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Measurement of solvent-independent polymer–polymer Flory–Huggins interaction parameters with the use of non-random partitioning solvents in inverse gas chromatography

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Abstract

Flory–Huggins interaction parameters of two well-known immiscible binary polyolefin blends consisted of high-density polyethylene (HDPE) and isotactic polypropylene (i-PP) and of HDPE and atactic polystyrene (a-PS) were measured by inverse gas chromatography (IGC). In particular, the data analysis approach recently proposed by the authors was used to test whether non-random partitioning solvents could be one of the causes for the solvent dependence problem commonly observed in IGC measurements. Current results reinforced our previous claim that the solvent dependence problem is mainly attributed to the use of the molar volumes of the solvents used in the experiment concurrently for the calculations of the solvent–stationary phase interaction parameters and not to the use of non-zero $\Delta\chi$ ($\Delta\chi = \chi_{12} - \chi_{13}$) (i.e. non-random partitioning) solvents. In other words, solvent independent χ_{23} can be obtained so long as a single common reference volume is used for the data analysis. The interaction parameters for the HDPE/i-PP and HDPE/a-PS blends were found to be in the range of 0.03–0.10 and of 0.03–0.13, respectively. In the cases of 50/50 blends, the results were comparable to those obtained from neutron reflectivity measurements. © 2002 Published by Elsevier Science Ltd.

Keywords: Inverse gas chromatography; HDPE/i-PP and HDPE/a-PS blends; Non-random partitioning solvents

1. Introduction

Recently, we have demonstrated that the solvent dependence problem commonly encountered in the inverse gas chromatography (IGC) measurement of polymer–polymer Flory–Huggins interaction parameter (χ_{23}) is mainly attributed to the use of the molar volumes of the solvents used in the experiment concurrently for the calculations of the solvent–stationary phase interaction parameters (i.e. χ_{12}, χ_{13} and $\chi_{1(23)}$). And simply by using a single common reference volume for such calculations, solvent-independent χ_{23} can be obtained [1]. In the previous work, the proposed data analysis approach was tested on blends of high-density polyethylene (HDPE) and low-density polyethylene (LDPE) at several elevated temperatures. Owing to the chemical similarity of HDPE and LDPE, all the solvents used exhibited very small or near to zero $\Delta\chi$ ($\Delta\chi = \chi_{12} - \chi_{13}$) in the range of 0.01–0.02. This coincidentally matched Su and Patterson's argument that zero $\Delta\chi$ solvents should be used to obtain solvent independent interaction parameters [2]. As a result, it was unclear whether the newly proposed data analysis approach is applicable to the systems that solvents used do not meet the zero $\Delta\chi$ criterion.

Here, according to Su and Patterson's argument, the difference between χ_{12} and χ_{13} reflects the degree of non-random partitioning of the solvent molecules in the two constituent polymers of the blend. They as well as many other researchers believed that it is the non-random partitioning behavior that causes the solvent dependence problem. This is because, to obtain χ_{23}, all χ_{12}, χ_{13}, and $\chi_{1(23)}$ are required (see Eq. (3)). Strictly speaking, both χ_{12} and χ_{13} correspond to the interaction parameters between the solvent (i.e. component 1) and polymers 2 and 3, respectively, in a blend environment in which both polymers are present. Obviously, it is practically impossible to do so. As a result, χ_{12} and χ_{13} used in Eq. (3) are usually obtained with the use of IGC columns containing pure polymers 2 and 3. It is conceivable that χ_{12} obtained from

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the binary system (solvent + polymer 2) must be different from that from the ternary system (solvent + polymers 2 and 3) because of the presence of polymer 3. So is χ_{13}. Consequently, using different solvents will produce different χ_{23}. They suggested that in order to obtain the solvent independent interaction parameter, one should use the solvents that meet the criterion of $\chi_{12} = \chi_{13}$ or $\Delta\chi = 0$. In this case, the presence of polymer 3 will not alter the interaction between polymer 2 and the solvent so that, χ_{12} in the ternary system is the same as that obtained from the binary system. Therefore, they claimed that χ_{23} calculated from each solvent should be the same. However, by extending Su and Patterson's argument, if the third component has significant effect on the interaction between the other two components, the presence of the solvent will also interfere with the interaction between the two polymers as well. Obviously, each solvent will have different degree of influence on the measured χ_{23} even when the solvents used meet the criterion of $\chi_{12} = \chi_{13}$. As a result, χ_{23} obtained using different solvents will still be different. Therefore, in order to obtain the probe independent χ_{23}, the solvent and polymers used should meet $\chi_{12} = \chi_{13} = \chi_{23}$ instead of $\chi_{12} = \chi_{13}$. Systems that meet such a criterion might not exist. In fact, with the results of our previous work, we suspected that meeting such a criterion was not necessary for the attainment of solvent independent χ_{23}.

