscibility in a dilute solution. In this study, the system analyzed was a poly(vinyl chloride) (PVC)/polystyrene (PS) mixture, and the viscosity measurements of the polymer system were performed with six viscometry methods: the Krigbaum–Wall<sup>10</sup> method of classical dilution; Garcia et al.'s<sup>11</sup> method of treating the viscosity interaction parameter; Chee's<sup>15</sup> and Zhu's<sup>16</sup> methods, which are based on the arithmetic and geometric differential intermolecular interactions, respectively; Jiang and Han's<sup>17</sup> method, which is based of the cross-Huggins parameter of the mixture; and Pan et al.'s<sup>12</sup> method, which is based on simple cluster theory. The results obtained by viscometry method were compared with the RI and FTIR spectroscopy measurements.

### Theoretical background

Huggins proposed the following expression for the viscosity of a solution of macromolecules:<sup>18</sup>

$$\eta_{\text{red}} = [\eta] + K[\eta]^2 C \quad (1)$$

where  $\eta_{\text{red}}$  is the reduced viscosity of the solution,  $C$  is the concentration of the solution,  $[\eta]$  is the intrinsic viscosity of the solution, and  $K$  is the Huggins coefficient. In ternary system (polymer A–polymer B–solvent), an analogue of eq. (1), as proposed by Krigbaum and Wall,<sup>10</sup> can be obtained in the following form:

$$\eta_{\text{red}m} = [\eta]_m + K[\eta]_m^2 C \quad (2)$$

where  $\eta_{\text{red}m}$  is the reduced viscosity of the mixture and  $[\eta]_m$  is the intrinsic viscosity of the mixture, and at infinite dilution, the molecules have no influence over each other. The  $[\eta]_m$  value obtained for an ideal polymer mixture is represented by eq. (3):<sup>19</sup>

$$[\eta]_m = w_A[\eta]_A + w_B[\eta]_B \quad (3)$$

where  $w_A$  and  $w_B$  are the weight fractions of polymers A and B, respectively, and  $[\eta]_A$  and  $[\eta]_B$  are the intrinsic viscosities of polymers A and B, respectively. The viscosity of a dilute solution containing a mixture of two polymers defines the value of the interaction parameter ( $b_m$ ) by the expression:<sup>10,13</sup>

$$b_m = b_A w_A^2 + b_B w_B^2 + 2b_{AB} w_A w_B \quad (4)$$

When eqs. (2)–(4) are combined, we have the following expression:

$$\eta_{\text{red}m} = [\eta]_A w_A + [\eta]_B w_B + (b_A w_A^2 + b_B w_B^2 + 2b_{AB} w_A w_B) C \quad (5)$$

where  $b_A$ ,  $b_B$ , and  $b_{AB}$  are the viscosity interaction parameters of polymers A and B and the mixture of polymers A and B, respectively. The values of  $b_A$  and  $b_B$  are determined from the plot of the reduced viscosity versus  $C$  (Huggins plot). The slope of the curve gives the corresponding  $b^{\text{exp}}$  value.<sup>18</sup>

$$b_A = K_A [\eta]_A^2 \quad (6)$$

$$b_B = K_B [\eta]_B^2 \quad (7)$$

The value of  $b_{AB}$  is determined by eq. (8):

$$b_{AB} = K_{AB} [\eta]_A [\eta]_B \quad (8)$$

where  $K_A$ ,  $K_B$ , and  $K_{AB}$  are the Huggins coefficients of polymers A and B and the polymer mixture, respectively.

The theoretical foundations of the applied methods are based on considerations from Krigbaum and Wall<sup>10</sup> and Cragg and Bigelow.<sup>13</sup> Krigbaum and Wall<sup>10</sup> defined the ideal value of the interaction parameter ( $b_m^{\text{id}}$ ) with the following expression:

$$b_m^{\text{id}} = b_A w_A^2 + b_B w_B^2 + 2b_{AB}^{\text{id}} w_A w_B \quad (9)$$

It is usually difficult to obtain the parameter  $b_{AB}^{\text{id}}$ . Thus, for simplification, the concept *ideal mixed polymer solution* was suggested. It is assumed that in an ideal mixed polymer solution, no interaction besides hydrodynamic interaction exists and the interaction coefficient between unlike polymer chains may be defined as  $b_{AB}^{\text{id}}$ .  $b_{AB}^{\text{id}}$  may be obtained by eq. (10) or (11):<sup>20</sup>

$$b_{AB}^{\text{id}} = \sqrt{b_A b_B} \quad (10)$$

$$b_{AB}^{\text{id}} = \sqrt{\frac{b_A + b_B}{2}} \quad (11)$$

The evaluation of the experimental interaction parameter of the mixture ( $b_m^{\text{exp}}$ ) is done on the basis of

the classical Huggins equation [eq. (1)] with the plot of  $\eta_{redm}$  versus  $C$  (Huggins plot of the mixture).

