ELSEVIER

Polymer 42 (2001) 1075–1081

polymer

www.elsevier.nl/locate/polymer

Determination of solvent-independent polymer–polymer interaction parameter by an improved inverse gas chromatographic approach

L. Zhao, P. Choi*

Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2G6

Received 1 November 1999; received in revised form 24 May 2000; accepted 24 May 2000

Abstract

The solvent-dependence problem generally observed in the determination of polymer–polymer interaction parameters from inverse gas chromatography (IGC) measurements has been examined and resolved. The problem is mainly attributed to the use of different reference volumes in the calculations of χ_{12}, χ_{13}, and $\chi_{1(23)}$ from the raw IGC data for different solvents. Upon selection of a common reference volume for all the solvents used, IGC data were found to be well described by the ternary version of the Flory–Huggins lattice theory; unique solvent-independent χ_{23} values were obtained. Our data on blends of high-density polyethylene (HDPE) and low-density polyethylene (LDPE) have also confirmed the validity of the zero $\Delta\chi$ criterion suggested by Su and Patterson twenty odd years ago (Macromolecules, 10 (1977) 708) so long as a common reference volume is used in the data analysis. If the latter criterion is not satisfied, measured χ_{23} values still vary with the solvent used. However, it is uncertain whether the present approach can be applied to the situation in which the solvents used do not meet the zero $\Delta\chi$ criterion. The χ_{23} values obtained in the present work suggest that HDPE/LDPE blends may exhibit a closed-loop phase behavior. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Inverse gas chromatography; Reference volume; Polymer–polymer interaction parameter

1. Introduction

Much attention has been paid to polymer blends in the past few decades inasmuch as such multi-component systems can offer desirable processing and performance properties at reasonable costs that would otherwise be difficult to obtain by synthesizing new polymers. This, in turn, has created considerable interest in developing reliable and convenient experimental methods that can be used to characterize and to understand the miscibility of different polymers [1,2]. Although numerous methods have been developed for such purposes, only a few of them can be used to obtain thermodynamic parameters relevant to the miscibility issue. Among the frequently used techniques, inverse gas chromatography (IGC) has gained popularity in recent years because of its simplicity, rapidity, and the general availability of GC equipment [3,4]. However, the technique suffers from the drawback that the measured polymer–polymer interaction parameters have been found to be dependent on the chemical nature of the solvent used in the experiment in many systems. And it is generally believed that the phenomenon is attributed to the inappropriateness of the application of the original Flory–Huggins lattice theory to ternary systems [3,4].

In order to eliminate the problem and to enhance the applicability of IGC, numerous modifications have been proposed but none of them has been found satisfactory [5–11]. In particular, Munk and co-workers suggested that uncontrolled experimental artifacts and errors could cause the observed variability of χ_{23} with solvent [5]. Later, they pointed out that the solvent-dependence observation is real. Shi and Schreiber tackled the problem by correcting the concentrations used in the original Flory–Huggins expression based on the argument that the mixed stationary phase is not homogeneous (i.e. the surface and bulk concentrations are not the same) but they cannot totally eliminate the problem [6]. Horta and co-workers and Sanchez applied an equation-of-state approach and found that the contribution of the excess volume effect (one of the major deficiencies of the Flory–Huggins lattice theory) to the solvent-dependence problem is not significant [7–9]. Chee developed a method that can provide unique interaction density parameters (B_{23}), but not χ_{23}, based on an equation developed by Guillet et al. for the calculation of Hildebrand solubility parameters of polymers [10,12]. More recently, Farooque and Deshpande compared χ_{23} values obtained from various IGC approaches proposed in the literature as

---

* Corresponding author. Tel.: +1-780-492-9018; fax: +1-780-492-2881.
E-mail address: phillip.choi@ualberta.ca (P. Choi).

PII: S0032-3861(00)00412-2

well as their newly developed extrapolation method based upon the equation-of-state theory for polystyrene/polybutadiene blends at several elevated temperatures and found that none of the approaches is satisfactory [11].

All of the above findings led us to revisit the $\Delta\chi$ (i.e. $\chi_{12} - \chi_{13}$) effect proposed by Su and Patterson twenty odd years ago [13]. In particular, they suggested that in order to obtain solvent-independent χ_{23}, one must select solvents that give $\chi_{12} = \chi_{13}$. This is because such solvents can partition in a mixed stationary phase in a completely random fashion. As one can imagine, identifying such solvents is rather difficult in practice for many polymer blends. Nonetheless, we have been able to do so for high-density polyethylene (HDPE)/low-density polyethylene (LDPE) blends. But the measured χ_{23} values still vary with the solvent used. When such data were further examined, we discovered that the solvent-dependence problem essentially originates from the improper choice of reference volumes used in the calculations of the binary interaction parameters between various solvents and the pure polymers as well as their blends. When a common reference volume was used, the data conformed to the ternary version of the Flory–Huggins lattice theory and unique χ_{23} values were obtained. The rationale behind this new data analysis approach will be discussed in detail in Section 2. The new approach is illustrated with the use of the HDPE/LDPE blend since the materials are readily available and have been studied extensively by other researchers using techniques such as DSC, SANS, and TEM [14–18].

