

Analysis of the Thermodynamic Compatibility of Poly(vinyl chloride) and Nitrile Rubbers from Inverse Gas Chromatography

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ABSTRACT: The solubility parameter method was applied to an analysis of the solution thermodynamic data of several solutes (probes) in polymers obtained by inverse gas chromatography. Experimental data previously reported by different authors were analyzed. The polymers used as the stationary phases were poly(vinyl chloride) (PVC), two nitrile rubbers (NBRs), and PVC/NBR blends. From the retention volumes of the probes, the Flory–Huggins interaction parameters at infinite dilution were calculated. The interaction parameters, in turn, were related to the solubility parameters of the solutes and stationary phases. With a series of probes, the solubility parameters of PVC and NBRs were determined. Differences existed between the experimental

values of the size-corrected free energies of solutions and the values calculated with solubility parameters. The differences were generally negative values. When these differences obtained from two NBR rubbers were plotted versus PVC, a correlation was found. Methods for obtaining the interaction parameters of polymer blends were examined. A modified plotting method gave a linear line and an interaction parameter between two polymers consistent with the results of the solubility parameters. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1242–1249, 2003

Key words: thermodynamics; poly(vinyl chloride) (PVC); nitrile rubber; blends

INTRODUCTION

The knowledge of the interaction parameter between two polymers is very important to the study of their miscibility. Many techniques have been used to study the miscibility of different polymers.^{1,2} Among them, gas–liquid chromatography is an effective tool for measuring the thermodynamic properties of solute (probe) vapors in high molecular weight polymers, particularly at the infinite dilution state.^{3–8} The molecular probe technique of gas–liquid chromatography, generally known as inverse gas chromatography (IGC), reveals information about the interaction between probes and polymeric stationary phases as well as the interaction between components of polymer mixtures.

In IGC measurements, a known amount of a non-volatile stationary phase is dissolved in a volatile solvent and coated on a porous and inert support. After the solvent is evaporated, the support is packed into a gas chromatography column. In the operation of IGC, a carrier gas passes through the column continuously. When a volatile probe liquid is injected into the column, the probe flows with the carrier gas. The retention time is a measure of the time that a sample stays

in the stationary phase. The retention time can also be represented by the volume of the carrier gas measured at the outlet pressure. After an adjustment to 0°C, the retention volume (V_g^0) is obtained. Both the retention time and volume represent the solubility of the probe vapors in the stationary phase. By the nature of IGC, the probes are volatile and have low molecular weights; the stationary phase is usually a low vapor pressure solvent or a high molecular weight polymer. When a stationary phase with a known molecular weight is used, the retention volume can be related to the activity coefficient of the probe in the stationary phase.^{5–8} When a high molecular weight polymer stationary phase is used, the retention volume of probes is related to the Flory–Huggins interaction parameter between the solvents and polymer (χ) by the following equation:^{1–8}

$$\chi = \ln\left(\frac{273.16Rv_2}{V_g^0 P_1^0 V_1}\right) - 1 - \frac{P_1^0}{RT}(B_{11} - V_1) \quad (1)$$

where R is the gas constant; T is the column temperature; v_2 is the specific volume of the stationary phase; and P_1^0 , V_1 , and B_{11} are the vapor pressure, molar volume, and second virial coefficient of the probe, respectively. When χ is less than 0.5, the probe liquid is generally characterized as a good solvent for the polymer, whereas a value higher than 0.5 indicates a poor solvent and may lead to phase separation.⁹

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SOLUBILITY PARAMETER

IGC was first applied to the study of the thermodynamics of probe-polymer interactions with a polymer as the stationary phase. The interaction between probes and a polymer is usually represented by the values of χ and analyzed by the solubility parameters of the probes and polymer.¹⁻⁶ In 1916, Hildebrand pointed out that the relative solubility of a given solute in a series of solvents¹⁰ is determined by the internal pressure of the solvents. Later, Scatchard introduced the concept of cohesive energy density into Hildebrand's theory, identifying this quantity with the cohesive energy per unit volume.¹⁰ In 1949, Hildebrand proposed the term *solubility parameter* and the symbol δ , which is defined as follows:¹⁰

$$\delta = \left(\frac{\Delta E_{\text{vap}}}{V} \right)^{1/2} \quad (2)$$

where ΔE_{vap} is the energy of vaporization and V is the molar volume of the liquid. The square of δ is often called the cohesive energy density. The concept of the solubility parameter was initially used in polymer-solvent systems, particularly by the coating industry and the elastomer industry. Years later, the extension of the concept of the solubility parameter to polymer-polymer systems was made by Bohn.¹¹ The solubility parameter model has been successful in describing thermodynamic properties of solutions, especially when the component liquids are nonpolar. It has been shown that χ can be related to the solubility parameters of two components as follows:¹⁰

$$\chi = (V_1/RT)(\delta_1 - \delta_2)^2 \quad (3)$$

where δ_1 and δ_2 are the solubility parameters of the probe and polymer, respectively, and V_1 is the volume of the probe. This equation implies that χ is always positive. A negative experimental value of χ can occur in systems with a specific interaction.

