Studies on Thermodynamic Compatibility of Nitrile Rubber and Polybutadiene by Inverse Gas Chromatography

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SYNOPSIS

Inverse gas chromatography technique has been used to study the thermodynamic compatibility of the industrially important elastomers polybutadiene (BR) and polybutadiene copolymerised with acrylonitrile (NBR). The NBR used in this study had nitrile contents of 18 and 34%. The ratio of BR/NBR in blends varied between 1 and 0.25 in both cases and retention volume of twelve probes was measured at 80°C. The Flory–Huggins interaction parameter χ'_{23}, computed using a standard procedure, and also the interaction parameter B_{23} showed that BR and NBR are incompatible in all compositions and that incompatibility increases with nitrile content. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Inverse gas chromatography technique (IGC) is one method of studying thermodynamic compatibility of polymers.[1,2] It is convenient, quick and precise, provided experiments are carefully designed and proper precautions are taken in data acquisition and reduction. Munk[3] et al. have recently refined the procedure for calculation of Flory–Huggins interaction parameter χ'_{23} from net retention volume of the probe (V_g) and suggested that the solubility parameters of polymer blends obtained through IGC data should be matched with the solubility parameter of the probe for a better understanding of compatibility of the two components of the blend.

The first use of the IGC technique for studying polymer–polymer interaction was made by Deshpande et al. in the early 1970s,[4] who used this technique to determine thermodynamic interaction between components of a mixture of a polymer and a nonpolymer compound. Since then this technique has been used to study interaction in systems such as poly(vinyl chloride) (PVC)–dioctyl phthalate,[5] oligomeric polystyrene–poly(vinyl methyl ether)[6] and poly(*n*-butyl methacrylate),[7,8] poly(methyl methacrylate)–poly(vinylidene fluoride),[9] PVC with polycaprolactone, chlorinated polyethylene, acrylates and methacrylates,[10–12] chlorinated polyethylene–ethylene vinyl acetate copolymers[13,14] and poly(dimethyl siloxane) with tetracosane, dioctyl phthalate (DOP),[4] and styrene dimethyl siloxane copolymers.[15,16] Recently, thermodynamic compatibility studies on PVC and nitrile rubber blends have been reported from this laboratory.[17] It was perhaps the first study of thermodynamic compatibility between a plastomer and elastomer, and resulted in interesting findings which prompted us to study an industrially important system comprised of two elastomers: polybutadiene (BR) and nitrile rubber with different nitrile contents (18% and 34%), designated NBR-18, and NBR-34 in this paper.

Polybutadiene and poly(butadiene-*co*-acrylonitrile) should be conditionally compatible, at least when nitrile content is low.[18] However, Corish found the BR–NBR blends incompatible even at low nitrile contents by glass transition temperature (T_g) studies. The ratios of BR and NBR he used for these studies were 50/50 and 60/40 for high nitrile content and medium to low nitrile content in NBR, respectively.[19,20] Consequently, BR and NBR mixed in different ratios should give rise to a two-phase mixture. In IGC studies, the two-phase mixture

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Journal of Applied Polymer Science, Vol. 58, 1681–1688 (1995)
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Table I Specific Retention Volume V_g of Various Probes on Polybutadiene/NBR-18 Blend at 80°C

Solvent	NBR-18 Pure	75% NBR-18	50% NBR-18	75% NBR-18	Polybutadiene Pure
1. *n*-decane	548.00	898.53	1112.35	1233.46	1161.35
2. *n*-nonane	256.03	407.68	514.08	568.45	514.35
3. *n*-octane	116.37	165.81	229.35	252.73	228.66
4. *n*-heptane	52.07	72.50	101.12	110.21	102.93
5. *n*-hexane	23.75	23.89	44.77	47.07	41.54
6. Chloroform	97.07	109.53	119.18	103.16	78.61
7. Benzene	115.15	134.88	151.05	140.87	111.20
8. Toluene	261.34	317.94	355.90	338.13	279.93
9. Acetone	34.79	33.47	36.41	26.63	18.00
10. THF	79.99	90.76	100.92	95.75	74.75
11. 1,4-Dioxane	199.64	218.55	234.26	204.59	161.49
12. Ethyl Acetate	62.42	66.43	74.34	65.54	49.79

would probably lead to a structure that is more open for interaction of probe molecules than is a continuous film of a single component in its pure state. The Flory–Huggins interaction parameters should be positive in such cases and their values should indicate the extent of phase separation, provided a proper probe is selected for interaction studies.

