Probe Dependency of Polymer-Plasticizer and Polymer-Polymer Interaction Parameters in Inverse Gas Chromatography

Jan-Chan Huang

Plastics Engineering Department, University of Massachusetts Lowell, Lowell, Massachusetts 01854

ABSTRACT: Inverse gas chromatography has been widely used to determine the Flory–Huggins parameter, χ, between a plasticizer and a polymer, or between two polymers. Many studies showed that interaction parameters may be probe dependent. In a recent study it was proposed that, when a specific interaction occurred between two polymers, the probes had less interaction with the polymers, leading to a lower solubility parameter for polymer blends than the volume average of the components. An equation was derived to relate the probe dependency to the deviation of solubility parameter of polymer mixtures. Here this approach is applied to plasticized poly(vinyl chloride) (PVC) and a copolymer, and to poly(vinylidene fluoride)–poly(ethyl methacrylate) blends. For a PVC and epoxidized oil system the relative deviation of specific retention volume showed two trends, with saturated hydrocarbons as one group, and polar and aromatic probes as another group. For the poly(vinylidene fluoride)/poly(ethyl methacrylate) system the plot of retention volume deviation versus solubility parameter of probes also showed separate trends for n-alkanes, esters, and alcohols. But the plot of $\phi_2\phi_3 RT(\chi_{23}/V_2)$ versus solubility parameter had better linearity for the systems studied. The slope of this plot was used as an indicator for miscibility. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 4110–4116, 2007

Key words: inverse gas chromatography; interaction parameter; poly(vinylidene fluoride); poly(ethyl methacrylate); poly(vinyl chloride)

INTRODUCTION

The knowledge of the interaction parameters between two polymers is very important in the study of their miscibility and thermodynamic properties of solutions. Inverse gas chromatography (IGC) has been demonstrated to be an effective tool for measuring the thermodynamic properties of solute (probe) vapors in polymers.[1–4] The name IGC was used because the subject of the study is the stationary phase rather than the probes. In IGC measurement a known amount of nonvolatile stationary phase is dissolved in a solvent and coated on a porous inert support. When a liquid probe is injected into the column the probe vaporizes and flows with the carrier gas, and a characteristic specific retention volume can be measured. Using Flory–Huggins theory,[5] the Flory–Huggins interaction parameter between a polymer and a probe, χ, can be related to the specific retention volume of the probe, V_g^0, by the following eqs. (1)–(4):

$$\chi = \ln\left(\frac{273.16 R v_2}{V_g^0 P_1^0 V_1}\right) - 1 - \frac{P_1^0}{RT}(B_{11} - V_1) \qquad (1)$$

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, the liquid molar volume, and the second virial coefficient of the probe, respectively. When a polymer blend is used in an IGC study the corresponding specific retention volume and density data of blends can be used in Eq. (1). The interaction parameter obtained is called $\chi_{1(23)}$. Applying the Flory–Huggins equation of polymer solutions[5] to a ternary system with two polymers and one probe, the interaction parameter $\chi_{1(23)}$ can be related to the difference between pair of interactions of probe-polymers, χ_{12} and χ_{13}, and polymer–polymer χ_{23}:[3,4]

$$\chi_{1(23)} = \phi_2\chi_{12} + \phi_3\chi_{13} - \phi_2\phi_3\chi_{23}(V_1/V_2) \qquad (2)$$

Here ϕ is the volume fraction of the two stationary phases. Since molar volumes of polymers may not be accurately known, it is a practice in IGC study to define a probe normalized interaction parameter, χ_{23}' $= \chi_{23}(V_1/V_2)$. The advantage of this parameter is

Correspondence to: J.-C. Huang (jan_huang@uml.edu).

that it can be calculated through the specific retention volume by the following formula without calculating the individual interaction parameters:[6]

$$\ln\left(\frac{V_{g,\text{blend}}^0}{w_2 v_2 + w_3 v_3}\right) = \phi_2 \ln\left(\frac{V_{g,2}^0}{v_2}\right) + \phi_3 \ln\left(\frac{V_{g,3}^0}{v_3}\right) + \phi_2 \phi_3 \chi'_{23} \quad (3)$$