2. Theoretical background

Determination of solvent–polymer and polymer–polymer interaction parameters (i.e. χ_{12} or χ_{13} and χ_{23}) using IGC is well documented in the literature [4]. We, therefore, will only review the theoretical aspects that are pertinent to the present work in this section. Traditionally, when the Flory–Huggins lattice theory is applied to a solvent–polymer system [19], the molar volume of the solvent (V_1) is usually taken as the reference volume (V_0) to define the size of the lattice. Difficulties arise when one wants to compare interaction strengths between different solvents with the same polymer since these interaction parameters are calculated based on different lattice sizes. As a result, the apparent differences in the interaction parameters among different solvents with the same polymer do not necessarily completely originate from the differences in the intermolecular interactions but also the lattice sizes used. This is problematic especially when the ternary version of the Flory–Huggins theory is used to correlate experimental data involving more than one solvent. This is essentially the situation encountered in all IGC measurements and in our opinion, is the major cause for the observed solvent-dependence problem. In fact, when such data are analyzed using a common reference volume, the problem vanishes (see Section 4).

The question here is which V_0 should be used in the data analysis when a number of solvents are involved. According to the spirit of the original Flory–Huggins lattice theory, one should choose the smallest among the molar volumes of the solvents and polymers comprising the mixture in question. Here, for the polymers, the molar volumes of their repeat units rather than those of the whole molecules should be considered. Therefore, for this particular work, one should choose the molar volume of an ethylene repeat unit as the reference volume since all solvents used have molar volumes larger than that of the ethylene repeat unit. The molar volume of the ethylene repeat unit was calculated based on the experimental melt density and number average molecular weight of HDPE at the chosen experimental temperatures. With the adoption of such a reference volume, the Gibbs free energy change on mixing for a solvent–polymer system is given as follows:

$$\Delta G_{\mathrm{mix}} = \mathrm{R}T\left(n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi_{12} \frac{V_1}{V_0}\right). \tag{1}$$

Note that if V_1 is used as the reference volume, it follows that the V_1/V_0 term in the above expression will become 1 (i.e. the original Flory–Huggins expression for ΔG_{mix}). For a ternary system that consists of one solvent and two polymers, the expression takes the following form:

$$\Delta G_{\mathrm{mix}} = \mathrm{R}T\left(n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + n_1 \phi_2 \chi_{12} \frac{V_1}{V_0} + n_1 \phi_3 \chi_{13} \frac{V_1}{V_0} + n_2 \phi_3 \chi_{23} \frac{V_2}{V_0}\right). \tag{2}$$

In the above expressions, R is the universal gas constant; T is the temperature; n_i is the number of moles of component i where $i = 1$, 2 and 3 signifies the solvent and the two polymers; ϕ_i is the volume fraction of component i; V_i is the molar volume of component i where $i = 0$ signifies the reference volume and in the cases of the polymers, V_i corresponds to the molar volume of the polymer; and χ_{12}, χ_{13} as well as χ_{23} are the Flory–Huggins binary interaction parameters. It should be pointed out that in the original ternary version of the Flory–Huggins lattice theory, both χ_{12} and χ_{13} are defined based on V_1 while χ_{23} is defined based on either V_2 or V_3 but not V_1.

Having reviewed the rationale behind choosing the reference volume and incorporation of such a choice into the original Flory–Huggins lattice theory, we now turn our attention to the application of the above expressions to IGC measurements. In IGC, the parameter that manifests the elution behavior of a solvent is the specific retention volume, V_{g}^0, which is related to other experimental