The Krigbaum–Wall viscosity interaction parameter ( $\Delta b^{KW}$ ) of the mixture is obtained from the difference between the experimental and ideal values. The polymer mixture is miscible if  $\Delta b^{KW} = b_m^{exp} - b_m^{id} \geq 0$  and immiscible if  $\Delta b^{KW} = b_m^{exp} - b_m^{id} < 0$ .

Garcia et al.<sup>11</sup> ascertained that there is an arbitrary assumption with respect to the definition of the  $b_{AB}^{id}$  value proposed by Krigbaum and Wall,<sup>10</sup> which consists of its calculation by means of the geometric means value, as shown in eq. (10). The authors proposed another miscibility criterion, where another ideal parameter ( $b_m^{id'}$ ) is calculated. According to Garcia et al.,<sup>11</sup> the expression is as follows:

$$b_m^{id'} = b_A w_A^2 + b_B w_B^2 \quad (12)$$

The Garcia et al.<sup>11</sup> interaction parameter ( $\Delta b^G$ ) of the mixture is obtained from difference between  $b_m^{exp}$  and  $b_m^{id'}$ . If  $\Delta b^G \geq 0$ , the system is miscible, and if  $\Delta b^G < 0$ , the system is immiscible. Shanfeng et al.<sup>14</sup> reported that the arbitrary assumption proposed by Krigbaum and Wall<sup>10</sup> in eq. (9) and described in Garcia et al.'s<sup>11</sup> report does not exist, and the authors discussed  $K_{AB}$ .

Pan et al.<sup>12</sup> proposed that an ideal mixed polymer solution should be defined as one in which there is not any yet attractive interaction between unlike polymers that could result in an interchain association between unlike polymers. The new viscometry criterion proposed by Pan et al.<sup>12</sup> is based on simple cluster theory<sup>21</sup> and involves two basic assumptions: (1) the Einstein viscosity law is valid for individual polymer chains in dilute solution with total  $C$ , and (2) any deviation is due to interchain association or cluster formation.

With the viscometry criterion proposed by Pan et al.,<sup>12</sup> the apparent association constant ( $K_m$ ) is calculated by eq. (13):

$$K_m = \frac{b_m^{exp}}{6[\eta]_m^{exp}} \quad (13)$$

With the polymer mixture regarded as a simple solute, the viscosity data of an ideal mixed polymer solution presents an ideal association constant ( $\langle K_m \rangle^{id}$ ) calculated by the following expression:

$$\langle K_m \rangle^{id} = \frac{(b_A w_A + b_B w_B)^2}{6([\eta]_A w_A + [\eta]_B w_B)} \quad (14)$$

Here, both  $K_m$  and  $\langle K_m \rangle^{id}$  are related to the viscosity interaction parameters for simplification. For a mixed polymer solution, the positive deviation of its experimental overall  $K_m$  from its  $\langle K_m \rangle^{id}$  due to eq.

(14) can be regarded as an indication of attractive interaction between unlike polymers; that is, the mixture is miscible. On the other hand, the negative deviation of  $K_m$  from its ideal value indicates that repulsive interactions exist between the polymers, and that means immiscibility of the system.

Chee<sup>15</sup> proposed a criterion using the parameter  $\Delta B$  [eq. (15)] to determine the polymer–polymer miscibility, whereas Zhu<sup>16</sup> proposed a study method of polymer–polymer miscibility using the parameter  $\Delta b$  [eq. (16)]:

$$\Delta B = \frac{b_{AB} - (b_A + b_B)}{2} \quad (15)$$

$$\Delta b = b_{AB} - \sqrt{b_A b_B} \quad (16)$$

When  $\Delta B \geq 0$  or  $\Delta b \geq 0$ , it indicates there are attractive interactions between different polymers (miscibility); otherwise, there are repulsive interactions (immiscibility).