Here v is the specific volume and w is the weight fraction. Equation (2) then becomes:[3,4]

$$\chi_{1(23)} = \phi_2 \chi_{12} + \phi_3 \chi_{13} - \phi_2 \phi_3 \chi'_{23} \quad (4)$$

Equation (4) was frequently used to study the interaction of two stationary phases using the IGC method. But many studies have shown that the value of χ'_{23} depend on the probe used.[6–11] In examining literature data it is found that in many systems, when probe dependency occurred, the values of χ'_{23} were positive when χ_{12} and χ_{13} were positive, and decreased toward negative when χ_{12} and χ_{13} decreased. In most systems that were miscible some negative χ'_{23} values were generally observed for probes with low χ_{12} and χ_{13}. This trend caused the slope of $\chi_{1(23)}/V_1$ versus $(\phi_2 \chi_{12} + \phi_3 \chi_{13})/V_1$ plot to deviate slightly from unity.[12–14]

APPARENT SOLUBILITY PARAMETERS OF POLYMER MIXTURES

Because polymer–polymer mixtures have little entropy of mixing, the miscibility is largely decided by the sign of the heat of mixing. If the heats of vaporization of a mixture and its components are known the heat of mixing can be calculated. The heat of vaporization is related to the solubility parameter, δ, of the liquid by the relation:[15]

$$\delta = \left(\frac{\Delta E_{\text{vap}}}{V}\right)^{1/2} \quad (5)$$

where ΔE_{vap} is the energy of vaporization and V is the molar volume of the solvent. The ratio $\Delta E_{\text{vap}}/V$ is the cohesive energy density; it represents the energy required to separate the liquid molecules into the ideal gas state. Experimental values of χ have been used to estimate the solubility parameters of polymers using the method of DiPaola-Baranyi and Guillet.[16,17] In their studies, the Flory–Huggins parameter between a solute and a polymer was assumed to have the following expression:

$$\chi = (V_1/RT)(\delta_1 - \delta_2)^2 + \chi_s \quad (6)$$

Here χ_S is the entropy term. Equation (6) can be changed into the following linear expression:[16,17]

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi}{V_1}\right) = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \left(\frac{\delta_2^2}{RT} + \eta\right) \quad (7)$$

where η is the average value of χ_S/V_1. From a linear regression method δ_2 can be determined.

In a previous study it was proposed to examine the miscibility of polymer blends by comparing the solubility parameters of components and blends.[18] When a mixture is used as the stationary phase the solubility parameter of the mixture, δ_m, can be compared with the prediction of the regular solution method, which predicts δ_m to be the volume average of the two components:[15]

$$\delta_m = \phi_A \delta_A + \phi_B \delta_B \quad (8)$$

If there were a specific interaction that produced negative enthalpy of solution, the value of δ_m would be higher than the prediction of eq. (8), to account for the separation of the additional specific interaction of the mixtures in the vaporization process. A measurement of the solubility parameter of polymer mixtures would be a good indicator to predict their miscibility. In the previous study[18] this argument was tested using the data of Munk and coworkers[19] on the poly(ε-caprolactone) (PCL)/poly(epichlorohydrin) (PECH) system at 80°C. It was found that the solubility parameter of the mixture was lower than the prediction of eq. (8). This was opposite to the above argument, even though there were some specific interactions between PCL and PECH and the system was miscible. When a deviation from eq. (8) occurs, the deviation of the solubility parameter of the mixture, Δ, can be defined as:

$$\delta_1 - \delta_m = \delta_1 - \delta_{m,r} + \Delta \quad (9)$$

Here Δ is the deviation of the solubility parameter of the polymer mixture from the regular solution value, $\delta_{m,r}$, which is calculated from eq. (8). A mechanism was then proposed to explain this observation.[18] When two polymers with specific interactions are brought together, some functional groups interact with each other and are less available to the probes. Relative to the average values based on nominal composition, the probes will have less specific interaction with the mixture. Therefore, polar probes show a decrease in retention volume than the average of the components, and for n-alkane probes the decrease may be smaller. This difference between probes is exhibited as the probe dependency. The solubility parameter of mixtures measured by the IGC method also reflects the change in the interaction between the probe and the polymer mixtures. It

can no longer be related to the cohesive energy density by eq. (5). But the extent of such solubility parameter change, as measured by the parameter Δ, could be an indicator of the interaction between the two polymers.