Table 1
Characteristics of HDPE and LDPE

Resin	Density at 25°C (g/cm^3)	M_n	M_w	Branch content (branches/1000 carbon atoms)
HDPE	0.957	28,000	137,000	~0
LDPE	0.919	17,000	94,000	22

parameters as shown in the following expression [3]:

$$V_g^0 = \frac{273.15 t_R F J}{wT} \tag{3}$$

where t_R is the net retention time; F is the carrier-gas flow rate measured at the experimental temperature T; w is the mass of polymer(s) coated in the column; and J is the James-Martin correction factor that is used to correct the pressure gradient across the column. On the other hand, V_g^0 is also related to the partition coefficient of the solvent, which is defined as the ratio of the concentration of the solvent in the liquid phase, c_1^l, to that in the gaseous phase, c_1^g. For columns containing one polymer, the relationship reads:

$$V_g^0 = \left(\frac{c_1^l}{c_1^g}\right)\upsilon_2\left(\frac{273.15}{T}\right). \tag{4}$$

For columns which consist of two polymers

$$V_g^0 = \left(\frac{c_1^l}{c_1^g}\right)(w_2\upsilon_2 + w_3\upsilon_3)\left(\frac{273.15}{T}\right). \tag{5}$$

In expressions (4) and (5), υ_i and w_i are the specific volume and weight fraction, respectively, of polymer i in the liquid phase.

In general, a fast equilibrium of the solvent between the liquid and gaseous phases is established in a chromatographic column. Under such conditions, the chemical potentials of the solvent in both phases are the same; this means

$$\mu_1^l = \mu_1^g. \tag{6}$$

Here, the chemical potential of the solvent in the gaseous phase is given by the following expression [20]:

$$\mu_1^g = \mu_1^0 + \mathrm{R}T \ln \frac{\mathrm{R}Tc_1^g}{M_1} \tag{7}$$

where μ_1^0 is the chemical potential of the solvent in an arbitrarily chosen standard state, and M_1 is the molecular weight of the solvent. The chemical potential of the solvent in the liquid phase is depicted as follows [20]:

$$\mu_1^l = \mu_1^0 + \mathrm{R}T\left(\ln \alpha_1 + \ln P_1^0 + \frac{(B_{11} - V_1)P_1^0}{\mathrm{R}T}\right) \tag{8}$$

where P_1^0 is the vapor pressure of the solvent at temperature T; B_{11} is the second virial coefficient of the solvent in the gaseous phase; and α_1 is the activity of the solvent in the liquid state. According to thermodynamics, $\ln \alpha_1$ is related to the Gibbs free energy change on mixing through the following expression [19]:

$$\mathrm{R}T \ln \alpha_1 = \left(\frac{\partial \Delta G_{\mathrm{mix}}}{\partial n_1}\right)_{n_2,n_3,P,T} \tag{9}$$

Here, the partial derivative can be evaluated with the use of either expression (1) or (2) depending on the number of components in the liquid phase. If the concentration of the solvent in the liquid phase is very low (i.e. infinitely dilute), for a pure liquid phase, $(\partial \Delta G_{\mathrm{mix}}/\partial n_1)$ is given by:

$$\left(\frac{\partial \Delta G_{\mathrm{mix}}}{\partial n_1}\right)_{n_2,n_3=0,P,T} = \mathrm{R}T\left(\ln \phi_1 + 1 - \frac{V_1}{V_2} + \chi_{12}\frac{V_1}{V_0}\right). \tag{10}$$

If the liquid phase contains a binary polymer blend,

$$\left(\frac{\partial \Delta G_{\mathrm{mix}}}{\partial n_1}\right)_{n_2,n_3,P,T} = \mathrm{R}T\left(\ln \phi_1 + 1 - \frac{V_1}{V_2}\phi_2 - \frac{V_1}{V_3}\phi_3 + \phi_2\chi_{12}\frac{V_1}{V_0} + \phi_3\chi_{13}\frac{V_1}{V_0} - \phi_2\phi_3\chi_{23}\frac{V_1}{V_0}\right). \tag{11}$$

By combining expressions (8)–(10) and then equating the resultant expression to expression (7), after some manipulation, the final expression reads:

$$\chi_{12} = \frac{V_0}{V_1}\left(\ln \frac{273.15\mathrm{R}\upsilon_2}{V_g^0 V_1 P_1^0} - 1 + \frac{V_1}{M_2\upsilon_2} - \frac{(B_{11} - V_1)}{\mathrm{R}T}P_1^0\right). \tag{12}$$

By performing similar manipulation of the corresponding expressions for ternary systems, one obtains the following expression:

$$\phi_2\chi_{12} + \phi_3\chi_{13} + \phi_2\phi_3\chi_{23} = \frac{V_0}{V_1}\left(\ln \frac{273.15\mathrm{R}(w_2\upsilon_2 + w_3\upsilon_3)}{V_g^0 V_1 P_1^0} - 1 + \frac{V_1}{M_2\upsilon_2} + \frac{V_1}{M_3\upsilon_3} - \frac{(B_{11} - V_1)}{\mathrm{R}T}P_1^0\right). \tag{13}$$