To verify such speculation, we furthered our proposed data analysis approach to blends that consisted of polymers that are chemically rather different. In this regard, we have deliberately chosen two well-known immiscible polyolefin blends. And they are blends of HDPE and isotactic polypropylene (i-PP) and of HDPE and atactic polystyrene (a-PS). It is expected that the solvents used would exhibit fairly large $\Delta\chi$ values for these blends. In addition, since miscibility of the HDPE/i-PP and HDPE/a-PS blends has been extensively investigated using a wide variety of experimental as well as computational techniques, findings from the present study can be readily compared with results obtained from those techniques to determine whether the new IGC data analysis approach yields reasonable χ_{23} values.

2. Theory

In the following, we will only review the key expressions that are crucial to the present work. Interested readers should refer to our previous article for detailed derivation of those equations that require the use of a single common reference volume (V_0) rather than the individual molar volumes of the solvents used in the IGC experiment for the calculations of the solvent–stationary phase interaction parameters [1].

With the adoption of a common reference volume, the original Gibbs free energy change on mixing expression derived upon the Flory–Huggins lattice theory for a solvent–polymer system is simply modified by multiplying the enthalpy part by V_0/V_1. Note that χ_{12} in the original Flory–Huggins theory is expressed based on the solvent's molar volume (V_1) [3]. By combining the derivative of the modified Gibbs free energy change on mixing expression with that of the solvent's activity coefficient obtained from thermodynamics, χ_{12} or χ_{13} can be estimated by the following expression [4,5]

$$\chi_{12(\text{or }3)} = \frac{V_0}{V_1}\left(\ln\frac{273.15Rv_{2(\text{or }3)}}{V_g^0 V_1 P_1^0} - 1 + \frac{V_1}{M_{2(\text{or }3)}v_{2(\text{or }3)}} - \frac{(B_{11}-V_1)}{RT}P_1^0\right) \tag{1}$$

where $\chi_{12(\text{or}3)}$ is the interaction parameter between a particular solvent and the polymer of interest; V_0 is the reference volume and V_1 is the molar volume of the solvent. R is the universal gas constant and T is the experimental temperature; v_2 is the specific volume of the polymer; and V_g^0 is the specific retention volume that is determined from the net retention time of the solvent and is calculated using the standard chromatographic relation given in Ref. [6]. P_1^0 is the vapor pressure of the solvent; M_2 is the number average molecular weight of the polymer; and B_{11} is the second virial coefficient of the solvent in the gaseous phase. Here, the reference molar volume used is the one of an ethylene repeating unit at the experimental temperature T, as explained in our previous published work. For a ternary system that contains one solvent and two polymers, the interaction parameter between the solvent and the blend composed of polymers 2 and 3, $\chi_{1(23)}$, is given by:

$$\chi_{1(23)} = \frac{V_0}{V_1}\left(\ln\frac{273.15R(w_2v_2 + w_3v_3)}{V_{g\,\text{blend}}^0 V_1 P_1^0} - 1 + \frac{V_1}{M_2v_2} + \frac{V_1}{M_3v_3} - \frac{(B_{11}-V_1)}{RT}P_1^0\right) \tag{2}$$

Here, $\chi_{1(23)}$ is related to the other binary interaction parameters as shown in the following expression:

$$\chi_{1(23)} = \phi_2\chi_{12} + \phi_3\chi_{13} - \phi_2\phi_3\chi_{23} \tag{3}$$

If χ_{23} is assumed to be constant for a given blend at a fixed concentration (i.e. independent of the solvent used), Eq. (3) basically predicts that a plot of $\chi_{1(23)}$ versus $(\phi_2\chi_{12} + \phi_3\chi_{13})$ will yield a straight line with a slope of 1 and an intercept of $-\phi_2\phi_3\chi_{23}$. Therefore, solvent independent χ_{23} can be obtained from the intercept of such a plot. It should be noted that the plot does not require the solvents that must meet the zero $\Delta\chi$ criterion. Another noteworthy point is that, if all the solvent–stationary phase interaction parameters (i.e. χ_{12}, χ_{13} and $\chi_{1(23)}$) for each solvent are calculated using the corresponding solvent molar volume, the linear relationship between $\chi_{1(23)}$ and $(\phi_2\chi_{12} + \phi_3\chi_{13})$ will be destroyed and solvent independent χ_{23} cannot be obtained. It is evident that once V_g^0 and other physical

Table 1
Characteristics of HDPE, i-PP and a-PS used

Resin	Density at 25 °C (g/cm^3)	M_n	M_w
HDPE	0.962	13,700	49,400
i-PP	0.90	N/A	270,000
a-PS	1.04	200,000	N/A

parameters of the solvent and polymers used in the experiment appeared in Eqs. (1) and (2) have been determined, χ_{12}, χ_{13} and $\chi_{1(23)}$ can be readily calculated. Here, such parameters were estimated using correlations obtained from other sources and will not be described here [7–10].