The solubility parameters of low molecular weight liquids can be determined experimentally from heat of vaporization data. Because polymers have no appreciable vapor pressure and their molar volume is not known, the definition in eq. (2) cannot be used for polymers. Experimental values of χ have been used in the determination of the solubility parameters of polymers. Guillet and coworkers^{12,13} demonstrated the use of IGC in the determination of χ and the solubility parameters of polymers. In their studies, eq. (3) was modified as follows:

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi}{V_1} \right) = \left(\frac{2\delta_2}{RT} \right) \delta_1 - \left(\frac{\delta_2^2}{RT} \right) \quad (4)$$

With a series of probes with different solubility parameters, the solubility parameter of the polymer (δ_2)

can be calculated from the slope or intercept. However, the solubility parameters of a polymer determined from the slope and intercept terms obtained from eq. (4) are frequently different. A related difficulty associated with this problem is that eq. (3) predicts a positive value for χ . In practice, this is not the case because some specific interactions exist between a particular probe and a stationary phase. This is a fundamental problem with the solubility parameter model. One way of overcoming this problem is the addition of an entropy term into χ so that χ is equal to $\chi_H + \gamma$,¹²⁻¹⁴ where γ is an entropy term that can be used to accommodate a negative value or temperature dependence. χ represents the size-corrected free energy of solution and is calculated as $RT\chi$.⁷ The enthalpy of solution is calculated on the basis of eq. (3) as $RT\chi_H = (\delta_1 - \delta_2)^2 V_1$. The entropy term can take either a positive or negative value and represents the deviation from the solubility parameter model. It is more appropriate to call this new entropy term the residual free energy of solution because it can include interactions with both enthalpy and entropy characteristics. The residual free energy term includes any specific interaction other than that from solubility parameter calculations. With the addition of this new term, eq. (4) becomes^{12,13}

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi}{V_1} \right) = \left(\frac{2\delta_2}{RT} \right) \delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\gamma}{V_1} \right) \quad (5)$$

In the application of eq. (5) to IGC data, it is assumed that the γ term depends largely on the polymer or remains constant for a series of probes. Therefore, δ_2 can be determined from the slope term of the plot, and the intercept is used to calculate γ . The results of γ measured by the IGC method for hydrocarbon probes in ethylene-propylene rubber, *cis*-polyisoprene, and amorphous polypropylene were around 0.3 and showed a small probe dependence. γ was higher for linear alkanes and smaller for aromatic probes.¹³

INTERACTION PARAMETERS OF POLYMER BLENDS BY IGC

When a polymer blend is used in an IGC study, the corresponding retention volume data and density of blends can be used in eq. (1). The interaction parameter obtained is called $\chi_{1(23)}$. With the application of the Flory-Huggins equation of polymer solutions to a ternary system with two polymers and one probe, $\chi_{1(23)}$ can be related to the difference between pair interactions between probes and polymers (χ_{12} and χ_{13}) and polymers and polymers (χ_{23}):

$$\chi_{1(23)} = \phi_2\chi_{12} + \phi_3\chi_{13} - \phi_2\phi_3\chi_{23}(V_1/V_2) \quad (6)$$

where ϕ is the volume fraction of polymers.

Because molar volumes of polymers may not be accurately known, it is a practice in IGC studies to define a probe-normalized interaction parameter:^{4,6,8}

$$\chi'_{23} = \chi_{23}(V_1/V_2) \quad (7)$$

The advantage of this parameter is that it can be related to the retention volume directly by the following formula without the calculation of the individual interaction parameters:^{4,6,8}

$$\chi'_{23} = \frac{1}{\phi_2\phi_3} \left[\ln\left(\frac{V_{g,\text{blend}}^0}{w_2v_2 + w_3v_3}\right) - \phi_2\ln\left(\frac{V_{g,2}^0}{v_2}\right) - \phi_3\ln\left(\frac{V_{g,3}^0}{v_3}\right) \right] \quad (8)$$