In view of the above, it was thought worthwhile to study compositionally dependent thermodynamic compatibility between BR and NBR by the IGC technique. The temperature chosen for compatibility studies was 80°C, i.e., about 150°C above the T_g of either component of the blend. Ideal chromatographic conditions may be assumed to exist for retention volume measurement of probes (solvents) having a wide variety of chemical groups and covering a range of polarities.

THEORY

The retention volume V_g per unit weight of stationary phase for any solvent (probe) corrected for gas compressibility, for dead volume of column, and also for effect of support is related to the Flory–Huggins interaction parameter χ_{1i} by eq. (1).[21,22] (In all of the following equations, subscript 1 denotes the probe, and 2 and 3 the two polymers studied.)

$$\chi_{1i} = \frac{\ln 273.15RV_{\text{isp}}}{P_1^o V_g V_1} - \frac{P_1^o(B_{1i} - V_i)}{RT} - \left[1 - \frac{V_1}{V_{\text{isp}}}\right]\phi_2 \quad (1)$$

Table II Specific Retention Volume V_g of Various Probes of Polybutadiene/NBR-34 Blend at 80°C

Solvent	NBR-34 Pure	75% NBR-34	50% NBR-34	25% NBR-34	Polybutadiene Pure
1. *n*-decane	253.39	517.93	710.87	936.95	1161.35
2. *n*-nonane	123.50	242.79	327.88	433.32	514.35
3. *n*-octane	59.39	114.58	150.60	199.38	228.66
4. *n*-heptane	28.38	52.66	63.86	89.59	102.93
5. *n*-hexane	11.12	25.16	30.50	29.77	41.54
6. Chloroform	89.29	97.49	86.34	95.34	78.61
7. Benzene	95.70	138.86	136.40	129.95	111.20
8. Toluene	191.26	230.49	298.71	290.09	279.93
9. Acetone	53.15	48.89	45.32	32.39	18.00
10. THF	91.51	91.29	89.60	89.79	74.75
11. 1,4-Dioxane	278.30	258.81	244.82	197.63	161.49
12. Ethyl Acetate	61.77	68.90	67.37	60.88	49.79

Table III Thermodynamic Interaction Parameter (χ_{1i}) for Solvent and Single Polymer Systems at 80°C

Solvent	Polybutadiene Pure χ_{12}	χ_{13} NBR-18	χ_{13} NBR-34	$\Delta\chi = \chi_{12} - \chi_{13}$ BR/NBR-18	$\Delta\chi = \chi_{12} - \chi_{13}$ BR/NBR-34
1. *n*-decane	−0.11	0.59	1.32	0.70	1.43
2. *n*-nonane	−0.06	0.59	1.28	0.65	1.39
3. *n*-octane	−0.00	0.62	1.25	0.62	1.25
4. *n*-heptane	0.05	0.68	1.25	0.63	1.20
5. *n*-hexane	0.12	0.62	1.34	0.50	1.22
6. Chloroform	−0.26	−0.52	−0.48	0.26	0.22
7. Benzene	−0.13	−0.22	−0.07	0.07	0.06
8. Toluene	−0.29	−0.27	0.00	0.02	0.29
9. Acetone	1.14	0.43	−0.04	0.71	1.18
10. THF	0.00	−0.12	−0.30	0.12	0.30
11. 1,4-Dioxane	0.30	0.04	−0.34	0.26	0.64
12. Ethyl Acetate	0.45	0.13	0.14	0.32	0.31

where V_{isp} and ϕ_2 are specific volume and volume fractions of polymers used as the stationary phase. P_1^o, V_1 and B_{1i} are the vapor pressure, molar volume, and second viral coefficient of the solvent probe, respectively. The denominator in the third term in eq. (1) contains the specific volume of the polymer in its denominator, therefore it can be neglected.