3. Experimental

3.1. Materials

Two immiscible binary blends, composed of HDPE and i-PP and of HDPE and a-PS, respectively, were studied at three different concentrations over the temperature range of 170–230 °C. The HDPE sample was supplied by NOVA Chemicals Corporation. The i-PP sample was obtained from Dow Chemicals while the a-PS sample from Exxon Chemicals. The average molecular weights, which were determined by gel permeation chromatography (GPC), and the solid-state density of the homo-polymers are listed in Table 1. It should be pointed out that the molecular weights of the samples used are very comparable to those of the samples that were used in the neutron reflectivity (NR) measurements of Bucknall et al. [11]. High purity solvents including both aliphatic and aromatic hydrocarbons were purchased from Fisher Scientific Company and used without further purification.

3.2. Sample preparation and data collection

The IGC columns, both the pure and blend ones, were prepared using the standard procedure described elsewhere [1]. The loadings and mass of polymer coated 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 that was used to prepare the coated Chromosorb before data collections. 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 in the range from 18 to 21 ml/min that were measured at the corresponding experimental temperatures with the use of a soap bubble flow-meter. The inlet and outlet pressures of the column were monitored with pressure gauges during the experiments. 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 and the net retention times were subsequently converted into the specific retention volume V_g^0. And all the solvent–stationary phase and polymer–polymer interaction parameters were calculated using the foregoing described equations.

Table 2
Loadings and mass of HDPE, i-PP, a-PS and their blends used in the GC columns

Column number	Composition (wt% of HDPE)	Loading (% w/w)	Mass of polymer (g)
1	100% HDPE	8.80	0.05396
2	100% i-PP	7.09	0.04582
3	30% HDPE + 70% i-PP	6.95	0.04303
4	50% HDPE + 50% i-PP	8.32	0.05273
5	70% HDPE + 30% i-PP	7.15	0.04726
6	100% a-PS	8.85	0.05658
7	30% HDPE + 70% a-PS	8.66	0.05986
8	50% HDPE + 50% a-PS	8.45	0.05207
9	70% HDPE + 30% a-PS	8.35	0.05791

4. Results and discussion

For each column, specific retention volumes for each solvent were calculated from the experimental retention times. Substituting those average specific retention volumes along with the corresponding physiochemical properties of polymers and solvents into Eqs. (1) and (2), interaction parameters for the pure polymers, χ_{12} and χ_{13}, and their blends $\chi_{1(23)}$ were obtained. Here, the specific volumes of a-PS at high temperatures are calculated using the following equation [12]:

$$v = (1.0865 - 6.19 \times 10^{-4}T + 1.36 \times 10^{-7}T^2)^{-1} \qquad (4)$$

And the specific volumes of HDPE and i-PP at the experimental temperatures were obtained from the work of Rudin et al. [13].

The resultant interaction parameters of different solvents with pure HDPE, a-PS, and with their 50/50 blend from 170 to 230 °C are listed in Table 3. It can be seen from this table that all solvents used exhibited rather different χ_{12} and χ_{13} (they vary from 0.03 to 0.06). Here, it should be noted that the $\Delta\chi$ range for the HDPE/LDPE blends used in our previous work was about 0.01–0.02. It is clear that the $\Delta\chi$ values shown by the blends used in the present work are significantly greater than those of the HDPE/LDPE systems and do not meet the zero $\Delta\chi$ criterion. However, when $\chi_{1(23)}$ was plotted against $(\phi_2\chi_{12} + \phi_3\chi_{13})$ for the same set of data, it was found that all data points followed a straight line with reasonably good linearity as shown in Fig. 1. This suggests that the data can be described quite well by Eq. (3) even if χ_{12} and χ_{13} differed considerably. Therefore, solvent independent χ_{23} can still be obtained between the two polymers by using a common reference volume although the

Table 3
Measured Flory–Huggins interaction parameters between the selected solvents and pure HDPE, a-PS and their 50/50 blend at 170, 190, 210 and 230 °C