Sun et al.<sup>22</sup> proposed the  $\alpha$  criterion, which is a thermodynamic parameter and is the function of the cross-Huggins parameter of the polymer mixture, mixture composition, and  $[\eta]$  of the constituent polymer. The thermodynamic parameter proposed by Jiang and Han<sup>17</sup> ( $\beta$ ) was a revision of the  $\alpha$  criterion proposed by Sun et al.<sup>22</sup> We rewrote the  $\beta$  parameter [eq. (17)] as a function of the viscosity interaction parameters:

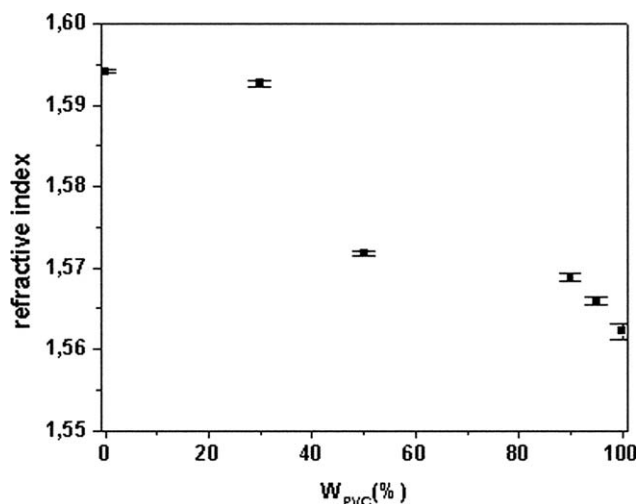
$$\beta = \frac{2 \left( \frac{b_{AB}}{[\eta]_{AB}^2} - \sqrt{\frac{b_A}{[\eta]_A^2}} \times \sqrt{\frac{b_B}{[\eta]_B^2}} [\eta]_A [\eta]_B w_A w_B \right)}{(w_A [\eta]_A + w_B [\eta]_B)^2} \quad (17)$$

When  $\beta \geq 0$ , the mixture is miscible, and when  $\beta < 0$ , the mixture is immiscible.

## EXPERIMENTAL

### Material and preparation of the films

In this study, PVC ( $5 \times 10^4$  g/mol) and PS ( $1.4 \times 10^5$  g/mol) samples were supplied by Tiletron S. A. (Brazil) and Companhia Brasileira de Estireno S. A. (Brazil), respectively. The polymers were dispersed in methanol and refluxed at 50°C for 24 h for purification. The PVC, PS, and PVC/PS mixture films ( $\sim 0.1$  mm) were prepared by solvent casting from methyl ethyl ketone (MEK) solvent by slow evaporation in air at room temperature. The MEK was dried with  $\text{Na}_2\text{SO}_4$  and purified by distillation. Any remaining MEK was removed by the drying of the films at 80°C for about 10 h. All of the samples were stored in a desiccator for 72 h before use in the experiments. The PVC/PS mixtures were prepared



**Figure 1** Variation of RI of the PVC/PS mixture with the PVC weight fraction.

at different weight compositions: 95/5, 90/10, 50/50, and 30/70.

### Viscosimetry measurements

The viscosity of the samples was calculated from the relative viscosity ( $\eta_{rel} = v/v_0 \approx t/t_0$ ), where  $v$  and  $v_0$  are the cinematic viscosities of the polymer solution and the solvent, respectively, and  $t$  and  $t_0$  are the solution and solvent tetrahydrofuran (THF) flow times, respectively, which result in the cinematic viscosity measure. These measures were carried out with an Ostwald-type capillary (75 mm) viscometer immersed in a thermal bath at a temperature of  $25.0 \pm 0.1^\circ\text{C}$ , and the flow times were measured with an accuracy of  $\pm 0.01$  s. After the  $\eta_{rel}$  values were obtained, the specific viscosity ( $\eta_{sp} = \eta_{rel} - 1$ ) and  $\eta_{red}$  ( $\eta_{red} = \eta_{rel}/C$ ), where  $C$  is 0.1 g/dL, were calculated.  $[\eta]$  was determined by extrapolation to infinite dilution (zero-solute  $C$ ) by Huggins plots, that is,  $\eta_{red}$  versus  $C$ .