Equation (8) was frequently used to study the interaction of two stationary phases with the IGC method. Deshpande et al.³ applied this technique for the determination of thermodynamic interactions between components of a mixture of a polymer and a nonpolymeric compound. Su et al.⁸ used this technique to measure the interaction parameter of poly(vinyl chloride) (PVC) and dioctyl phthalate as a plasticizer to study their compatibility. Later, this method was also used to measure the compatibility of polymer blends. However, many studies have shown that the polymer–polymer interaction parameter determined by this technique depends on the probes used. Hsu and Prausnitz¹⁵ and Patterson and coworkers^{16,17} suggested that the compatibility of polymeric components in solution should reflect not only the interaction between the components themselves, that is, χ_{23}' , but also the difference in the strengths of the polymer–probe interactions, that is, $\Delta\chi = |\chi_{12} - \chi_{13}|$. They called it the $\Delta\chi$ effect, and a large $\Delta\chi$ value, in addition to a high χ_{23}' value, suggests incompatibility. Su and Patterson¹⁸ suggested that the probe dependency of χ_{23}' arises from the difference between χ_{12} and χ_{13} . Accordingly, for studying the blend, one must select probes that give $\chi_{12} = \chi_{13}$. Klotz et al.¹⁹ selected probes that were thermodynamically symmetric with respect to the polymers to be evaluated. After careful study of the results of the poly(epichlorohydrin)–poly(methylacrylate) system, Al-Saigh and Munk²⁰ concluded that the probe dependence was real. Chee²¹ used eqs. (1) and (5) and the corresponding retention volume and density of blends to calculate the solubility parameters of blends and the interaction parameter of blends. His method provided a single interaction parameter for one blend composition for the whole set of probes used, but the interaction parameter of the blend is generally a function of composition. Shi and Schreiber²² attributed the probe dependence to the difference between the bulk and surface composition of the stationary phase. El-Hibri et al.²³ found a correlation between the average values of an interaction

density parameter, $B_{23} = RT\chi_{23}'/V_1$, and the solubility parameter of the probe.

There were several attempts to explain a probe- or concentration-dependent interaction parameter through the equation-of-state approach by Flory and coworkers.^{24,25} Prolongo et al.^{26,27} derived a modified form of Flory's equation that allowed the calculation of the probe-independent interaction parameter χ'_{23} . His equation took into account the equation-of-state parameters. Sanchez²⁸ suggested that a full description of polymer mixture thermodynamics required the definition of four different parameters. These methods allow us to evaluate the polymer–polymer interaction parameter for each of the probes used. Etxeberria and coworkers^{29,30} used an approach based on the lattice-fluid theory in an attempt to eliminate the probe dependence of the thermodynamic parameters calculated by IGC. Farooque and Deshpande³¹ tested the aforementioned methods on polystyrene–polybutadiene blends and found that the interaction parameters were still probe-dependent. A simpler method was proposed to obtain the interaction parameter. This method was reexamined in this study with literature data.

RESULTS AND DISCUSSION

Determination of the solubility parameters

Sen and Mukherjee³² determined the retention volume of a series of solutes with PVC with a number-average molecular weight of 98,000, a nitrile rubber (NBR) with 28 wt % acrylonitrile (NBR28), and an NBR with 34 wt % acrylonitrile (NBR34). Both NBRs had a number-average molecular weight of 110,000. NBR is sometimes used as a high molecular weight plasticizer for PVC. These authors also measured the retention volumes of solutes in several mixtures of PVC and NBR at weight ratios of 25/75, 50/50, and 75/25. The probes used included *n*-octane, *n*-nonane, *n*-decane, benzene, toluene, *o*-xylene, butyl acetate, tetrahydrofuran, methyl ethyl ketone, ethylene dichloride (EDC), dioxane, and cyclohexanone. Molar volumes and solubility parameters of solutes were listed by Sen and Mukherjee.³² In this study, the specific volumes of PVC and NBR34 at 130°C were taken from Zoller and Walsh.³³ The values were 0.7515 and 1.0623 cm³/gm, respectively. For NBR28, the specific volume was estimated from NBR34 and polybutadiene with the group addition rule. The number was 1.0878 cm³/gm.