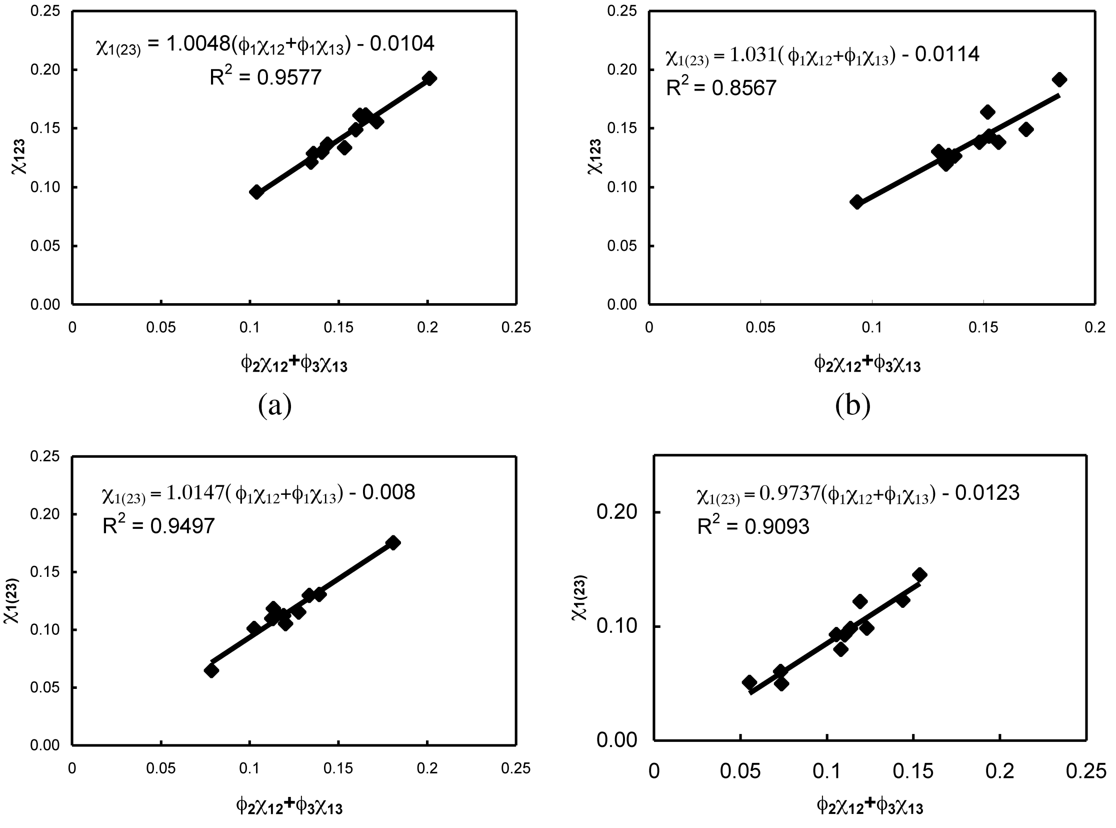
Probe	170 °C			190 °C			210 °C			230 °C		
	χ_{12}	χ_{13}	$\chi_{1(23)}$	χ_{12}	χ_{13}	$\chi_{1(23)}$	χ_{12}	χ_{13}	$\chi_{1(23)}$	χ_{12}	χ_{13}	$\chi_{1(23)}$
1-Hexene	0.15	0.19	0.16	0.13	0.18	0.14	0.11	0.13	0.11	0.04	0.07	0.05
1-Octene	0.13	0.16	0.14	0.11	0.15	0.13	0.12	0.14	0.12	0.10	0.11	0.09
Benzene	0.24	0.17	0.19	0.21	0.16	0.19	0.21	0.15	0.18	0.17	0.13	0.14
Cyclohexane	0.15	0.18	0.16	0.13	0.18	0.16	0.12	0.15	0.13	0.11	0.13	0.12
n-Hexanes	0.14	0.18	0.16	0.12	0.19	0.14	0.11	0.13	0.11	0.06	0.09	0.06
n-Dodecane	0.08	0.13	0.10	0.07	0.11	0.09	0.07	0.09	0.06	0.07	0.08	0.05
n-Heptane	0.13	0.18	0.13	0.12	0.18	0.14	0.09	0.13	0.12	0.09	0.13	0.09
n-Nonane	0.11	0.16	0.12	0.11	0.16	0.12	0.09	0.12	0.10	0.08	0.14	0.08
n-Octane	0.12	0.16	0.13	0.11	0.16	0.13	0.10	0.12	0.11	0.09	0.14	0.10
Toluene	0.19	0.13	0.15	0.18	0.16	0.15	0.15	0.11	0.13	0.15	0.13	0.12
Xylenes	0.15	0.12	0.13	0.14	0.13	0.13	0.13	0.10	0.11	0.13	0.12	0.10