In addition, MEK and THF are good solvents for PVC and PS; however, cast films from MEK presented better quality than those cast from THF. Thus, MEK was used to make the films, and THF was used in the viscosity measurements.

### Spectroscopy

The infrared spectra of PVC, PS, and PVC/PS mixtures were obtained by FTIR spectroscopy. The analysis were done in a Bruker IFS66 instrument at a resolution of  $2\text{ cm}^{-1}$  in transmittance mode. PVC/PS mixtures were granulated with dehydrated KBr powder in a mortar press molded to prepare disk specimens. In all of the FTIR measurements, a minimum of 50 scans were signal-averaged.

### RI

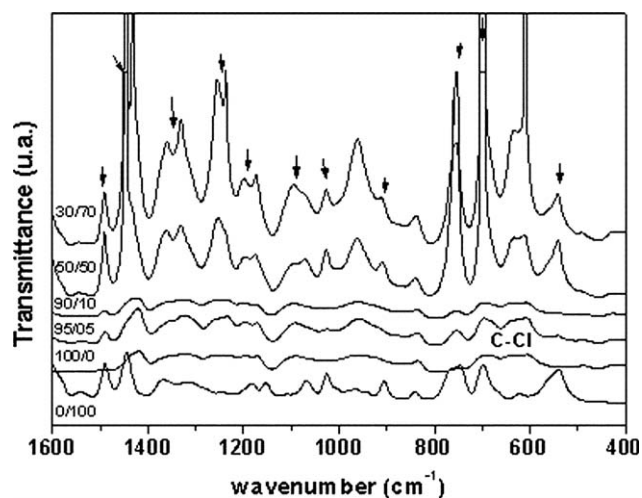
RI was evaluated by an Abbe's refractometer at  $25^\circ\text{C}$  with  $\alpha$ -bromonaphthalene as a contact liquid.

## RESULTS AND DISCUSSION

### RI and FTIR measurements of the PVC/PS mixture

We used a simple technique to investigate the miscibility of the PVC/PS mixtures, and the variation of RI of the polymer mixture is shown in Figure 1. If the polymer mixture was miscible, the system was a single-phase mixture and exhibited RI values intermediate to those of the components. The linear variation of RI as function of the mixture components was expected.<sup>6</sup> As shown in Figure 1, it was evident that the variation of RI as a function of mixture composition was nonlinear. This result was attributed to the immiscible behavior of the PVC/PS mixture. If a polymer mixture is immiscible, the system is phase-separated with differing RIs in each one, and this results in a mismatch in the RIs of the phases. Thus, the PVC/PS mixture did not exhibit RI values intermediate between the PVC and PS in the compositions studied.

Figure 2 shows the FTIR spectra of the PVC, PS, and PVC/PS mixtures films in the  $1600\text{--}400\text{-cm}^{-1}$  region. The main vibrational bands of PVC and PS ( $1600\text{--}400\text{ cm}^{-1}$ ) were identified and are shown in Table I. The PS addition to PVC influenced its spectrum, and the signals originating from the aromatic bond appeared (see the arrow in Fig. 2). The  $700\text{--}600\text{-cm}^{-1}$  frequency could be used to determine the existence of interactions between the chlorine group of PVC and the hydrogen groups of the backbone of PS in the PVC/PS mixture. The frequency region was attributed to C–Cl stretching vibration in the



**Figure 2** FTIR spectra of PVC, PS, and the PVC/PS mixture.

TABLE I  
Main Vibrational Bands of PVC and PS

Main bands in the PVC spectrum (cm <sup>-1</sup> )	Assignment	Main bands in the PS spectrum (cm <sup>-1</sup> )	Assignment
1429	CH <sub>2</sub>	1600 and 1505	C=C (in-plane aromatic ring)
1330 and 1255	C—H (of CHCl)	1440 and 1431	CH <sub>2</sub>
1095	C—C	1000 and 994	C—H (aromatic out-of-plane)
961	CH <sub>2</sub> (rocking)	829 and 765	C=C (out-of-plane aromatic ring)
689, 636, and 613	C—Cl	699 and 694	C—H (out-of-plane)
		620 and 557	C=C—H (twisting vibration)

PVC molecule.<sup>23</sup> The PVC frequency region did not shift with PS addition in the system. This result indicates negligible intermolecular interactions between the components of the PVC/PS mixture, and the miscibility of the polymer pair was limited for the compositions studied. The results obtained by FTIR spectroscopy were in agreement with the results obtained by RI measurements.

