

Study of the Effect of Branch Content of Octene-Based Linear Low-Density Polyethylene on Its Melt Miscibility with High-Density Polyethylene by Inverse Gas Chromatography

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ABSTRACT: Inverse gas chromatography was used to measure Flory–Huggins interaction parameters (χ_{23}) for five binary blends consisting of high-density polyethylene (HDPE) and octene-based linear low-density polyethylene (LLDPE) with different compositions at four elevated temperatures. The branch content of the LLDPE used in each pair of the blends ranged from 2 to 87 branches per 1000 backbone carbons. To obtain solvent-independent χ_{23} , the data analysis approach recently proposed by Zhao and Choi (Polymer 2001, 42, 1075) was used. The results indicate that the higher the branch content of LLDPE, the higher the

measured χ_{23} , signifying that HDPE/LLDPE blends with low branch content LLDPEs are relatively more miscible than those with high branch contents. In particular, when the branch content of LLDPE is higher than 50 branches per 1000 backbone carbons, phase separation may occur. This result is in good agreement with other researchers' results obtained from different techniques. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1927–1931, 2004

Key words: blends; miscibility; inverse gas chromatography (IGC); branch content; polyethylene (PE)

INTRODUCTION

Recently, we reported an improved way of analyzing inverse gas chromatography (IGC) data so that the solvent-independent Flory–Huggins interaction parameter (χ_{23}) can be obtained.¹ In particular, we used a blend consisting of high-density polyethylene (HDPE) and low-density polyethylene (LDPE) to illustrate the method. Later, we applied the proposed approach to two well-known immiscible blends [blends of HDPE/isotactic polypropylene (i-PP) and of HDPE/atactic-polystyrene (a-PS)] to measure their corresponding interaction parameters and found that the results are in good agreement with those obtained from neutron reflectivity measurements.^{2–4} However, when one compares the resultant χ_{23} values of all the above-mentioned blends from IGC with those obtained from small-angle neutron scattering (SANS) measurements and molecular dynamics (MD) simulations on comparable systems, they are generally one to two orders of magnitude larger.^{5–8}

This raises the question as to which technique would yield reliable χ_{23} values for these polyolefin

blends. To some extent, the discrepancy in the magnitudes of the measured χ_{23} values from different techniques is somewhat expected. This is because all the techniques are subjected to different experimental conditions and require the fitting of data using various theories that are formulated based on different assumptions. Nonetheless, it is speculated that any observed functional dependency of χ_{23} (e.g., temperature dependency) may be retained, although not necessarily. In this regard, we decided to apply the technique to study the effect of branch content (i.e., number of branches per 1000 backbone carbons) of octane-based linear low-density polyethylene (LLDPE) on its melt miscibility with high-density polyethylene (HDPE) because such systems have been extensively studied and the branch content dependency of χ_{23} is available.^{5–9} In particular, Hill et al.⁹ found that HDPE/LLDPE blends containing LLDPE with branch contents above 60 show extensive phase-separation behavior. Alamo et al.⁵ suggested that the blends are miscible if the branch content of LLDPE is lower than 40 and immiscible if the branch content of LLDPE is higher than 80. Rhee and Christ⁶ contended that 60 branches per 1000 carbons is the critical value to induce phase separation of HDPE/LLDPE blends. Recent molecular modeling results based on MD simulation at temperatures as high as 250°C have also indicated that 40 branches, regardless of the branch length, is the threshold value above which phase separation occurs in those blends.^{7,8} Therefore, it is interesting to check whether

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TABLE I
Characteristics of HDPE and LLDPE Used

Resin	Density at 25°C (g/cm ³)	M_n	M_w	Branch content (branches/1000 carbons)
HDPE	0.962	13,700	49,400	~ 0
LLDPE-1	0.938	34,600	69,200	2
LLDPE-2	0.922	38,700	77,400	11.4
LLDPE-3	0.914	20,300	69,000	18.1
LLDPE-4	0.874	53,800	96,900	49.7
LLDPE-5	0.881	52,000	104,000	87.2

IGC can capture the miscibility trend of these blends. In this work, five different octane-based LLDPEs with branch contents ranging from 2 to 87 were used.