For convenience, we define a new variable here, $\chi_{1(23)}$, as shown in the following expression to replace the left hand side of the above expression. Here, $\chi_{1(23)}$ can be thought of as the interaction between the solvent and the polymer blend.

$$\chi_{1(23)} = \phi_2\chi_{12} + \phi_3\chi_{13} - \phi_2\phi_3\chi_{23}. \tag{14}$$

Eq. (14) predicts that a plot of $\chi_{1(23)}$ versus $(\phi_2\chi_{12} + \phi_3\chi_{13})$ will give a straight line with a slope of 1 and an intercept of $-\phi_2\phi_3\chi_{23}$. Therefore, attainment of solvent-independent χ_{23} for a blend with polymer concentrations ϕ_2 and ϕ_3 and (note that $\phi_1 \cong 0$) essentially boils down to the determination of χ_{12}, χ_{13}, and $\chi_{1(23)}$ based on Eqs. (12) and (13). Other parameters (e.g. B_{11}) appearing in those equations can be calculated from the physical properties of the corresponding

Table 2
Loadings and mass of HDPE, LDPE and their blends used in the GC columns

Column number	Composition (weight% of HDPE)	Loading (% w/w)	Mass of polymer (g)
1	100% HDPE	8.80	0.05396
2	100% LDPE	7.14	0.04920
3	30% HDPE + 70% LDPE	8.55	0.05431
4	50% HDPE + 50% LDPE	8.05	0.05411
5	70% HDPE + 30% LDPE	6.76	0.04173

solvents and polymers. These were obtained or estimated using correlations obtained from Refs. [21–23].

3. Experimental

3.1. Materials

Both HDPE and LDPE samples used in this work were supplied by NOVA Chemical Corporation based in Calgary, Canada. Here, LDPE used is a homopolymer made by a high-pressure process. The molecular weight averages and branch contents of the polymers, which were determined by gel permeation chromatography (GPC) and Fourier transform infrared spectroscopy (FTIR), are listed in Table 1. Solvents used including aliphatic and aromatic hydrocarbons were purchased from Fisher Scientific Company. They were reagent grade and used without further purification.

3.2. Columns

The pure polymers and their blends were first dissolved in xylene at about 100–120°C and mixed with an inert solid support chromosorb W (60/80 mesh). The solvent was then evaporated slowly at the same temperature using a rotary evaporator in order to deposit the polymer(s) onto the surfaces of the solid support. The resultant coated chromosorb was dried in a vacuum oven at 50°C for 4 h and packed into an acetone-washed stainless steel tube (0.18 cm inner diameter and 100 cm in length) with gentle tapping. The tubes were ended by glass wool. The amount of polymer deposited on the chromosorb (i.e. loading) was determined by an ashing method with blank corrections. The loadings and weights of polymer coating of the columns are listed in Table 2. Each column was conditioned in a gas chromatograph at 60°C for 2 days under a helium flow to eliminate residual solvent before data collections. In addition, the variation from column to column has also been checked and it was found that the data is highly reproducible.