#### Measurements of the PVC/PS mixture in the dilute solution

The reduced viscosity values showed a good linear nature with  $C$  of all compositions of the PVC/PS mixture studied. The  $R$  values (Table II) were the correction factors in the linear regression analysis; the values were almost equal to unity, which showed a good fit. From linear regression analysis, we obtained the values of experimental intrinsic viscosity ( $[\eta]^{\text{exp}}$ ) and  $b^{\text{exp}}$  of PVC, PS, and the PVC/PS mixture. The values of  $[\eta]^{\text{exp}}$ ,  $b^{\text{exp}}$  and other parameters calculated from the equations mentioned in the theoretical section are summarized in Table II.

The changes in  $[\eta]_m$  in the PVC/PS mixture in solution were attributed to polymer–polymer interactions, especially the thermodynamic interactions. As pointed out by Tewari and Srivastava,<sup>24</sup> thermodynamic interactions include the intramolecular excluded effect, which results in an expansion of the coil in solution, and the intermolecular excluded volume effect, which results in the contraction of the coil.  $[\eta]^{\text{exp}}$  of PVC ( $[\eta]_{\text{PVC}}^{\text{exp}}$ ) was compared with  $[\eta]^{\text{exp}}$  of the 95/5 PVC/PS mixture ( $[\eta]_{95/5}^{\text{exp}}$ ), 90/10 PVC/PS mixture ( $[\eta]_{90/10}^{\text{exp}}$ ), 50/50 PVC/PS mixture ( $[\eta]_{50/50}^{\text{exp}}$ ), and 30/70 PVC/PS mixture ( $[\eta]_{30/70}^{\text{exp}}$ ). As shown in Table II, although the  $[\eta]_{\text{PVC}}^{\text{exp}}$  value was less than the  $[\eta]_{95/5}^{\text{exp}}$  value, the  $[\eta]_{\text{PVC}}^{\text{exp}}$  value was larger than the  $[\eta]^{\text{exp}}$  values of other mixture compositions ( $[\eta]_{90/10}^{\text{exp}}$ ,  $[\eta]_{50/50}^{\text{exp}}$ , and  $[\eta]_{30/70}^{\text{exp}}$ ). The reasonable interpretation may be that the attractive interaction between PVC and PS may have caused the expansion of the PVC coils in solution with a small number of PS molecules, whereas the intermolecular excluded volume effect may have caused the contraction of PVC coils in solution with a greater

amount of PS. At a lower weight fraction of PS (95/5 composition), the attractive interaction between PVC and PS was believed to be dominant; this resulted in an increase in  $[\eta]_{95/5}^{\text{exp}}$ . On the contrary, with increasing PS fraction (in the 90/10, 50/50, and 30/70 compositions), the intermolecular excluded volume effect was believed to be dominant; this resulted in decreases in  $[\eta]_{90/10}^{\text{exp}}$ ,  $[\eta]_{50/50}^{\text{exp}}$ , and  $[\eta]_{30/70}^{\text{exp}}$ . Thus, our results show that both the polymer–polymer interactions and intermolecular excluded volume effects were PS weight-fraction-dependent.

The criteria proposed by Krigbaum and Wall<sup>10</sup> ( $\Delta b^{\text{KW}}$ ) were negative for the 90/10, 50/50, and 30/70 compositions and exceeded the range of experimental error. The  $\Delta b^{\text{KW}}$  value obtained for the 95/5 composition was equal zero in the range of the experimental error, as shown Figure 3. On the other hand, the PVC/PS mixture with all compositions satisfied the miscibility criteria proposed by Garcia et al.<sup>11</sup> for  $\Delta b^{\text{G}} \geq 0$ . The results obtained with the Krigbaum and Wall<sup>10</sup> and Garcia et al.<sup>11</sup> criteria only agreed for the 95/5 composition (see Fig. 4). The cause of equivocal conclusion from the criteria of Krigbaum and Wall<sup>10</sup> and Garcia et al.<sup>11</sup> was a different definition of the  $b_{\text{PVC/PS}}^{\text{id}}$  value.