Table 4
Measured polymer–polymer interaction parameters between HDPE and i-PP

HDPE (wt%)	170 °C	190 °C	210 °C	230 °C
30	0.074 ± 0.026	0.051 ± 0.024	0.062 ± 0.022	0.070 ± 0.015
50	0.053 ± 0.021	0.043 ± 0.020	0.031 ± 0.019	0.064 ± 0.013
70	0.048 ± 0.028	0.062 ± 0.027	0.10 ± 0.025	0.13 ± 0.018

Table 5
Measured polymer–polymer interaction parameters between HDPE and a-PS

HDPE (wt%)	170 °C	190 °C	210 °C	230 °C
30	0.13 ± 0.048	0.051 ± 0.040	0.116 ± 0.038	0.092 ± 0.024
50	0.042 ± 0.030	0.046 ± 0.030	0.032 ± 0.019	0.049 ± 0.018
70	0.061 ± 0.035	0.070 ± 0.040	0.066 ± 0.031	0.19 ± 0.024



(a) (b)

(c) (d)

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

Table 6
Comparison of χ values from current work and the literature

Interaction parameter χ	Technique used	HDPE/i-PP blend	HDPE/a-PS blend
Current work	IGC	0.053 (50/50, 170 °C)	0.042 (50/50, 170 °C)
Refs. [11,16]	Neutron reflectivity	0.020 (175 °C)	0.053 (150 °C)
Ref. [14]	Monte Carlo simulation	0.090 (0.45/0.55, 200 °C)	N/A
Ref. [15]	Small angle neutron scattering	0.0038 (50/50, 167 °C)	N/A

solvent molecules exhibited non-random partitioning behavior. This result indicates that the contribution of non-zero $\Delta\chi$ to the probe dependence problem is negligible and the problem is mainly attributed to the improper use of the reference volume.

Tables 4 and 5 summarize the χ_{23} values, as a result of the plot of $\chi_{1(23)}$ versus $(\phi_2\chi_{12} + \phi_3\chi_{13})$, for the HDPE/i-PP and HDPE/a-PS blends at different compositions and temperatures, along with the associated uncertainties. From Table 4, it can be seen that depending on the temperature and composition, χ_{23} values of the HDPE/i-PP blends are in the range from 0.04 to 0.13 with uncertainties at about 0.03 and most of them are above 0.05 indicating that the blend components are immiscible which is consistent with observations of other techniques reported in the literature. It should be noted that the χ_{23} values were calculated based on the reference volume of molar volume of an ethylene repeating unit. Table 6 lists the χ_{23} values for the HDPE/i-PP blends obtained from the present work as well as those from other researchers using different techniques. It is clear that the current IGC approach, NR measurements [11] and molecular simulation [14] yielded χ_{23} in the same order of magnitude. However, all such results are at least one order of magnitude larger than χ_{23} value from SANS, which is 3.8×10^{-3} at 167 °C based on the same reference volume [15]. Here, it is uncertain whether NR or SANS yields more reliable χ_{23} value. Nevertheless, the results obtained from NR lend some support to the approach we propose here. For the HDPE/a-PS blends, our χ_{23} values are in the range of 0.04–0.19. The errors for χ_{23} were determined to be 0.03. Hermes et al. used NR to study similar systems and found that χ_{23} values are in the range of 0.038–0.08 at 150 °C [16], as also shown in Table 6. It is obvious that χ_{23} values obtained in this work are consistent with results of Hermes et al. The current results also indicated that HDPE and a-PS should form an immiscible blend.

5. Conclusions

In this paper, we have demonstrated that solvent independent χ_{23} can be obtained for systems in which solvents used did not meet the zero $\Delta\chi$ criterion (i.e. the solvent molecules exhibited non-random partitioning in the two components of the blend). The non-random partitioning behavior of solvents is not the real reason to the probe dependence problem. The probe dependence problem is mainly attributed to the improper use of the reference volume in the calculations of the solvent–stationary phase interaction parameters (i.e. χ_{12}, χ_{13} and $\chi_{1(23)}$). The interaction parameters of the HDPE/i-PP blends obtained in this work were in the range from 0.04 to 0.13 and from 0.04 to 0.19 for the HDPE/a-PS blends, which were consistent with those obtained from NR measurements. The measured χ_{23} indicated that both blends were immiscible in the melt state which was in good agreement with findings of other researchers.

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