3.3. Instrumentation

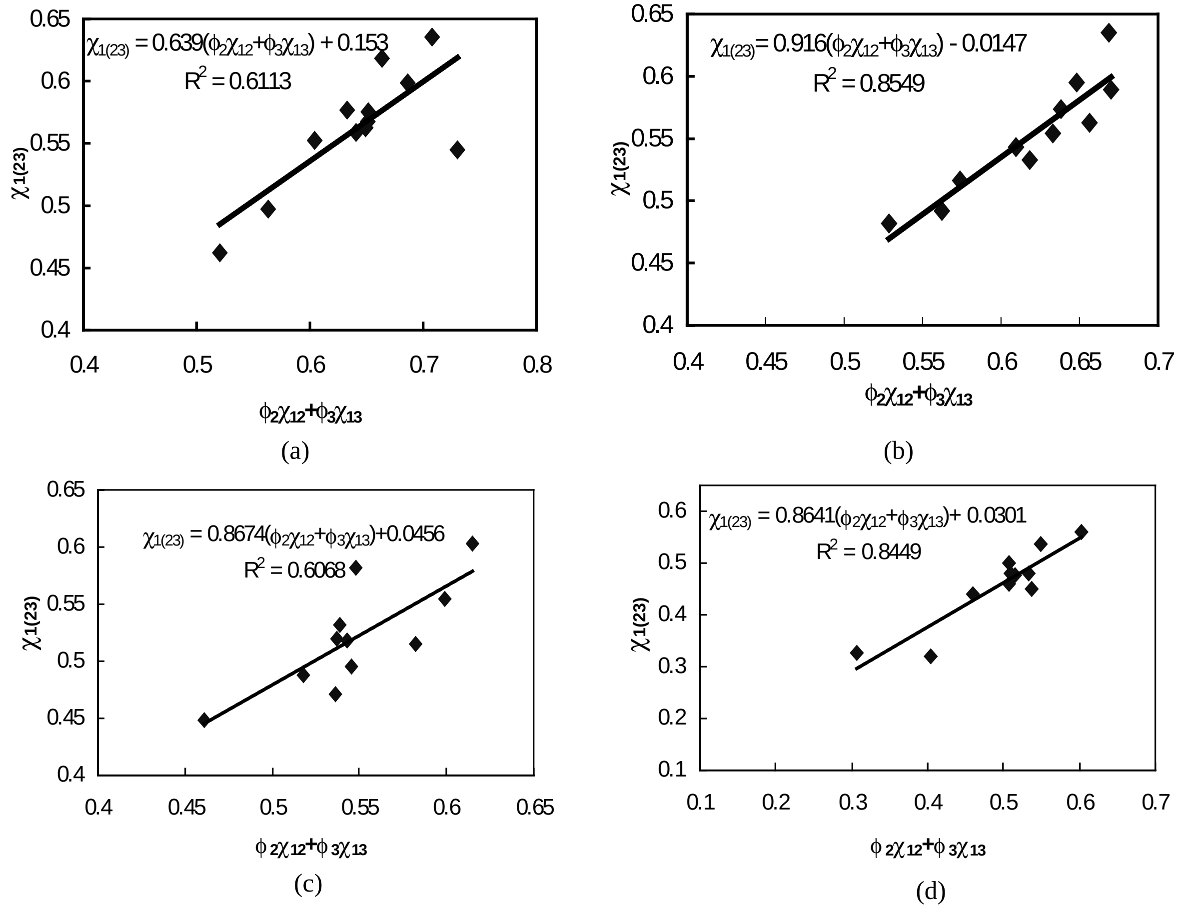
Measurements were carried out using a Hewlett-Packard 4890 gas chromatograph, equipped with a flame ionization detector (FID). Pre-purified Helium was used as the carrier gas at flow rates over the range from 18 to 21 ml/min, which were measured at the corresponding experimental temperatures with the use of a soap bubble flowmeter. The inlet and outlet pressures of the column were monitored with the manometers. For each solvent, three injections of 1 μl of its vapor were made to measure the retention time with a reproducibility of within 3%. The net retention times were determined using methane as the marker.

4. Results and discussion

By substituting measured V_g^0 in expressions (12) and (13),

Table 3
Measured Flory–Huggins interaction parameters between the selected solvents and pure HDPE, LDPE and their 50/50 blend at four elevated temperatures. We omit the corresponding tables for 30/70 and 70/30 blends for clarity

Probe	170°C			190°C			210°C			230°C		
	χ_{12}	χ_{13}	$\chi_{1(23)}$	χ_{12}	χ_{13}	$\chi_{1(23)}$	χ_{12}	χ_{13}	$\chi_{1(23)}$	χ_{12}	χ_{13}	$\chi_{1(23)}$
1-hexene	0.15	0.14	0.13	0.13	0.14	0.12	0.11	0.093	0.11	0.043	0.040	0.044
1-octene	0.13	0.11	0.11	0.11	0.12	0.10	0.12	0.099	0.099	0.097	0.089	0.091
benzene	0.24	0.22	0.21	0.21	0.22	0.20	0.21	0.17	0.19	0.17	0.18	0.16
cyclohexane	0.15	0.13	0.12	0.13	0.15	0.13	0.12	0.11	0.11	0.11	0.11	0.10
n-hexane	0.14	0.13	0.13	0.12	0.13	0.12	0.11	0.089	0.093	0.056	0.061	0.046
n-dodecane	0.078	0.072	0.066	0.074	0.075	0.065	0.071	0.072	0.062	0.069	0.069	0.058
n-heptane	0.13	0.12	0.11	0.12	0.12	0.10	0.094	0.099	0.093	0.087	0.081	0.076
n-nonane	0.11	0.098	0.092	0.11	0.093	0.087	0.089	0.087	0.080	0.080	0.075	0.073
n-octane	0.12	0.11	0.10	0.11	0.11	0.095	0.100	0.099	0.088	0.091	0.073	0.081
toluene	0.19	0.17	0.16	0.18	0.17	0.15	0.15	0.14	0.14	0.15	0.12	0.12
xylenes	0.15	0.14	0.13	0.14	0.13	0.13	0.13	0.12	0.12	0.13	0.11	0.11