If the IGC column comprises a binary stationary phase, the overall interaction parameter from Scott's solution theory treatment[23] $\chi_{1(2,3)}$ is given by

$$\chi_{1(2,3)} = \frac{\ln 273.15R(w_2V_{2sp} + w_3V_{3sp})}{P_1^oV_{g23}^oV_1} - \frac{P_1^o(B_{1i} - V_1)}{RT} - 1 \quad (2)$$

Equation (2) can be simplified to

$$\chi_{1(2,3)} = \left[\frac{\chi_{12}}{V_1}\phi_2 + \frac{\chi_{13}\phi_3}{V_1} - \frac{\chi_{23}}{V_2}(\phi_2\phi_3)\right]V_1 \quad (3)$$

where w_i and ϕ_i represent weight fraction and volume fraction of polymer, respectively. $\chi_{1(2,3)}$ normalized to the size of probe denoted by χ_{23} can be written as follows:

$$\chi_{23} = \frac{\chi_{23}V_1}{V_2} = \frac{\chi_{12}}{\phi_3} + \frac{\chi_{13}}{\phi_2} - \frac{\chi_{1(2,3)}}{\phi_2\phi_3} \quad (4)$$

The interaction parameter in the form of energy B_{23} is related to χ'_{23} by eq. (5):

$$B_{23} = \frac{RT\chi'_{23}}{V_1} \quad (5)$$

The solubility parameter δ_2 of polymers is calculated using the following equation, obtained by Hildebrand–Scatchard[26] solution theory with Flory[27,28] interaction theory.

$$\left[\frac{\delta_i^2}{RT} - \frac{\chi}{V_1}\right] = \left[\frac{2\delta_2}{RT}\right]\delta_1 - \left[\frac{\delta_2^2}{RT} + \frac{\chi_s}{V_1}\right] \quad (6)$$

In practice, $[(\delta_i^2/RT) - (\chi/V_1)]$ is plotted against δ_1 (solubility parameter of probe at working temperature) and regression analysis enables the calculation of δ_2 (assumed to be constant for all the probes).[28,29] The values of various parameters, e.g., δ, V, P, etc., were obtained from literature.[23–25]

EXPERIMENTAL

Polybutadiene (pure, from IPCL Baroda) and nitrile rubber (NBR) with 18% and 34% acrylonitrile content were received from Bayer India, Ltd. The solvents were of high purity when received from manufacturers, around 99.98%. IOLAR-grade hydrogen from Indian Oxygen, Ltd., was used as a carrier gas. The viscosity average molecular weight (mol wt) of polybutadiene, NBR-18, and NBR-34, as determined by viscometry, were 3.32×10^5, 1.00×10^5, and 1.11×10^5, respectively.

An Aimil Nucon 5700 dual column GC from Nucon Engineers (New Delhi, India) with thermal

Table IV Polymer–Polymer Thermodynamic Interaction Parameters (χ'_{23} and B_{23}) at 80°C of Different Blend Ratios (w/w)

	χ'_{23} of Polybutadiene/NBR-18/Blend				
Solvent	75% NBR-18	50% NBR-18	25% NBR-18	χ'_{23}	B_{23}
1. *n*-decane	1.55	1.30	1.32	1.39	4.172
2. *n*-nonane	1.48	1.36	1.47	1.44	4.780
3. *n*-octane	0.93	1.33	1.44	1.24	4.607
4. *n*-heptane	0.74	1.26	1.28	1.09	4.640
5. *n*-hexane	0.08	1.39	1.42	0.96	4.810
6. Chloroform	0.92	1.26	1.22	1.13	8.950
7. Benzene	0.93	1.16	1.26	1.12	8.150
8. Toluene	0.93	1.63	1.13	1.23	7.270
9. Acetone	0.69	1.54	1.28	1.17	10.66
10. THF	0.75	0.73	1.27	0.92	7.790
11. 1,4-Dioxane	0.76	1.08	1.62	1.15	9.150
12. Ethyl Acetate	0.63	1.17	1.21	1.00	6.560

conductivity detector was used for this study. The temperature of the IGC oven was measured using a mercury thermometer with an accuracy of 0.5°C. The flow rate of carrier gas was measured by a soap bubble flowmeter with an accuracy of 0.1 ml at room temperature and atmospheric pressure. A Hewlett Packard (HP3394-A) integrator with an accuracy of 0.01 min was used for retention time measurement. "Retention time" refers to the apex of a peak. The HP3394-A locates the apex by finding a segment from which three further segments show downslope: that segment locates the region of the apex. The HP3394-A uses the segments immediately preceding and immediately following the maximum in a quadratic fit to find the true apex.