On the basis of these arguments two methods were proposed to test the miscibility.[18] One was to examine the trend of deviation of the specific retention volume from the weight average rule for different probes. The second method was based on a more quantitative criterion derived using the solubility parameter model. From eqs. (4), (6), and (9) the following equation was obtained in the previous study:[18]

$$\phi_2\phi_3RT(\chi_{23}/V_2) = \phi_2\phi_3(\delta_2 - \delta_3)^2 - 2\Delta(\delta_1 - \delta_{m,r}) - \Delta^2 \\ + RT(\phi_2\chi_{s,2} + \phi_2\chi_{s,3} - \chi_{s,m})/V_1 \tag{10}$$

The left hand side can be plotted versus the solubility parameter of the probe, δ_1. In the plot, a linear trend with negative slope was predicted for miscible blends. The slope was proportional to the deviation of the solubility parameters of the polymer mixtures from the volume average, Δ, which could be used as a measurement of miscibility. The advantage of plotting $\phi_2\phi_3RT(\chi_{23}/V_2)$ versus δ_1 is that the former can be calculated from the specific retention volume results without additional calculation. It can be calculated from eq. (3) using the specific retention volume data. This plot was demonstrated for PCL/PECH in the previous study.[18]

## EVALUATION OF MISCIBILITY OF PLASTICIZED PVC AND A COPOLYMER

In this study the plasticized systems of poly(vinyl chloride) (PVC) and a copolymer, PV(DC-VC), reported by Demertzis et al.[20–22] were used for further examination of the procedure. PV(DC-VC) is a copolymer with 80 wt % vinyl chloride (VC) and 20 wt % vinylidene dichloride (DC). In their study the interaction parameters of probes in polymers and plasticizers were reported for 90, 100, and 110°C. The polymer-plasticizer interaction parameters were reported for 92/8 wt polymer/plasticizer mixtures for the same temperatures. The molecular weight of PVC was 100,000. For PVC the plasticizers used were epoxidized soybean oil (ESO) and a polyadipate (Santicizer 409A).[20,21] For PV(DC-VC) the plasticizers used were polyadipate and triiso-nonyl trimellitate (TiNT).[22] The plasticized PVC systems were analyzed previously by Huang and Deanin.[14] It was concluded that the systems were more miscible at high PVC concentration but became less miscible at low PVC concentration.

In the present study, interaction parameters, χ'_{23}, reported by Demertzis et al., were used for further calculation. The required physical properties were taken from a standard source, and molar volumes of probes were calculated using the method of Spencer and Danner.[23] Enthalpy of vaporization of probes was calculated by the Clausius–Clapeyron equation. Figure 1 shows the plot of relative deviation of specific retention volume from the weight average rule versus $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ for the PVC/ESO system at 90°C. It can be seen that the data appeared as two groups. The results of n-alkanes were located at the right hand side, and the left hand side was aromatic and polar probes, which had smaller χ values. Both groups had separate upward trends, as in the previous case in the PECH/PCL system. For the 60/40 wt composition the data of polar probes were located at the left side of the 82/8 wt composition. This was because polar probes had smaller χ in ESO. With higher percentage of ESO, the values of $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ were smaller. But the percentage deviation of polar probes in the 60/40 composition was more positive than in 92/8. This suggested that the latter system might be more miscible than the former. This was confirmed by the value of χ'_{23} for each composition reported by Demertzis et al.[22] The χ'_{23} for 60/40 was more positive than for 92/8. PVC-polyadipate and plasticized PV(DC-VC) also showed similar behavior and are not presented here.