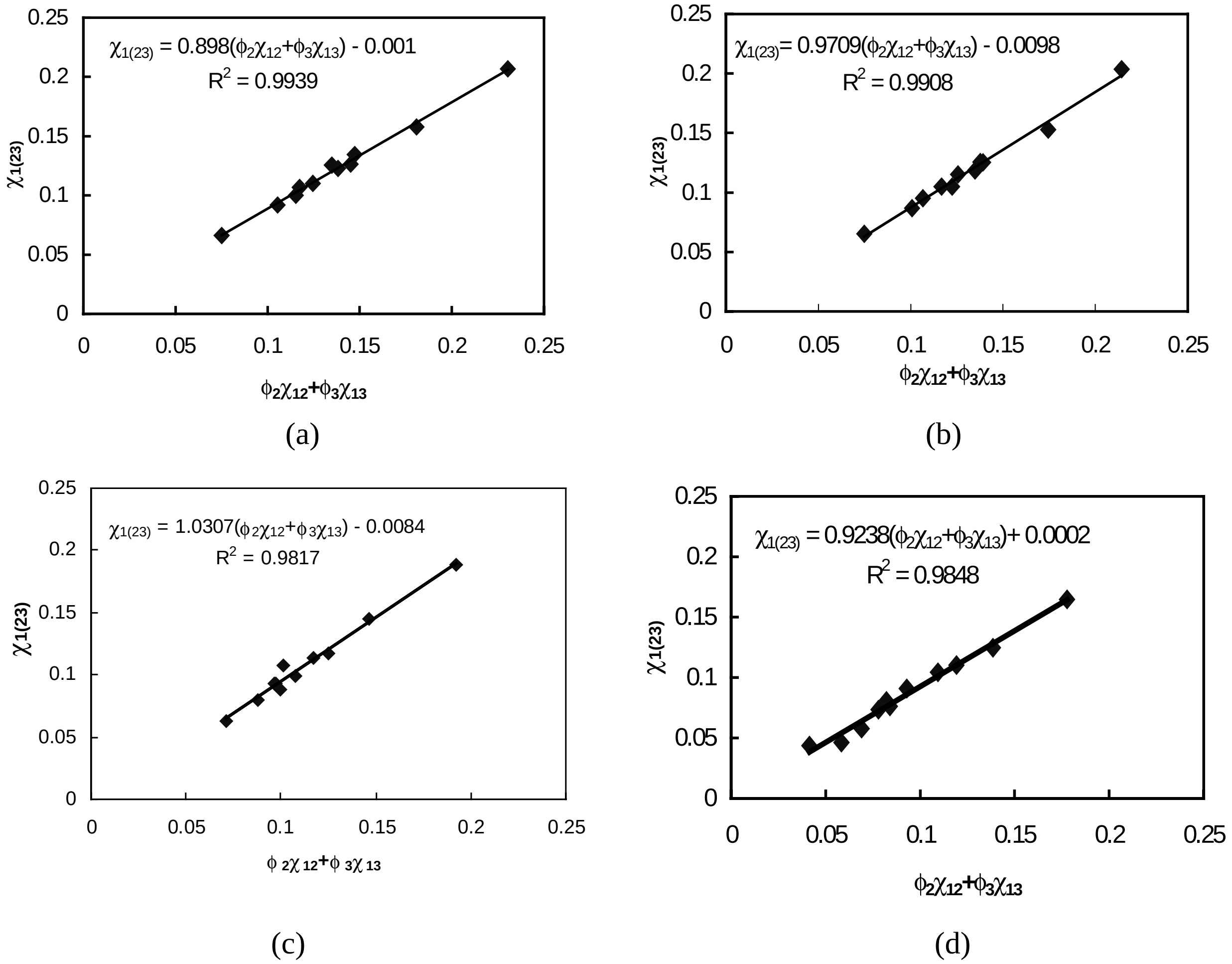


(a) (b)

(c) (d)

Fig. 1. Plots of $\chi_{1(23)}$ vs. $(\phi_2\chi_{12} + \phi_3\chi_{13})$ for the 50:50 HDPE/LDPE blends at four elevated temperatures: (a) $T = 170$°C; (b) $T = 190$°C; (c) $T = 210$°C; and (d) $T = 230$°C (solvent as V_0).