The polybutadiene polymers and the nitrile rubber make a clear solution in methylene dichloride in their pure states as well as in a mixture of any ratio of the two. The columns were prepared and conditioned by the same method described in a previous communication.[17] Ten system compositions (including one of pure support) were studied, out of which three columns showed 10% polymer loading of pure butadiene, NBR-18, and NBR-34; six col-

Table V Polymer–Polymer Thermodynamic Interaction Parameters (χ'_{23} and B_{23}) at 80°C of Different Blend Ratios (w/w)

	χ'_{23} of Polybutadiene/NBR-34 Blend				
Solvent	75% NBR-34	50% NBR-34	25% NBR-34	χ'_{23}	B_{23}
1. *n*-decane	1.58	0.95	0.80	1.11	3.330
2. *n*-nonane	1.51	0.99	0.91	1.14	3.780
3. *n*-octane	1.44	0.91	0.87	1.07	3.980
4. *n*-heptane	1.41	0.56	0.92	0.96	4.090
5. *n*-hexane	2.38	1.29	0.64	1.44	7.210
6. Chloroform	0.63	0.14	0.92	0.56	4.430
7. Benzene	1.52	1.12	1.08	1.24	9.020
8. Toluene	0.44	1.00	0.71	0.72	4.250
9. Acetone	1.06	1.65	1.89	1.53	13.90
10. THF	0.27	0.35	0.77	0.46	3.900
11. 1,4-Dioxane	0.38	0.64	0.44	0.49	3.900
12. Ethyl Acetate	0.86	0.81	0.86	0.84	5.510

umns showed loading of mixtures of BR and NBR having 25%, 50% and 75% polybutadiene content and the balance either NBR–18 or NBR-34. Fixed quantities of solid support, i.e., DMCS treated chromosorb, WAW (2.0 g), and the pure polymer or mixture (0.2 g), were used in each column. The probes used were of diverse polarity, including *n*-decane, *n*-heptane, *n*-hexane, *n*-octane, *n*-nonane, chloroform, benzene, toluene, acetone, THF, 1,4-dioxane, isobutyl alcohol, and ethyl acetate. The quantity injected, always 0.2 μL of each probe, was maintained throughout the measurement. The injections were made a number of times to obtain a constant value of retention time. The method of calculation of V_g has been described in a previous paper.[17]

Before carrying out the experiments, the columns were conditioned at 120°C for 8 h to obtain a steady base line. The retention times were measured at 80°C.

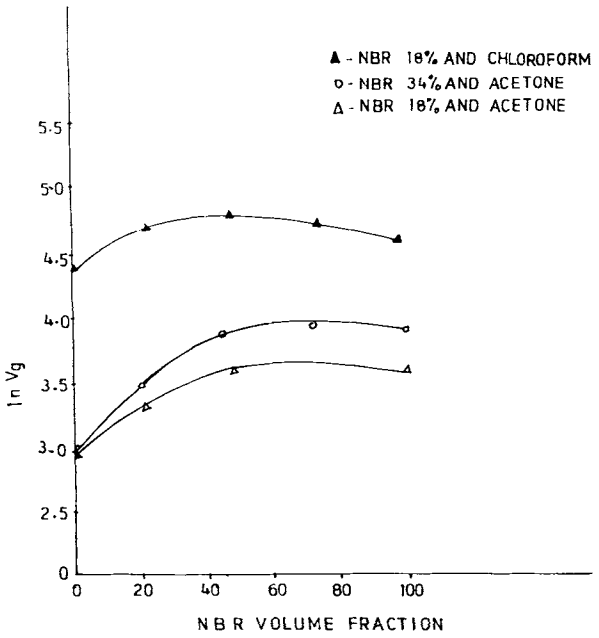

Figure 1 Plot of retention volume of selected probes against volume fractions of nitrile rubber. (▲) NBR 18% and chloroform; (O) NBR 34% and acetone; (Δ) NBR 18% and acetone.

RESULTS AND DISCUSSIONS

The specific retention volume corrected for gas compressibility, etc., were determined on pure and mixed stationary phases containing BR and NBR. The retention volume of each probe on a column, with the same quantity of support as used for filling a coated column, was subtracted from specific retention volumes of the probe on coated columns.

The corrected retention volumes of pure polymers and their blends, having different proportions of BR and NBR, are given in Tables I and II. Based on these values, χ_{1i} for the pure polymers were calculated using eq. (1) and are recorded in Table III.

The interactions in thermodynamic terms are measured in terms of interaction parameters. χ_{12} and χ_{13} values in Table III are for interaction [calculated using eq. (1)] between a given probe and BR and NBR, respectively. According to Patterson and others,[30-32] the χ_{1i} is directly proportional to the square of the difference in solubility parameters of probe and polymer. Thus, $\Delta\chi_{1i}$ values should give a fair indication of compatibility. In Table III, $\Delta\chi_{1i}$ values are given for each probe along with individual χ_{1i} values. The value of $\Delta\chi_{1i}$ increases with the nitrile content, and it may be inferred that the degree of incompatibility increases with the nitrile content of NBR. Even NBR-18 shows incompatibility with BR, as seen from the $|\Delta\chi|$ data.