The plots for the solubility parameters of the three polymers are shown in Figure 1(a–c). Each line has a linear trend with a different slope. The slope is highest for PVC, which is shown in Figure 1(a), and lowest for NBR28, which is shown in Figure 1(b). The correlation factor was high; EDC accounted for most of the scattering. The solubility parameters of the three polymers were calculated on the basis of the slopes and inter-

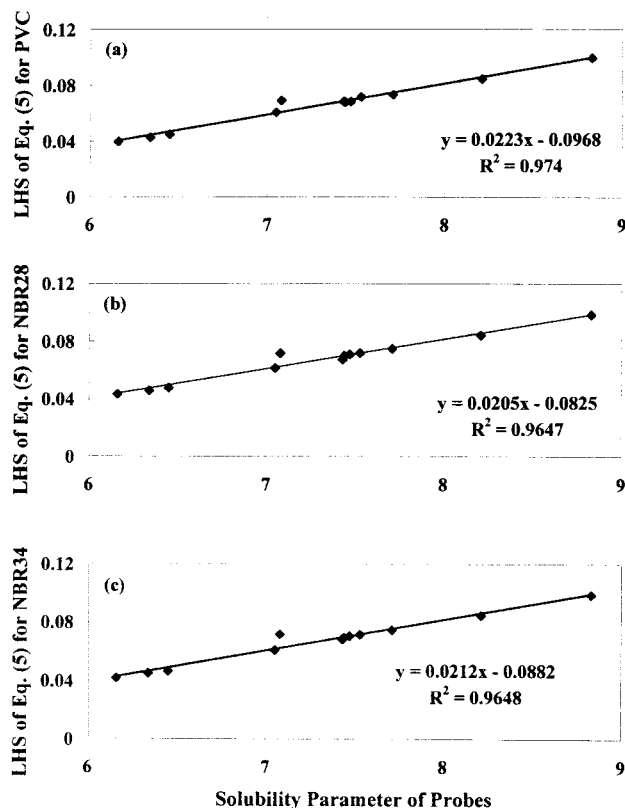


Figure 1 Left-hand side of eq. (5) versus the solubility parameters of probes for PVC stationary phases: (a) PVC, (b) NBR28, and (c) NBR34.

cepts and are listed in Table I. Two values of the solubility parameters were obtained for each polymer. The difference between the two values was about 0.1 ($\text{cal}^{0.5}/\text{cm}^{1.5}$). The solubility parameters determined from intercepts were lower than those from slopes. This indicated that the residual term, γ , was negative and different from the results of Guillet and coworkers.^{13,14} The values of the solubility parameters of NBR28 and NBR34 were close to the values calculated by Sen and Mukherjee,³² but the value of PVC was higher than that reported by them. The solubility parameter of PVC at 25°C reported in the literature ranges from 9.53 to 10.9 $\text{cal}^{0.5}/\text{cm}^{1.5}$.³⁴ EDC deviated from the linear lines in Figure 1 for all three plots. When EDC was removed from the calculation, the solubility parameters of the three polymers increased, but the numbers calculated from the intercepts were still smaller than those calculated from the slopes. The

TABLE I
Solubility Parameters of PVC and NBR [$(\text{cal}/\text{cm}^3)^{0.5}$]

| | Polymer | | |
|----------------|---------|-------|-------|
| | PVC | NBR28 | NBR34 |
| From slope | 8.93 | 8.21 | 8.49 |
| From intercept | 8.81 | 8.15 | 8.41 |

TABLE II
 $RT\chi$, $(\delta_1 - \delta_2)^2V_1$, and the Residual Free Energy of Solution of the Probes in PVC (cal/mol)

| Solute | $RT\chi$ | $(\delta_1 - \delta_2)^2V_1$ | Residual free energy |
|------------------------|----------|------------------------------|----------------------|
| 1. <i>n</i> -Octane | 1162 | 1445 | -283 |
| 2. <i>n</i> -Nonane | 1218 | 1374 | -156 |
| 3. <i>n</i> -Decane | 1250 | 1365 | -115 |
| 4. Benzene | 104 | 218 | -114 |
| 5. Toluene | 96 | 269 | -173 |
| 6. <i>o</i> -Xylene | 88 | 202 | -114 |
| 7. EDC | -545 | 342 | -887 |
| 8. Tetrahydrofuran | -80 | 186 | -266 |
| 9. Methyl ethyl ketone | 48 | 237 | -189 |
| 10. Butyl acetate | 160 | 540 | -380 |
| 11. Dioxane | -56 | 51 | -107 |
| 12. Cyclohexanone | -224 | 1 | -225 |

exclusion of a datum with a large negative value of χ still gave negative residual terms and did not change the aforementioned conclusion.

After the determination of the solubility parameters of the polymers, a comparison was made of the experimental values of the size-corrected free energy of solution and their predicted values based on solubility parameters. The experimental value of the size-corrected free energy of solution was calculated as $RT\chi$, and the predicted value based on the solubility parameter model was $(\delta_1 - \delta_2)^2V_1$. The residual free energy of solution was calculated as the difference between these two quantities. The results of the calculation for PVC are shown in Table II. The results of NBR28 and NBR34 are shown in Tables III and IV, respectively.