The  $b_{\text{PVC/PS}}^{\text{id}}$  ( $b_{\text{AB}}^{\text{id}}$ ) value was calculated by a geometric mean value [eq. (10)], as pointed out in the Krigbaum–Wall method.<sup>10</sup> Other authors<sup>25</sup> prefer to define  $b_{\text{AB}}^{\text{id}}$  as an arithmetic mean value [eq. (11)], especially for those systems in which the interaction parameter values are negative because then the geometric mean has no mathematical sense. The Garcia et al.<sup>11</sup> criteria proposed lies in the fact that it is not necessary to arbitrarily define the  $b_{\text{PVC/PS}}^{\text{id}}$  parameter (either as a geometric or arithmetic mean value) obtained with the respective binary polymer solvent systems, that is,  $b_{\text{PVC}}$  and  $b_{\text{PS}}$ . However, the value of the parameter  $b_{\text{PVC/PS}}^{\text{id}}$  is a complex interaction parameter including the thermodynamic and hydrodynamic interactions and associations existing in the system to estimate miscibility; it would be very helpful to know these particular contributions. The  $b_{\text{PVC/PS}}^{\text{id}}$  parameter also is used to calculate  $\Delta B$  by an arithmetic mean value [eq. (15)] and  $\Delta b$  by a

**TABLE II**  
**Comparison of the Experimental and Ideal Viscosimetric Parameters for the PVC/PS Solution Mixtures as Dependent on the Assumed Definition of the Ideal Values**

PVC/PS	R	$[\eta]^{exp}$ (dL/g)	$b^{exp}$ (dL/g) <sup>2</sup>	$b^{id}$ (dL/g) <sup>2</sup>	$\Delta b^{KW}$ (dL/g) <sup>2</sup>	$b^{id}$ (dL/g) <sup>2</sup>	$\Delta b^G$ (dL/g) <sup>2</sup>	$\Delta B$ (dL/g) <sup>2</sup>	$\Delta b$ (dL/g) <sup>2</sup>	$K_m$ (dL/g)	$\langle K_m \rangle^{id}$ (dL/g)	$\beta$ (dL/g) <sup>2</sup>
100/0	0.982	0.7238 ± 0.0307	0.7666 ± 0.0666	-	-	-	-	0.2088 ± 0.0750	0.2681 ± 0.0984	0.1765 ± 0.0269	0.1765 ± 0.0269	-
95/5	0.986	0.7914 ± 0.0259	0.7333 ± 0.055	0.7368 ± 0.0290	0 <sup>a</sup>	0.69261 ± 0.0277	0 <sup>a</sup>	0.0681 ± 0.0273	0.1273 ± 0.0188	0.1544 ± 0.0206	0.1639 ± 0.0278	-0.02903 ± 0.0054
90/10	0.984	0.6680 ± 0.0222	0.5925 ± 0.0479	0.7075 ± 0.0274	-0.1150 ± 0.0753	0.6238 ± 0.0249	0 <sup>a</sup>	0.0681 ± 0.0273	0.1273 ± 0.0188	0.1478 ± 0.0188	0.1518 ± 0.0256	-0.04366 ± 0.0136
50/50	0.992	0.6339 ± 0.0079	0.3012 ± 0.0171	0.4948 ± 0.0174	-0.1936 ± 0.0345	0.2622 ± 0.0106	0.0390 ± 0.0277	-0.2232 ± 0.0635	-0.1639 ± 0.0603	0.0792 ± 0.0058	0.0827 ± 0.0146	-0.45324 ± 0.0004
30/70	0.993	0.5427 ± 0.0086	0.3365 ± 0.0183	0.4027 ± 0.0143	-0.0661 ± 0.0326	0.2073 ± 0.0085	0.1292 ± 0.0268	-0.1879 ± 0.0603	-0.1286 ± 0.0615	0.1033 ± 0.0075	0.0768 ± 0.0148	-0.32833 ± 0.0367
0/100	0.980	0.3327 ± 0.0118	0.2823 ± 0.0255	-	-	-	-	-	-	0.1414 ± 0.0179	0.1414 ± 0.0179	-