Polybutadiene/Nitrile Rubber Interaction

The results of χ'_{23} calculations are reported in Tables IV and V. It is apparent from the results of χ'_{23} that the values are probe-dependent. Several authors have selected probes having ($\Delta\chi \rightarrow 0$) to interpret

Table VI Solubility Parameter (δ_2) of the Polymers and Their Blends at 80°C

Single Polymer	δ_2	NBR-18	δ_2	NBR-34	δ_2
Polybutadiene Pure	7.9961	75%	8.7130	75%	9.2291
18% AN Pure	8.9740	50%	8.9868	50%	8.5245
		25%	8.7336	25%	8.6545
34% AN Pure	9.6027	Average	8.8111	Average	8.9360
Average	8.8576				
				Average = 8.784	

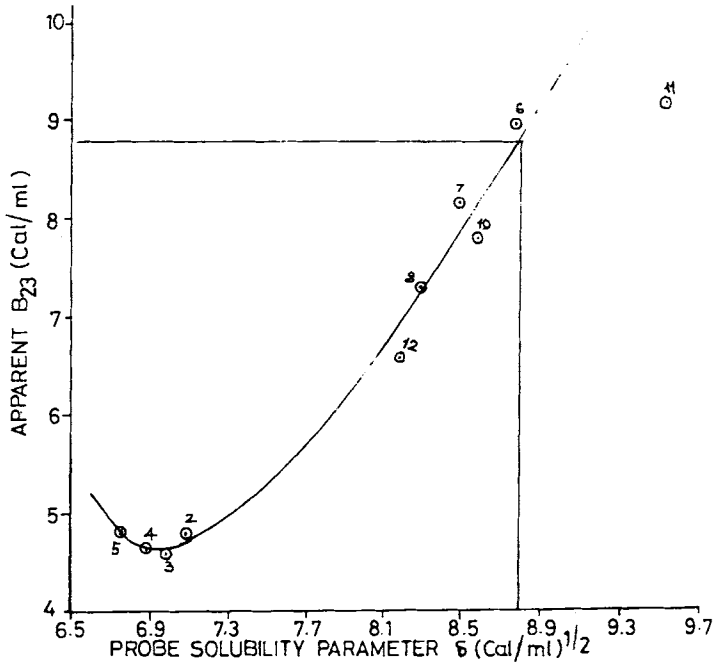

Figure 2 Plot between apparent B_{23} values against corresponding solubility parameter of different probes for BR/NBR-18 blends.

compatibility. El-Hibri et al.,[3] however, evolved another method for selecting the probe for more accurate evaluation of interaction parameters to interpret compatibility. It has been suggested by the author that the probe having a solubility parameter nearest to that of the solubility parameter of blend is most appropriate and that the values of χ'_{23} obtained from that probe should be used to interpret thermodynamic compatibility.

The method of estimation of solubility parameter δ_2 for stationary phase and δ_1 for probes have been described in our previous work.[17] The values of solubility parameter δ_2 for pure polybutadiene, acrylonitrile rubber, and their blends are given in Table VI. The average solubility parameter for a blend of NBR-18 is 8.8 and that of NBR-34 is 8.936. The probe having the nearest solubility parameter to that of the NBR-18 blend is $CHCl_3$ (8.78), and the acetone probe (9.01) is closest to the solubility parameter of NBR-34 blends. As such, the proper solvents for estimation of χ'_{23} for a polybutadiene/NBR-18 blend and a polybutadiene/NBR-34 blend are acetone/chloroform and acetone, respectively.

In Figure 1, the ln V_gs for selected probes having solubility parameters similar to polymer blends are plotted against NBR volume fraction for both NBR-18 and NBR-34 blends. In general, the downward deviation in such plots indicates the compatibility in blend components. In the present system, the convex curvature again indicates incompatibility in all compositions of BR and NBR.