THEORY

As mentioned, the essence of the new IGC data analysis approach is the use of a common reference volume for the calculations of all solvent-stationary phase-interaction parameters for different solvents.¹ In the following, we will present only the key expressions that are crucial to the present work. Interested readers should refer to Zhao and Choi¹ for detailed derivation of the equations. With the adoption of a common reference volume, the original expression for the Gibb's free energy change on mixing derived from the Flory-Huggins lattice theory is simply modified by multiplying the enthalpy part by V_0/V_1 . By combining the modified Gibb's free energy change on mixing expression with that of the solvent's activity coefficient, χ_{12} or χ_{13} can be obtained by the following expression:

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

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 (for the present work, the molar volume of an ethylene repeating unit at the experimental temperature T was used), and V_1 is the molar volume of the solvent. R is the universal gas constant, $v_{2(\text{or } 3)}$ is the specific volume of the polymer, and V_g^0 is the specific retention volume that can be determined from the net retention time of the solvent. P_1^0 is the vapor pressure of the solvent, $M_{2(\text{or } 3)}$ is the number-average molecular weight of the polymer, and B_{11} is the second virial coefficient of the solvent in the gaseous phase.

For ternary systems that contain 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

$$\chi_{1(23)} = \frac{V_0}{V_1} \left[\ln \frac{27315R(w_2 v_2 + w_3 v_3)}{V_g^0 V_1 P_1^0} - 1 + \frac{V_1}{M_2 v_2} + \frac{V_1}{M_3 v_3} - \frac{(B_{11} - V_1)}{RT} P_1^0 \right] \quad (2)$$

Here, $\chi_{1(23)}$ is related to χ_{12} , χ_{13} , and χ_{23} as shown in the following expression:

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

Equation (3) 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, solvent-independent χ_{23} can be obtained from the intercept of such a plot. It is evident that once V_g^0 and other parameters that appear 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.¹⁰⁻¹³

EXPERIMENTAL

Materials

Five binary blends composed of HDPE and octene-based LLDPE with branch contents ranging from 2 to 87 were studied. All polyethylene samples used were commercial products. In particular, the HDPE and three low branch content LLDPE samples were supplied by NOVA Chemicals Corp. (Calgary, Alberta, Canada), whereas the remaining two LLDPE samples were from Exxon Chemicals (Baytown, TX). The molecular weight averages and branch contents of the polymers are listed in Table I. For each pair of blends, three different compositions (30/70, 50/50, and 70/30) and four elevated temperatures (170, 190, 210, and 230°C) were investigated. The solvents including aliphatic and aromatic hydrocarbons were purchased from Fisher Scientific (Pittsburgh, PA) and used with-

TABLE II
Loadings and Mass of HDPE, LLDPE, and Their Blends Used in the GC Columns

Column number	Composition (wt % of HDPE)	Loading (% w/w)	Mass of polymer (g)
1	100%HDPE	9.14	0.06221
2	100%LLDPE-1	9.08	0.06478
3	30%HDPE + 70%LLDPE-1	8.55	0.05431
4	50%HDPE + 50%LLDPE-1	10.33	0.07482
5	70%HDPE + 30%LLDPE-1	9.30	0.06883
6	100%LLDPE-2	7.50	0.04712
7	30%HDPE + 70%LLDPE-2	9.09	0.06628
8	50%HDPE + 50%LLDPE-2	11.07	0.08373
9	70%HDPE + 30%LLDPE-2	9.18	0.06958
10	100%LLDPE-3	9.40	0.06954
11	30%HDPE + 70%LLDPE-3	8.65	0.06193
12	50%HDPE + 50%LLDPE-3	8.49	0.06114
13	70%HDPE + 30%LLDPE-3	8.96	0.06836
14	100%LLDPE-4	9.95	0.06908
15	30%HDPE + 70%LLDPE-4	8.85	0.06447
16	50%HDPE + 50%LLDPE-4	8.72	0.06200
17	70%HDPE + 30%LLDPE-4	9.22	0.06741
18	100%LLDPE-5	9.10	0.06523
19	30%HDPE + 70%LLDPE-5	10.21	0.07440
20	50%HDPE + 50%LLDPE-5	7.91	0.05373
21	70%HDPE + 30%LLDPE-5	8.94	0.06547

out further purification. Methane was used as a marker for the determination of net retention times.

Sample preparation and data collection

The IGC columns were prepared using the standard procedure established in the IGC literature.¹⁴ The loading of the polymer on the solid support was determined by calcinations of the samples in a furnace. The loadings and mass of polymers coated on the columns are listed in Table II. Before data collections, each column was conditioned in a gas chromatograph with prepurified helium at 60°C for 2 days to eliminate residual solvent. A Hewlett–Packard 4890 gas chromatograph (Hewlett–Packard, Palo Alto, CA) with a flame ionization detector (FID) was used to carry out all measurements. For each solvent, three injections of 1 μ L of its vapor were made to measure the retention time, and the reproducibility was usually within 3%. The average retention times were used for subsequent calculations. Prepurified helium was used as the carrier gas and its flow rates were measured at the corresponding experimental temperatures with the use of a soap bubble flow meter. The flow rates ranged from 18 to 21 mL/min, as recommended by the GC manual. The inlet and outlet pressures of the column were monitored by a built-in pressure gauge and manometer attached to the outlet of the column, respectively. The specific retention volume V_g^0 was subsequently calculated from the net retention times.¹