The plot of $\phi_2\phi_3RT(\chi_{23}/V_2)$ versus δ_1 was made in Figure 2 for 92/8 wt compositions for plasticized PVC systems. The similar plot for the PV(DC-VC) copolymer is shown in Figure 3. The value of Δ of each system was calculated and reported in Table I. It can be seen that slopes of different systems were different. It can be concluded that PVC-ESO was
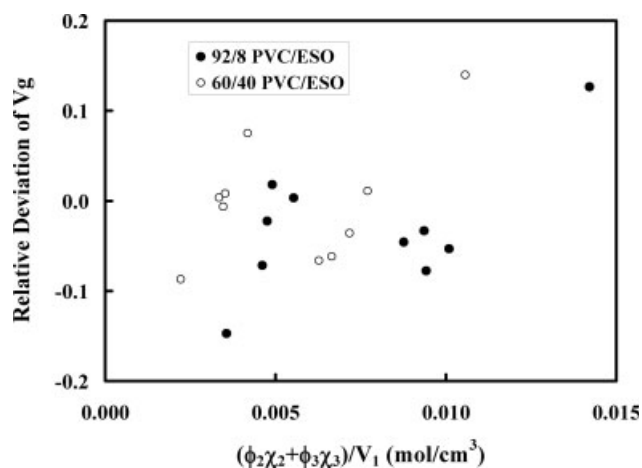

Figure 1 Plot of relative deviation of specific retention volume of polymer mixture from the weight average value versus $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ of solutes for 92/8 and 60/40 PVC/ESO at 90°C.
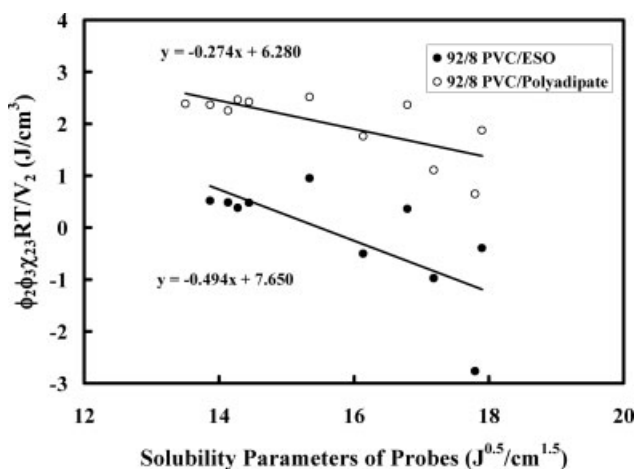
Figure 2 Plot of $\phi_2\phi_3RT\chi_{23}/V_2$ versus solubility parameter of probes, δ_1, at 90°C for PVC/ESO and PVC/Polyadipate at 92/8 wt composition. The latter were shifted upward by 2 J/cm^3. Unit: J/cm^3 = MPa.

more miscible than PVC-polyadipate, while for PV(DC-VC) systems, TiNT was slightly more miscible than polyadipate. The miscibility of PV(DC-VC), as measured by parameter Δ, was less than half of the polyadipate plasticized PVC systems, indicating a lower miscibility. The low miscibility of PV(DC-VC) was noted by Demertzis et al.[22] The reason was because it had a lower amount of tertiary hydrogen, which could form weak hydrogen bonding with plasticizers.[14,22]

It was noted that the data of Figures 2 and 3 could be correlated by a single line. This was different from Figure 1, which appeared as two trends. In Figure 1 the relative deviation of retention volume was the important variable, but the selection of $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ as the horizontal axis was some-
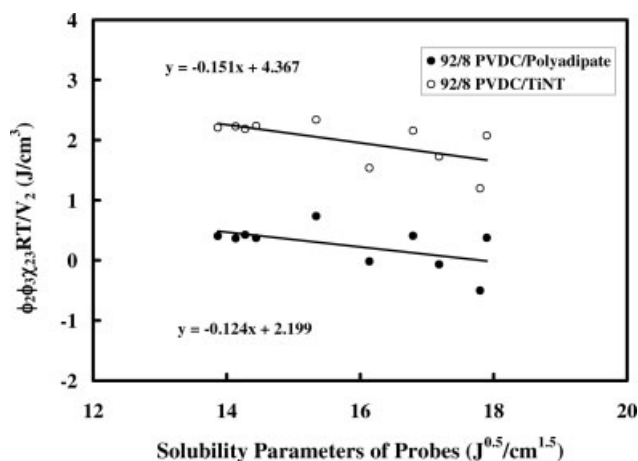
TABLE I
The Deviation Δ of Solubility Parameter from the Volume Average of Plasticized PVC and Its Copolymer at 92/8 wt Composition for Different Temperatures ($J^{0.5}/cm^{1.5}$ = $MPa^{0.5}$)