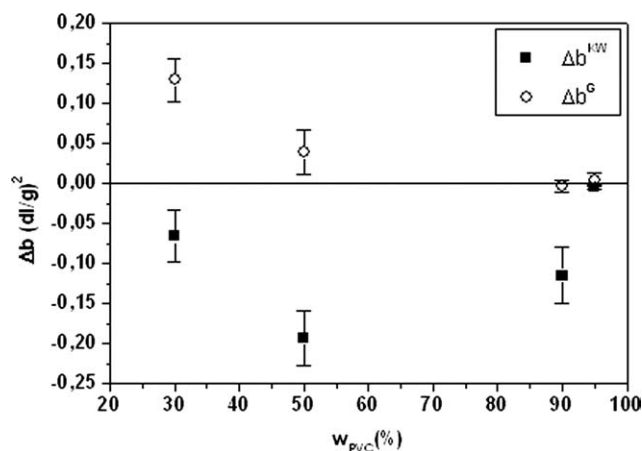
<sup>a</sup>Range of experimental error.

geometric mean value [eq. (16)], as proposed by Chee<sup>15</sup> and Zhu,<sup>16</sup> respectively. The conclusions obtained by  $\Delta B$  were the same from the results obtained by the  $\Delta b$  criteria, as shown Table II. The  $\Delta B$  and  $\Delta b$  values found were positive for the 95/5 and 90/10 compositions and satisfied the miscibility criteria proposed by the authors for  $\Delta B \geq 0$  and  $\Delta b \geq 0$ . The other compositions studied (50/50 and 30/70) satisfied the immiscibility criteria for  $\Delta B$  and  $\Delta b$  values of less than zero. These results were also in conflict with the conclusions obtained with the Krigbaum–Wall<sup>10</sup> and Garcia et al.<sup>11</sup> methods, and we must not ignore that the complex interaction parameter  $b_{PVC/PS}^{id}$  includes all kinds of physical interactions in solution, which may oppose one another. In both the  $\Delta B$  and  $\Delta b$  criteria,  $b_{AB}$  (or  $b_{PVC/PS}$ ) is defined with eq. (5), which means that  $b_{PVC}$  and  $b_{PS}$  in ternary system are the same as those in binary systems. However, there are facts that limit the effectiveness of these criteria:

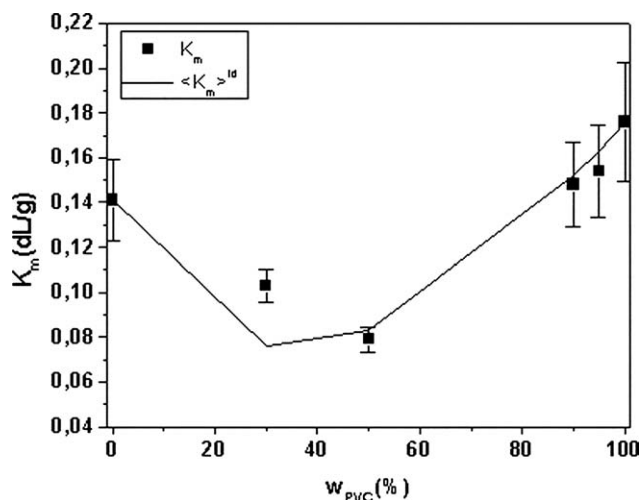
1.  $b_{PVC/PS}$  is not a thermodynamic parameter itself; it arises from the polymer–polymer interactions of finite  $C$ .<sup>10</sup> Because  $b_{PVC/PS}$  is not determined by the thermodynamic interactions alone, these criteria cannot be referred to as based on theoretical considerations.
2. In ternary systems, polymer–polymer interactions (attractive or repulsion) lead to changes in the effective hydrodynamic volume of polymers, which well influence the parameter  $b_{PVC/PS}$ .

So,  $b_{PVC}$  and  $b_{PS}$  obtained in a binary system are not the same as those obtained in ternary systems, as proposed by eqs. (15) and (16), except in the case of an ideal mixture.