RESULTS AND DISCUSSION

By substituting the measured V_g^0 into eqs. (1) and (2), interaction parameters between the selected solvents

and the pure polymers as well as their corresponding blends were calculated. They were then used to determine χ_{23} by plotting $\chi_{1(23)}$ against $(\phi_2\chi_{12} + \phi_3\chi_{13})$. The resultant χ_{23} values and the associated errors for all 50/50 blends are summarized in Figure 1. Because the results for the blends with 30 and 70% LLDPE showed similar trends, they are not presented here. As can be seen from Figure 1, χ_{23} values are generally not very sensitive to temperature. However, it seems that the temperature dependency of χ_{23} shows an inverse relationship for the blend containing LLDPE with a branch content of two. On the other hand, χ_{23} increases with increasing temperature for the blend containing LLDPE with 87 branches. In addition to the above-described trends, χ_{23} data show a maximum over the temperature range being used in the intermediate branch content region. In fact, researchers have found that χ_{23} is not necessary to follow an inverse relationship with temperature as predicted by the Flory–Huggins theory. Different temperature dependencies of χ_{23} were previously reported in the literature.¹⁵ For example, in the study of blends composed of deuterated polybutadiene (DPB) and protonated polybutadiene (HPB) with different vinyl contents by SANS, Jinnai et al.¹⁵ found if the vinyl contents of HPB are lower than 40%, χ_{23} decreases with increasing temperature; if higher than 65%, χ_{23} increases with increasing temperature, and no temperature dependency was observed for the blend with the intermediate vinyl contents. Nonetheless, because of the large errors associated with the measured χ_{23} , the temperature dependency of χ_{23} described previously may be questionable and reducing the errors is extremely impor-

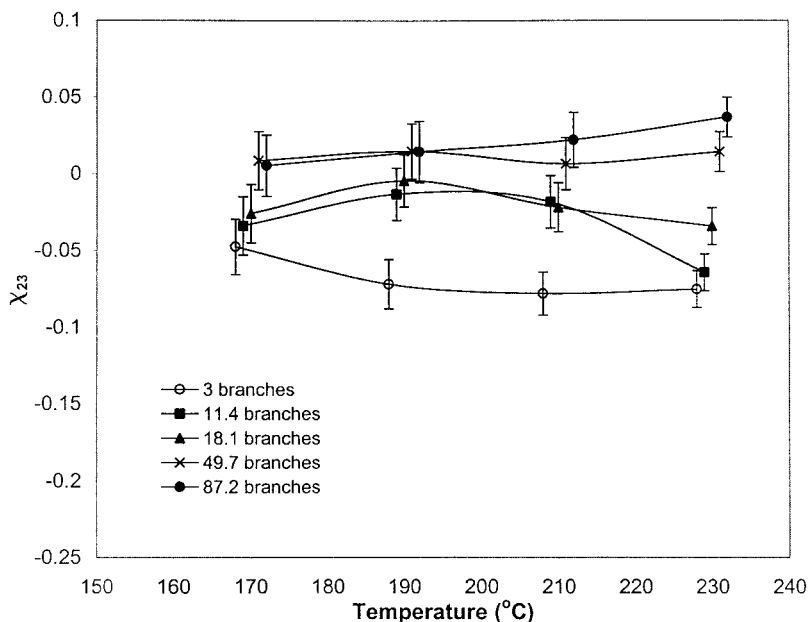


Figure 1 Temperature dependency of χ_{23} for 50/50 HDPE/LLDPE blends.

tant for identifying the temperature dependency of χ_{23} . In fact, the large errors associated with the measured χ_{23} for polyethylene blends have been encountered not only in IGC but also in other techniques such as PVT measurements, SANS, and MD simulations. For example, it has been reported that both χ_{23} and its errors for polyethylene blends obtained from PVT measurements were in the order of 10^{-3} . The change of χ_{23} with temperature has been found to be sufficiently negligible that no obvious trend could be drawn.¹⁶ Therefore, to obtain reliable temperature dependency of χ_{23} , especially for polyethylene blends, methods for reduction in measurement errors are highly desired.

The absolute value of χ_{23} is in the order of 10^{-3} to 10^{-2} , as shown in Figure 1. Here, χ_{23} values of the blends containing LLDPE with low branch contents (LLDPE-1, LLDPE-2, and LLDPE-3) were negative. In contrast, χ_{23} values of blends containing LLDPE with high branch contents (LLDPE-4 and LLDPE-5) showed positive values. The negative values of χ_{23} are unexpected, given that HDPE and LLDPE interact with each other by van der Waals forces. Therefore, their interaction energy is expected to conform to the geometric mean assumption, and the measured interaction parameters should be positive. It is worth noting that Jinnai et al.¹⁵ reported negative interaction parameters for blends with high vinyl content polybutadiene. Graessley et al.¹⁷ also reported negative values of χ_{23} for blends of hydrogenated polybutadiene and hydrogenated polyisoprene. The reason for the negative χ_{23} observed in our data is still not understood.