From Tables II–IV, it can be seen that the residual free energy of solution for most probes was generally negative. Two reasons can be given for the deviation from the solubility parameter model. One explanation is the free volume effect. A free volume effect occurs when a solvent molecule is moving from a solvent

TABLE III
 $RT\chi$, $(\delta_1 - \delta_2)^2V_1$, and the Residual Free Energy of Solution of the Probes in NBR28 (cal/mol)

| Solute | $RT\chi$ | $(\delta_1 - \delta_2)^2V_1$ | Residual free energy |
|------------------------|----------|------------------------------|----------------------|
| 1. <i>n</i> -Octane | 617 | 791 | -174 |
| 2. <i>n</i> -Nonane | 713 | 716 | -3 |
| 3. <i>n</i> -Decane | 729 | 678 | 41 |
| 4. Benzene | -96 | 56 | -152 |
| 5. Toluene | -104 | 72 | -176 |
| 6. <i>o</i> -Xylene | -90 | 34 | -114 |
| 7. EDC | -745 | 128 | -873 |
| 8. Tetrahydrofuran | -88 | 44 | -132 |
| 9. Methyl ethyl ketone | 120 | 64 | 56 |
| 10. Butyl acetate | 56 | 205 | -149 |
| 11. Dioxane | -16 | 0 | -16 |
| 12. Cyclohexanone | -112 | 45 | -157 |

TABLE IV
 $RT\chi$, $(\delta_1 - \delta_2)^2V_1$, and the Residual Free Energy
of Solution of the Probes in NBR34 (cal/mol)

| Solute | $RT\chi$ | $(\delta_1 - \delta_2)^2V_1$ | Residual free energy |
|------------------------|----------|------------------------------|----------------------|
| 1. <i>n</i> -Octane | 841 | 1022 | -181 |
| 2. <i>n</i> -Nonane | 849 | 974 | -95 |
| 3. <i>n</i> -Decane | 961 | 923 | 38 |
| 4. Benzene | -80 | 107 | -187 |
| 5. Toluene | -56 | 134 | -190 |
| 6. <i>o</i> -Xylene | -56 | 83 | -139 |
| 7. EDC | -745 | 199 | -944 |
| 8. Tetrahydrofuran | -64 | 88 | -152 |
| 9. Methyl ethyl ketone | 48 | 119 | -71 |
| 10. Butyl acetate | 152 | 317 | -165 |
| 11. Dioxane | -56 | 8 | -64 |
| 12. Cyclohexanone | -152 | 14 | -166 |

liquid into a polymeric matrix. A polymeric matrix tends to be dense and has a smaller free volume than solvents. Because low molecular weight compounds usually have more free volume between molecules than polymeric compounds, the thermodynamic properties of IGC should contain additional quantities, which represent the dissimilarity in the free volumes of solvents and polymers. Flory and coworkers^{24,25} developed a theory to account for the free volume effect in solution thermodynamics. Several authors have made modifications to their equations.³⁵⁻³⁷ I used the equation of Flory and coworkers for IGC results and showed that the effect of free volume in several stationary phases was on the order of 100 cal/mol.³⁸ Also, because probes generally have higher free volumes than polymers, the free volume effect usually contributes a positive term to the free energy of solution. Most results in Tables II-IV are negative numbers.

Another reason for the difference is the orientation effect of probes in the stationary phase. In a study by Langer et al.⁷ that used a series of probes in several gas chromatography stationary phases, it was found that there was some correlation between the enthalpy of solution and the entropy of solution after the size effect was made by the Flory-Huggins equation. This effect was called orientation entropy, which included the specific interaction between the probes and stationary phases and the effect of the geometry of the probes when they were moved from the probe liquid to the stationary phase. In IGC studies, the change in the thermodynamic properties is calculated between the pure liquid state and the infinite dilution state in polymers. It is usually assumed in regular solution theory that the entropy of the liquid state is the same for all probe liquids, and the value of χ reflects the difference in enthalpy. An unusual negative value of χ can happen when a pure probe liquid is in a more ordered state, which can create a larger entropy of

solution. The Trouton constant, which is the entropy of vaporization at the boiling point,^{7,13} can be used to compare the orders of different liquids. The values of the Trouton number were calculated from standard sources and ranged from 21.0 to 23.2 cal/K/mol, with no unusual deviation.