Tables IV and V give the χ'_{23} values for the various probes for different blends. The proper probe mentioned above for a polybutadiene/NBR-18 blend is acetone/chloroform. The χ'_{23} values calculated for chloroform probes of different compositions vary from 0.92 to 1.26, the average being 1.13; whereas the values calculated using the acetone probe vary from 0.69 to 1.54, the average being 1.17. For the polybutadiene NBR-34 blend, the values of χ'_{23} calculatedusing acetone, the appropriate probe, vary from 1.06 to 1.89, with an average of 1.53. Since the values of the interaction parameters are very high, the polybutadiene/NBR blends should be considered incompatible for all compositions of the blend system. The interaction parameter of the NBR-34 blend is higher than that of the NBR-18 blend system and shows higher incompatibility with increased acrylonitrile content, although it is not very apparent for an individual blend system of different compositions when considered separately, which is the limitation of the IGC technique.

Interaction Parameter Based on Munk's Analysis

Munk has utilized the term "interaction parameter B_{23}" to understand the compatibility of the polymer

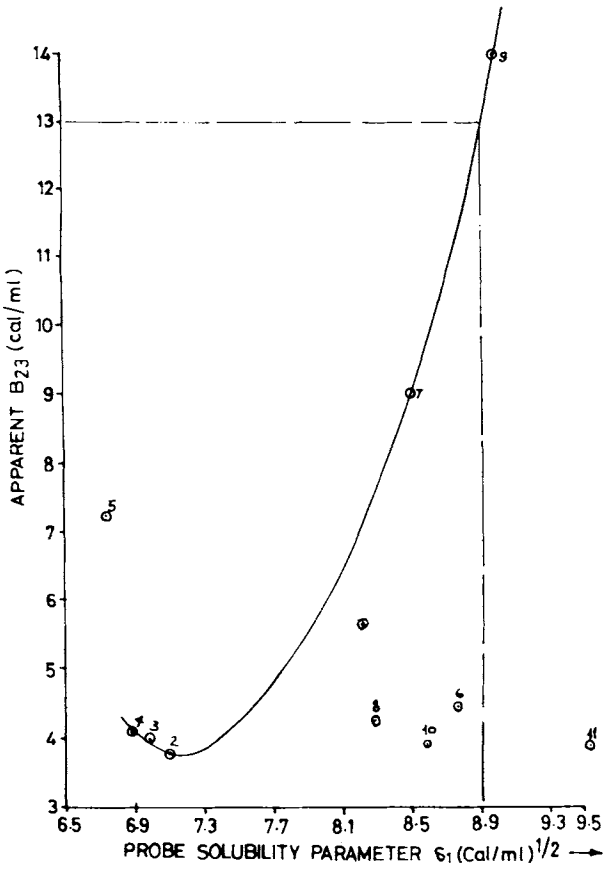

Figure 3 Plot between apparent B_{23} values against corresponding solubility parameters of different probes for BR/NBR-34 blends.

blends. The interaction parameter has been calculated for each probe from average values of χ_{23} given in Tables IV and V for the polybutadiene/NBR-18 and polybutadiene/NBR-34 blend systems. The B_{23} values for the polybutadiene/NBR-18 and polybutadiene/NBR 34 blends obtained for selected probes are 8.95 and 13.90 cal/mL, respectively, (derived by comparison with solubility parameter values of the selected probes at the corresponding solubility parameter of the blend). The B_{23} values for polybutadiene/NBR-18 and polybutadiene/NBR-34 have been plotted against solubility parameters of the probes studied in Figures 2 and 3, respectively. It is clear from these figures that the scatter is high in both cases. However, after drawing a smooth curve, the values of the apparent B_{23} were found to be 8.82 cal/mL for polybutadiene/NBR-18 and 13.00 cal/mL for polybutadiene/NBR-34 at the corresponding solubility parameter of the blend. The higher interaction energy of the blend shows incompatibility of polybutadiene/NBR blend systems; however, the incompatibility increases with nitrile content as indicated earlier.

CONCLUSION

Inverse gas chromatographic studies on thermodynamic compatibility of polybutadiene and nitrile rubber, and computation of Flory–Huggins interaction parameters obtained using the net retention volume of 12 probes having wide ranges of polarity, show a definite trend in incompatibility that increases with the nitrile content of NBR. The results obtained by various data reduction methods point toward the same conclusion and perhaps are best highlighted when χ'_{23} and B_{23} values for selected probes having same solubility parameter as those of polymer blends were used for interpretation.

The authors are highly indebted to Dr. S. N. Pandey, Director, D.M.S.R.D.E., Kanpur, for his valuable suggestions and encouragement during the course of this work.

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Received April 3, 1994
Accepted April 21, 1995