Flory–Huggins interaction parameters between the selected solvents and the pure polymers (i.e. χ_{12} and χ_{13}) as well as their corresponding blends (i.e. $\chi_{1(23)}$) were calculated at 170, 190, 210, and 230°C and are summarized in Table 3. It is evident from the table that both χ_{12} and χ_{13} are rather close to each other indicating that most of the solvents used satisfy the zero $\Delta\chi$ criterion. It is worth noting that the criterion was also satisfied even though the molar volumes of the solvents were used as reference volumes in the calculations of χ_{12} and χ_{13}. But when such interaction parameters were used for the plots of $\chi_{1(23)}$ versus $(\phi_2\chi_{12} + \phi_3\chi_{13})$, the data scatters considerably and the linearity, characterized by R^2, is poor (see Fig. 1). Here, we omit the corresponding figures of 30/70 and 70/30 blends for clarity. In contrast, when the molar volume of the ethylene repeat unit was used, the resultant data conforms remarkably well to Eq. (14). This observation is significant because this means that the ternary version of the Flory–Huggins lattice theory is, at least, applicable to the present set of data and unique interaction parameters can be obtained from the intercepts of the regression lines. Fig. 2 illustrates such plots of $\chi_{1(23)}$ versus $(\phi_2\chi_{12} + \phi_3\chi_{13})$ for the same 50/50 blend. As can be seen in Fig. 2, the linearity is excellent (high R^2 values) in all cases and the slopes are quite close to the expected value of 1. The solvent-independent χ_{23} values were then determined from the intercepts of these regression lines. The corresponding uncertainties were calculated based upon the measurement errors of the flow rate of the carrier gas, net retention time and mass of polymer(s) in the column. Both average χ_{23} values and their associated error bars are summarized in Table 4. It is noteworthy that the errors associated with $\chi_{12,}$ χ_{13}, and $\chi_{1(23)}$, not shown here, are rather small and within a range of 5%. It is unfortunate that due to error propagation, large error bars for χ_{23} were obtained. As a result, it is rather difficult to infer miscibility in those cases where measured χ_{23} values are close to the critical interaction parameter which is about 5×10^{-4} for the present blend. In other words, the present method is not suitable for measuring small χ_{23}. However, in the cases where the extrapolated χ_{23} values were far from the critical interaction parameter (e.g. the 70% blend at 210°C), it is believed that such a deviation is real, not due to random experimental errors. As shown in Fig. 3, χ_{23} exhibits a maximum over the temperature range under investigation indicating that the blend may show a closed-loop phase diagram. The location of the peak depends on the



(a) (b) (c) (d)

Fig. 2. Plots of $\chi_{1(23)}$ vs. $(\phi_2\chi_{12} + \phi_3\chi_{13})$ for the 50:50 HDPE/LDPE blends at four elevated temperatures: (a) $T = 170$°C; (b) $T = 190$°C; (c) $T = 210$°C; and (d) $T = 230$°C.

composition of the blend. A similar trend was observed for other polyethylene blends using the same technique in our laboratory and also obtained from our recent molecular dynamics (MD) calculations [24–25]. It should be noted that the MD results were obtained without the use of a third solvent and therefore, based upon the molar volume of the ethylene repeat unit.

It is evident in Fig. 2 that our data is well described by the Flory–Huggins lattice theory. This is somewhat surprising because the theory is known to be inadequate in many respects, the volume change on mixing, in particular. In our view, the following may probably explain our observation. First, different types of polyethylenes, regardless of their branching characteristics and/or content, have the same melt density above their melting temperatures [23]. This means that the free volumes as well as the expansion coefficients of both HDPE and LDPE at a given elevated temperature are identical and that volume change on mixing should be minimal. Secondly, as pointed out by Prolongo et al., the free volume differences between polymers are not the real cause for obtaining solvent-dependent χ_{23} [7–8]. Therefore, using more complicated solution theories such as the equation-of-state theory is not necessary. The Flory–Huggins lattice theory should be sufficient for describing the present set of data.

Table 4
Measured solvent-independent polymer–polymer χ_{23}

HDPE (wt%)	170°C	190°C	210°C	230°C
30	0.0098 ± 0.0088	0.073 ± 0.0091	0.025 ± 0.0097	0.0065 ± 0.0062
50	0.0040 ± 0.0074	0.039 ± 0.0075	0.034 ± 0.0087	−0.00080 ± 0.0053
70	0.033 ± 0.011	0.060 ± 0.011	0.098 ± 0.013	−0.0024 ± 0.0077