To investigate the source of the deviation from the solubility parameter model, we plotted the residual free energy of solution in NBR28 versus a similar property in PVC in Figure 2(a,b). The results were near the origin, with the exception of EDC. The location of data for PVC-NBR34 was very similar to that for PVC-NBR28. The former had smaller absolute values. This indicated the consistency of the experimental results. It also indicated that, whatever the reason for the residual free energy of solution, the mechanism was operative to a similar magnitude in both blends. This was because both blends had similar intermolecular forces toward solutes. In Figure 2(a,b), two parallel lines with slopes equal to unity were also plotted. The significance of these two lines is that data points falling within these boundaries have residual free energies of solution lying within 150 cal/mol of each other. The fact that most data fell within the two

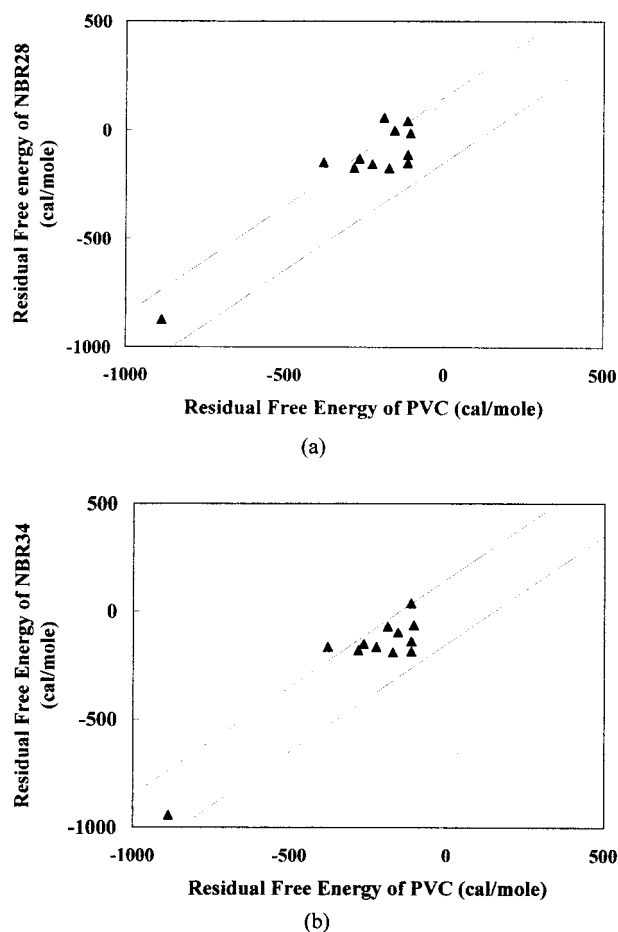


Figure 2 Residual free energy of the probe solution: (a) NBR28 versus PVC and (b) NBR34 versus PVC.

parallel lines indicates that probes did not have a specific interaction toward one of the polymer pairs. Note that in Figure 2, EDC also falls within the band of two parallel lines despite its large negative χ value in both polymers. It had a much more negative χ value, which accounted for the majority of the residual free energy. The difference in the solubility parameter contributed a smaller portion of the residual free energy. Its Trouton number was 22.3 cal/K/mol, which was within the range of the other probes. The reason that EDC fell away from other data is not clear.

Interaction parameters of the polymer blends

The values of χ_{23}' were calculated by Sen and Mukherjee³² and were used in this article. It has been noticed that the experimental value of χ_{23}' varies between different probes. A question has been raised concerning which probe is most suitable to use for measuring the interaction parameter. When the $\Delta\chi$ effect is considered, the probe that interacts similarly with both polymers should be selected. El-Hibri et al.,²³ however, used another method of selecting the probe for a more accurate evaluation of the interaction parameter. They argued that the probe, which possessed the nearest solubility parameter to that of the blend, was the most appropriate, and the value obtained from that probe should be used to interpret thermodynamic compatibility. The first approach is to use probes with similar χ values in the two polymers. The second approach is to use probes with similar χ_H values. Because the solubility parameters of the two polymers are generally not equal, finding a probe satisfying these conditions may not be easy with a blend made by two polymers with dissimilar structural units and solubility parameters. Also, one should consider the effect of the residual free energy when specific interactions exist between probes and polymers.