We compared  $K_m$  of the PVC/PS mixture with their  $\langle K_m \rangle^{id}$ , as shown in Figure 4. The  $K_m$  and  $\langle K_m \rangle^{id}$



**Figure 3** Variation of  $\Delta b$  of the PVC/PS mixture with the PVC weight fraction.



**Figure 4** Variation of  $K_m$  of the PVC/PS mixture with the PVC weight fraction.

values are shown in Table II. The 95/5, 90/10, and 50/50 compositions did not exhibit obvious deviation. This means that no evident attractive interaction existed between PVC and PS, and the mixture could be regarded as an ideal or immiscible mixture. That is, only hydrodynamic interactions existed. On the other hand, the  $\langle K_m \rangle^{\text{id}}$  value of the 30/70 composition had a slightly positive deviation. According to the Pan et al.<sup>12</sup> method, PVC and PS in this weight composition had certain attractive interactions, but the interactions were very weak. Thus, we also considered the polymer mixture immiscible at the 30/70 composition. If there were interactions between the PVC and PS polymers that resulted in intermolecular association between the PVC and PS chains, the extraneous terms to account for its contribution need to be added to eq. (14) to calculate the  $\langle K_m \rangle^{\text{id}}$  parameter.

The values of  $\beta$  were found to be negative for all PVC/PS compositions; this indicated the immiscibility of the pairs in the mixture. These results reinforced the conclusions obtained by analyses done by the Pan et al. method. Table III summarizes the results obtained by all of the techniques and criteria used in this study. The PVC/PS mixture analyzed with the Krigbaum and Wall<sup>10</sup> (partially miscible),

**TABLE III**  
Summary of the Results Obtained in this Study  
by Different Techniques

PVC/PS	$\Delta b^{\text{KW}}$	$\Delta b^{\text{G}}$	$\Delta B$	$\Delta b$	$\langle K_m \rangle^{\text{id}}$	$\beta$	FTIR	RI
95/05	M	M	M	M	I	I	I	
90/10	I	M	M	M	I	I	I	I
50/50	I	M	I	I	I	I	I	
30/70	I	M	I	I	I	I	I	

I = immiscible; M = miscible.

Garcia et al.<sup>11</sup> (miscible), Chee<sup>15</sup> (partially miscible), and Zhu<sup>16</sup> (partially miscible) showed conflicting results with the results obtained by the Pan et al.<sup>12</sup> and Jiang and Han<sup>17</sup> criteria and the RI and FTIR measurements, where the PVC/PS mixture was considered to be a immiscible mixture. PVC/PS was previously determined to be an immiscible mixture on the basis of its repulsive and attractive polymer-polymer interactions in dilute solutions.<sup>7,26</sup> However, this study showed that the interactions between PVC, PS, and the solvent and considerations about the ideal parameters of the mixture in dilute solutions played an important role in the conflicting results presented by the criteria analyzed in this study.

In addition, in our previous study,<sup>27</sup> we investigated the effect of  $\gamma$  irradiation on a PVC/PS system. When the films of a PVC/PS mixture were irradiated to 50 kGy, certain intermolecular interactions were observed by comparison of irradiated and non-irradiated data with the Pan et al.<sup>12</sup> method.

## CONCLUSIONS

Studies of the hydrodynamic properties of the solutions for PVC/PS mixtures measured by the method of classical dilution indicated that the satisfaction of the miscibility criterion depended on the definition of the ideal parameter  $b_m^{\text{id}}$ . If the  $b_m^{\text{id}}$  parameter value was defined according to Krigbaum and Wall, the investigated mixture satisfied the immiscibility criterion for all compositions, except that with a ratio of 95/5. On the other hand, the results obtained from the Garcia et al.<sup>11</sup> criterion showed that all of the PVC/PS compositions studied satisfied the miscibility conditions. The conclusions obtained with the Chee<sup>15</sup> and Zhu<sup>16</sup> methods agreed between themselves (partially miscible) but were in conflict with the conclusions obtained by the other criteria used in this study. The PVC/PS immiscibility conclusions obtained by the Jiang and Han<sup>17</sup> criterion were in agreement with the conclusions obtained with the Pan et al.<sup>12</sup> criterion and RI and FTIR measurements. Considerations of the ideal parameters of the mixture in dilute solutions played an important role in the conflicting results presented in the criteria analyzed in this study. In addition, our results show that both polymer-polymer interactions and intermolecular interactions excluded volume effects and were PS weight-fraction-dependent when the values of  $[\eta]$  of PVC and PVC/PS mixture obtained experimentally were analyzed.

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