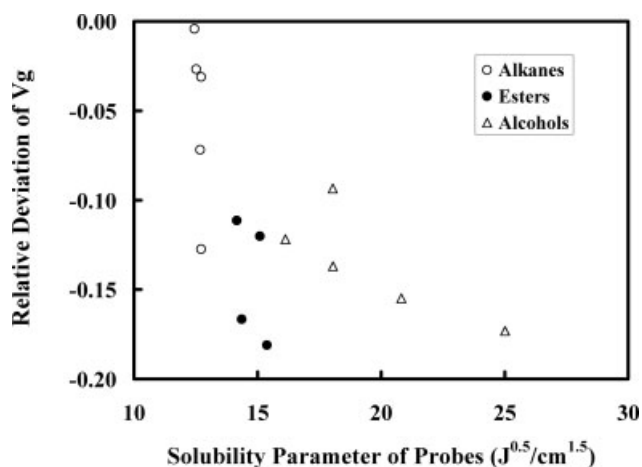| Systems	Temperatures		
	90°C	100°C	110°C
PVC-ESO	0.236	0.215	0.185
PVC-Polyadipate	0.137	0.124	0.058
PV(DC-VC)-TiNT	0.076	0.048	0.028
PV(DC-VC)-Polyadipate	0.062	0.041	0.030

what arbitrary. Although in the previous study a reasonable linear line correlated all data of the PCL/PECH system, such observation might not be viewed as typical for other systems. This is because, for many stationary phases, there are several types of specific interactions such as polar, hydrogen bonding, acid-base, and charge transfer complex. With the formation of specific interactions, the resulting products might still have some of these interactions besides dispersion interaction. When this happens, different homologous series will have different correlations compared with alkanes. This will also be seen later in a different system.

The results of Δ for different temperatures at 92/8 wt composition are compared in Table I. It can be seen that there was a definite decreasing trend when temperature increased. This can also be seen from the trend of the original χ'_{23} data. With decreasing Δ and increasing χ'_{23} the system could become incompatible at high temperatures. A comparison on the degree of miscibility of each system can be made based on the magnitude of Δ. It can be concluded that the miscibility was the highest for PVC-ESO and lowest for PV(DC-VC)-polyadipate within the temperature range studied.

EVALUATION OF MISCIBILITY OF PVDF/PEMA

In this study the miscible system of poly(vinylidene fluoride) (PVDF) and poly(ethyl methacrylate) (PEMA) reported by Al-Saigh and Chen[24] was used for further testing of eq. (10). In that study three types of probes were used: nonpolar hydrocarbons, polar acetate esters, and strongly polar alcohols. The two polymers and three mixtures were used as the stationary phases. Measurements were made at 175, 185, and 195°C. Specific retention volumes were listed as well as χ'_{23} of the mixtures. Because the interaction parameters of probes in pure polymer were not reported, the plot was made using the relative deviation of retention volume versus the solubility parameter of probes in Figure 4 for 195°C for the 50/50 wt composition. Enthalpy of vaporization of probes was calculated by the Clausius–Clapeyron

Figure 3 Plot of $\phi_2\phi_3RT\chi_{23}/V_2$ versus solubility parameter of probes, δ_1, at 90°C for PV(DC-VC)/Polyadipate and PV(DC-VC)/TiNT at 92/8 wt composition. The latter were shifted upward by 2 J/cm^3. Unit: J/cm^3 = MPa.