Because the value of χ_{23}' is generally probe-dependent, Farooque and Deshpande³¹ proposed rearranging eq. (6) into the following form:

$$(\chi_{1(23)} - \chi_{13})/V_1 = \phi_2(\chi_{12} - \chi_{13})/V_1 - \phi_2\phi_3\chi_{23}/V_2 \quad (9)$$

By plotting the left-hand side of eq. (9) versus $\phi_2(\chi_{12} - \chi_{13})/V_1$, we can obtain the interaction parameter from the intercept. This method was used by Etxeberria and coworkers^{39,40} and Lezcano et al.,⁴¹ and very good linear lines were obtained. Recently, Zhao and Choi⁴² suggested the use of an ethylene segment as a reference volume in the IGC study of blends of high-density polyethylene and low-density polyethylene. Their definition of χ was different from the traditional definition by a ratio of the reference volume to the probe volume (V_0/V_1). In terms of the nomenclature

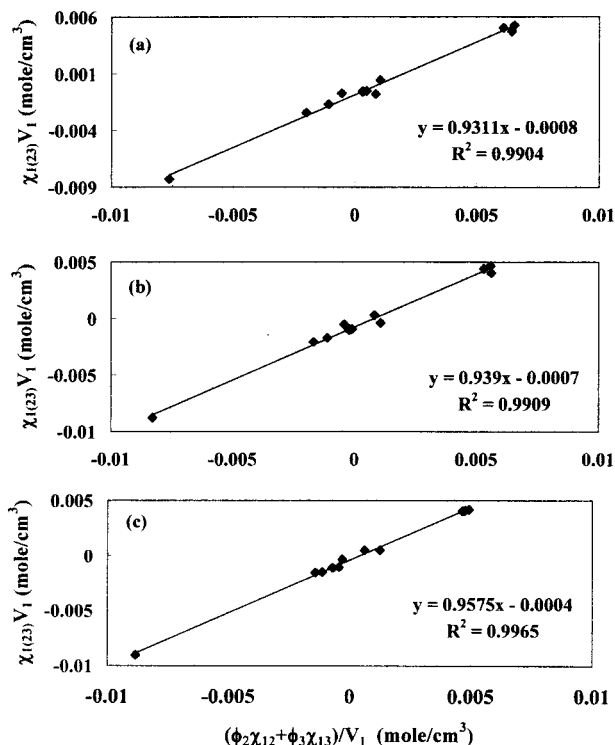


Figure 3 Plot of $\chi_{1(23)}/V_1$ versus $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ for three compositions of PVC/NBR28: (a) 75/25, (b) 50/50, and (c) 25/75.

of common definition, their equation has the following form:

$$[(V_0/V_1)\chi_{1(23)}] = \phi_2(V_0/V_1)\chi_{12} + \phi_3[(V_0/V_1)\chi_{13}] - \phi_2\phi_3[(V_0/V_2)\chi_{23}] \quad (10)$$

The quantities in brackets represent the new interaction parameters defined by Zhao and Choi. From the equation, a linear plot was obtained from the left-hand side versus $\phi_2[(V_0/V_1)\chi_{12}] + \phi_3[(V_0/V_1)\chi_{13}]$. Equation (10) is similar to eq. (9), with a difference in V_0 . Therefore, it is proposed in this study to use the following equation:

$$\chi_{1(23)}/V_1 = (\phi_2\chi_{12} + \phi_3\chi_{13})/V_1 - \phi_2\phi_3\chi_{23}/V_2 \quad (11)$$

A linear plot can be obtained from the left-hand side versus $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$. The plot has been made in Figure 3(a–c) for PVC–NBR28 and in Figure 4(a–c) for PVC–NBR34. The slope was near unity, and the intercept terms were negative; this indicated that χ_{23}/V_2 and B_{23} for both polymer blends were positive. Moreover, EDC was located in the linear lines without significant deviation despite its large negative χ values. The values of χ_{23}/V_2 were determined from the constant term in the regression lines shown in Figures 3 and 4 after division by the factor $\phi_2\phi_3$. Its values varied with the composition and indicated some con-