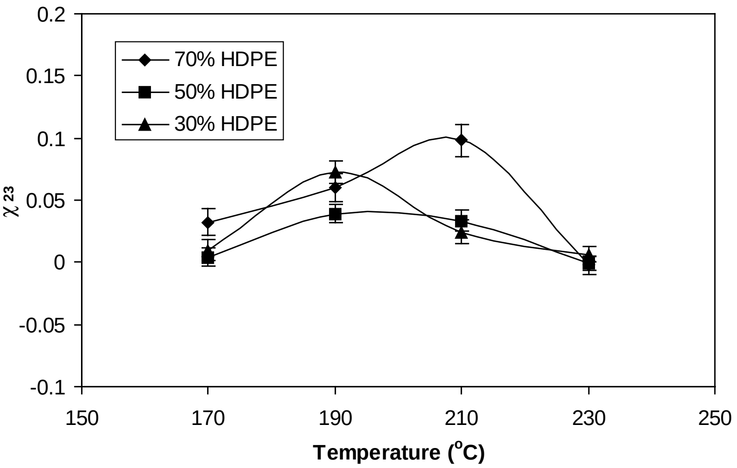


Fig. 3. Temperature-dependence of χ_{23} for the HDPE/LDPE blends at various compositions.

5. Conclusions

In summary, we have demonstrated that by selecting a proper common reference volume for analyzing IGC data, one can yield reliable solvent-independent χ_{23} so long as the solvents used satisfy the zero $\Delta\chi$ criterion suggested by Su and Patterson. However, it is uncertain whether such an approach can be used in the case of using solvents that do not meet the zero $\Delta\chi$ criterion. But it is anticipated that the method should be applicable to other polyolefin blends. The measured χ_{23} from the newly developed procedure for the HDPE/LDPE blend were found to be temperature- and concentration-dependent, as expected. The temperature-dependence was found to be non-$1/T$; instead, it exhibits a maximum over the temperature range being studied and the location of the peak varies with the composition of the blend.

Acknowledgements

We thank NOVA Chemicals Corporation and Natural Science Research Council of Canada for supporting this work financially. We would also like to thank Drs Charles Russell, Kam Ho, and Shiv Goyal of Nova Research and Technology Centre (NRTC) for valuable discussions.

References

[1] Olabisi O, Robeson LM, Shaw MT. Polymer–polymer miscibility. New York: Academic Press, 1979.
[2] Utracki LA. Polymer alloys and blends — thermodynamics and rheology. New York: Academic Press, 1989.
[3] Lloyd DR, Ward TC, Schreiber HP, editors. ACS Symposium Series 391Washington, DC: American Chemical Society, 1989.
[4] Al-Saigh ZY. Int J Polym Anal Charact 1997;3:249.
[5] El-Hibri MJ, Cheng W, Munk P. Macromolecules 1988;21:3458.
[6] Shi ZH, Schreiber HP. Macromolecules 1991;24:3522.
[7] Prolongo MG, Masegosa RM, Horta A. Macromolecules 1989;22:4346.
[8] Prolongo MG, Masegosa RM, Horta A. Macromolecules 1991;24:3788.
[9] Sanchez IC. Polymer 1989;30:471.
[10] Chee KK. Polymer 1990;31:1711.
[11] Farooque AM, Denshpande DD. Polymer 1992;33(23):5005.
[12] Lipson JEG, Guillet JE. J Polym Sci, Polym Phys Ed 1981;19:1199.
[13] Su CS, Patterson D. Macromolecules 1977;10:708.
[14] Hill MJ, Barham PJ, Keller A, Rosney CCA. Polymer 1991;32(8):1384.
[15] Hill MJ, Barham PJ. Polymer 1995;36(8):1523.
[16] Alamo RG, Londono JD, Mandelkern L, Stehling FC, Wignall GD. Macromolecules 1994;27:411.
[17] Agamalian M, Alamo RG, Kim MH, Londono JD, Mandelkern L, Wignall GD. Macromolecules 1999;32:3093.
[18] Alamo RG, Graessley WW, Krishnamoorti R, Lohse DJ, Londono JD, Mandelkern L, Stehling FC, Wignall GD. Macromolecules 1997;30:561.
[19] Flory PJ. Principles of polymer chemistry. New York: Cornell University Press, 1953.
[20] Denbigh KG. Principles of chemical equilibrium. 4th ed. Cambridge: Cambridge University Press, 1996.
[21] Reid RC, Prausnitz JM, Sherwood TK. The properties of gases and liquids. New York: McGraw-Hill, 1987.
[22] Tsonopoulos C. AIChE J 1974;20:263.
[23] Rudin A, Chee KK, Shaw JH. J Polym Sci, Part C 1970;30:415.
[24] Choi P. Polymer 2000;41:8741.
[25] Fan Z, Williams MC, Choi P, submitted for publication.