Figure 4 Plot of relative deviation of specific retention volume of polymer mixture from the weight average value versus the solubility parameters of probes for 50/50 wt PVDF/PEMA at 195°C.

equation. Because of the high measurement temperature, a correction for vapor phase imperfection was made using the method introduced previously.[25]

It can be seen in Figure 4 that the data appeared as three groups, with each type of probes in one trend. This was because three types of probes interacted differently with PVDF and PEMA and yielded different families of curves. But more important is that all of them had negative deviations, which was the evidence in the argument about interaction between two components and changing stationary phase environment. Alkane had the smallest deviation, because the polymer mixtures tended to become more "alkane-like" when specific interactions occurred. Among esters, methyl acetate had the highest negative deviation, while methanol had the highest deviation among alcohols. These were the first members of the series, with the highest weight fraction of the molecule as the functional group; thus they had the largest interaction with the polymers.

Because the probe interacts differently with the polymer components and their interacted products, a deviation of retention volume is the evidence that probes also have specific interactions toward one of the components and are competing with the other component. When two polymer components were interacting with each other, their functional groups interacted and the effective concentration was lower than the nominal concentration in the mixture. This created the deviation from the weight average rule. From this viewpoint, both esters and alcohols were competing with the polymers. Leonard et al.[26] used the FTIR method to show that PVDF interacted with the carbonyl group through hydrogen bonding. In contrast, ester probes would probably feel PEMA to be an ideal solvent, with zero or small χ, because of

structural similarity. Therefore, it can be said that ester probes were competing with PEMA for PVDF. Alcohols probably also interacted with PVDF and PEMA with hydrogen bonding. A different degree of interactions between probes and the two polymers was sufficient to cause the retention volume deviation through the mechanism described earlier.

The plot of $\phi_2\phi_3RT(\chi_{23}/V_2)$ versus the solubility parameter is shown in Figure 5 for three mixture compositions at 195°C. It can be seen that better correlations were obtained for each composition, even though Figure 4 did not show a simple correlation. This difference is also seen in the plasticized PVC system, when Figures 1 and 2 are compared. Therefore, the plot of eq. (10) is a better approach than a comparison of the relative deviation of retention volume, because there is no simple equation linking the deviation to probe solubility parameters or $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$ that were used previously as the horizontal variable. The deviation of the solubility parameters of polymer mixtures, Δ, at three temperatures is reported for each composition in Table II. It can be seen that the parameter Δ was also positive, indicating lower apparent solubility parameters for the mixtures than the volume average of the components. The temperature dependency was smaller than that of plasticized PVC and its copolymer. Both PVDF and PEMA are vinyl polymers with one functional group for every two carbon atoms in the main chain. The cooperative phenomena between the functional groups of two polymer chains probably made it more difficult to separate the interaction by thermal energy than in a polymer-plasticizer system. Cooperative phenomena[27] were observed in viscoelastic properties of a closely related system, PVDF
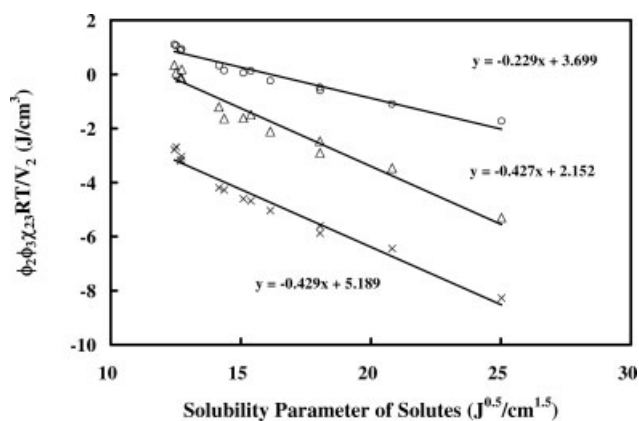
Figure 5 Plot of $\phi_2\phi_3RT\chi_{23}/V_2$ versus solubility parameter of probes, δ_1, at 175°C for PVDF/PEMA. Symbols: (O) 25/75 PVDF/PEMA; (Δ) 50/50 PVDF/PEMA; (X) 75/25 PVDF/PEMA. Data of 25/75 was shifted upward by 1 J/cm³ and data of 75/25 was shifted downward by 3 J/cm³. Unit: J/cm³ = MPa.
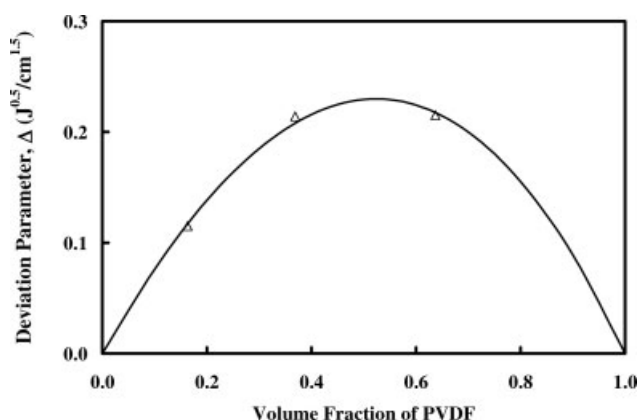
TABLE II
The Deviation Δ of Solubility Parameter from the Weight Average of PVDF/PEMA for Different Compositions and Temperatures ($J^{0.5}/cm^{1.5}$ = $MPa^{0.5}$)