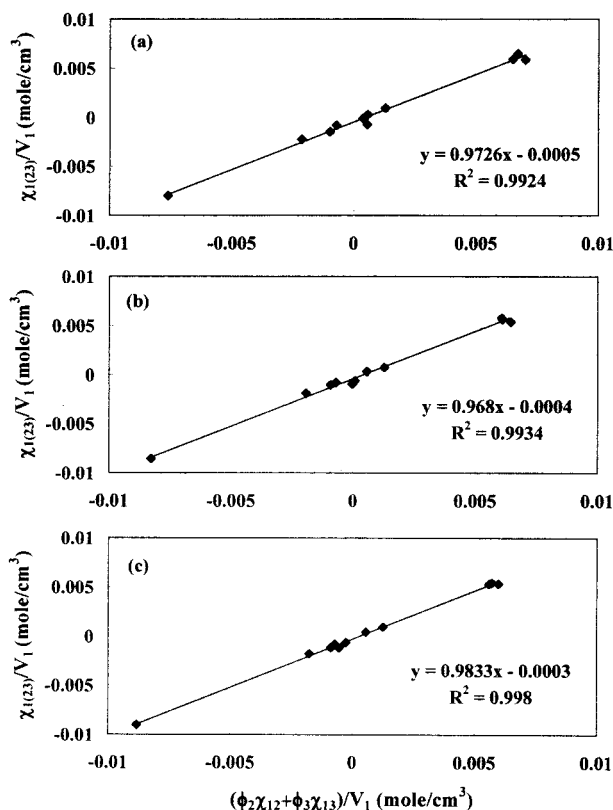


Figure 4 Plot of $\chi_{1(23)}/V_1$ versus $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ for three compositions of PVC/NBR34: (a) 75/25, (b) 50/50, and (c) 25/75.

centration dependence. The average values were calculated to be 0.0030 ± 0.00043 and 0.0019 ± 0.00042 for PVC–NBR28 and PVC–NBR34, respectively. Both numbers were higher than zero at a significant level. The difference between the two NBRs was also significant. The corresponding B_{23} values were 2.4 and 1.5 cal/cm³, respectively. This agreed with prior conclusions^{43,44} that the former system was less compatible than the latter. Because the solubility parameter of NBR34 was closer to that of PVC than that of NBR28, the order of compatibility also agreed with the prediction of the solubility parameter method. With the Flory–Huggins theory of ternary systems, the following formula could be obtained at the critical point of phase separation:^{1,2}

$$\chi'_{23} = \left[\left(\frac{V_1}{V_2} \right)^{0.5} + \left(\frac{V_1}{V_3} \right)^{0.5} \right]^2 \quad (12)$$

With a probe volume of 100 cm³/mol, the critical value for the interaction parameter was calculated to be 0.0017. This number was very close to the value of the PVC–NBR34 system (0.0019). This indicated that the system was close to a miscible system.

The deviation of slopes from unity is significant in explaining the probe and concentration dependence of

interaction parameters that have been reported in many studies. Because the slopes are not exactly unity, a systematic deviation exists when the last term in eq. (10), $\phi_2\phi_3\chi_{23}/V_2$, is calculated from the difference between $\chi_{1(23)}/V_1$ and $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$. The difference increases when $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ is increased from zero. This systematic difference is combined into the calculation of χ_{23} and has a tendency to distort its value. Generally, when the solubility parameter of probes is decreased from the average of two polymers, the value of $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ increases. Therefore, a line with a slope smaller than unity will have χ_{23} and B_{23} gradually increasing from zero to a positive value when the solubility parameter of the probe decreases away from the average of the two polymers. This was observed in this system and in the correlation of B_{23} versus the solubility parameter of probes by Munk et al.²³ Because the deviation of $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ from zero accounts for the probe dependency when a single probe is used to determine χ_{23} and B_{23} , it is better to use a probe whose $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ value is near zero. This also implies a probe with a solubility parameter close to both polymers and a probe with a low $\Delta\chi$ effect because both χ_{12} and χ_{13} are small. In practice, it is better to make a plot similar to Figures 3 and 4 with a series of probes.

In discussing the plotting method of Farooque and Deshpande,³¹ Etxeberria et al.⁴⁰ reached the following two conditions. First, the probes that had similar interaction parameters with both pure polymers were rejected because this implied similar specific retention volumes. Second, the probes were selected in an attempt to cover all possible chemical structures and polarities. The first condition was also suggested by Mandal and coworkers^{4,45} because a similar retention volume led to an error in the calculation. The second approach was intended to find a probe with a large value of $|\chi_{12} - \chi_{13}|$. In practice, it may not be feasible when a miscible blend is studied because similar interactions between the probe and polymers tend to create a small $\Delta\chi$ effect. These suggestions are different from the conclusion reached in the previous paragraph. This is because in the plotting based on eq. (9), the variable is the difference of two interaction parameters, whereas in this study, the variable is the summation of two interaction parameters. This method imposes fewer requirements on the selection of probes.

CONCLUSIONS

The solubility parameter method was used to analyze the χ values of PVC and two NBRs. The size-corrected free energy of most probes deviated from the solubility parameter by small values that could be explained by the free volume effect and orientation effect. A new plotting method was proposed for analyzing the IGC

data of blends. When this method was applied to PVC–NBR28 and PVC–NBR34, linear lines with slopes close to unity were observed. Both systems had positive interaction parameters, but the latter was smaller. This agreed with the observation that the PVC/NBR34 system was almost miscible.

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