When χ_{23} values were plotted against the branch content of LLDPE as shown in Figure 2, it may be seen that χ_{23} values were all negative if the branch content of LLDPE is lower than 50 for all temperatures and compositions of the blends. When the branch content of LLDPE was higher than 50, χ_{23} values became positive and deviated significantly from zero when the branch content was 87. This increasing trend of χ_{23} indicates that phase separation may occur in the blends containing LLDPE with high branch contents.

A similar miscibility trend for comparable systems was observed from SANS at a lower temperature range and from the MD simulation at comparable temperatures. Alamo et al.⁵ found that at 160°C if the branch content of LLDPE is lower than 40, HDPE/LLDPE blends are miscible, whereas if the branch content of LLDPE is higher than 80, the blends are immiscible. With the use of molecular dynamics simulation, Choi⁷ showed that 50 is the cutoff value to induce immiscibility. The present IGC results are in good agreement with these findings.

From a molecular structure perspective, such branch content dependency of χ_{23} is not unreasonable. This is because by adding more branches to the backbone of a polyethylene molecule, the distribution of the torsional angles of the backbone is disturbed. As a result, linear and branched molecules will have different local structures and such differences will lead to phase separation even though the molecules interact by similar van der Waals interactions. Moreover, the interaction energy of the CH_2 , CH_3 , and CH groups is not exactly the same and would also contribute to the immiscibility. The major interacting groups existing in

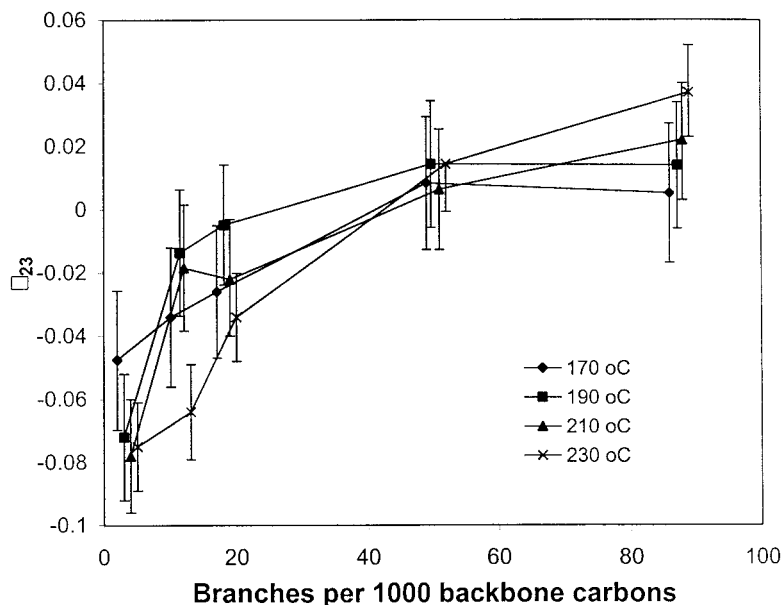


Figure 2 Effect of the branch content of LLDPE on χ_{23} for 50/50 HDPE/LLDPE blends at four elevated temperatures.

the HDPE molecules are the CH_2 groups. Because of the presence of the branches in LLDPE molecules, the above-mentioned three types of interacting groups exist in the LLDPE molecules. Increasing the number of branches on the LLDPE molecules would increase the number of non- CH_2 group interactions. Consequently, the HDPE molecules composed of only CH_2 groups (neglecting the end groups) will separate from highly branched LLDPE molecules, which contain numerous CH_3 and CH groups. The present results are also consistent with an experimental observation that if the branch content distribution of LLDPE chain molecules is broad enough, the highly branched molecules (>100 branches per 1000 backbone carbons) phase separate from the lightly branched matrix.¹⁸

CONCLUSIONS

The miscibility between HDPE and LLDPE with variable branch contents was studied at three compositions and four temperatures by IGC along with the newly proposed data analysis method. The results show that the branch content of LLDPE strongly influences the miscibility of the blends. Moreover, it seems that large differences in branch contents of the constituent polyethylenes induce immiscibility. In particular, our data suggest that when the branch content is higher than 50 branches per 1000 backbone carbons, the blend may phase separate. This result indicates that IGC yields a reliable miscibility trend, as demonstrated in the present work.

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