Systems	Temperatures		
	175°C	185°C	195°C
PVDF/PEMA 25/75	0.132	0.129	0.115
PVDF/PEMA 50/50	0.209	0.214	0.214
PVDF/PEMA 75/25	0.200	0.209	0.215

and poly(methyl methacrylate) (PMMA) blend. The blends showed a relaxation spectrum with a single characteristic relaxation time.

The composition dependency of polymer solubility parameter is also shown in Figure 6 for 195°C. Note that the value of Δ depended on the composition. The curve was an equation obtained from least square fitting of data: $\phi(1 - \phi)(0.829 + 0.176\phi)$ $J^{0.5}/cm^{1.5}$. This equation contained a symmetric portion and a term to account for the skewness. It was near symmetric to volume fraction with a maximum at 0.52. In Table II the weight fraction was used, and a considerable skewness was seen. A similar situation was observed in IGC study of PVDF-poly(methyl methacrylate) (PMMA) blends.[28] Ridel and Prud'Homme concluded that the composition dependency of χ'_{23} of PVDF-PMMA can be explained using Flory–Orwoll–Vrij theory with a surface-to-volume ratio, s_2/s_3, of 1.2.[29]

At the maximum composition, the deviation of solubility parameter, Δ, was about 0.23 $J^{0.5}/cm^{1.5}$. This was about the same value as the PCL/PECH system. Despite many negative values for χ'_{23} as measured by eq. (3), the systems appeared to have a similar Δ compared with the PCL/PECH system. Many of these χ'_{23} were negative because polar ester

and alcohol probes were used, and they followed eq. (9). When δ_1 is larger than $\delta_{m,r}$ the value of $\phi_2\phi_3 RT(\chi_{23}/V_2)$ becomes more negative. In many systems these probes would be expected to interact with both polymers with different strength and might overtake the interaction between the two polymers. When this happened the deviation of specific retention volume would be different from the trend of the other probes, and scattering data might be observed. It appeared that the interaction between PVDF and PEMA was so specific or strongly cooperative that even alcohols followed eq. (10) very well. Cooperative interaction between two polymer chains could also explain why PCL/PECH followed eq. (10) well,[8] but the plasticized polymers in Figures 2 and 3 had more scattering.

CONCLUSIONS

A mechanism previously proposed for the probe dependency of polymer–polymer interactions was tested using plasticized PVC and a copolymer, and PVDF-PEMA mixtures. Two methods were previously proposed to test the miscibility. One was to examine the relative deviation of specific retention volume from the weight average rule. The other was to plot $\phi_2\phi_3 RT(\chi_{23}/V_2)$ versus δ_1. This plot was more linear than a plot of relative deviation of specific retention volume versus δ_1 or $(\phi_2\chi_{12} + \phi_3\chi_{13})/V_1$. The slope of this plot could be used as an indicator of miscibility. For plasticized PVC and PV(DC-VC), a ranking of miscibility was made based on the values of Δ.

Figure 6 Plot of deviation of solubility parameter of polymers, Δ, versus volume fraction of PVDF at 195°C. The solid curve is the best fit equation for the data: $\phi(1 - \phi)$ $(0.829 + 0.176\phi)$. Unit: $J^{0.5}/cm^{1.5}$ = $MPa^{0.5}$.

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