# Studies on the thermodynamic compatibility of blends of poly(vinyl chloride) and nitrile rubber

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Inverse gas chromatography has been used to investigate the thermodynamic compatibility of blends of poly(vinyl chloride) (PVC) and nitrile rubber (NBR) as a function of blend composition and acrylonitrile (AN) content of NBR. The values of the polymer–polymer thermodynamic interaction parameters ($\chi'_{23}$ and $B_{23}$) and the solubility parameter ($\delta$) of the polymers and their blends were determined with the help of the measured retention data for various polar and non-polar probes in the pure and mixed stationary phases of these polymers. Out of all the probes studied only dioxane and cyclohexanone have similar $\delta$ values to those of the blends. The $B_{23}$ values for the PVC/NBR blends were $\sim -0.1$ and $-1.1$ cal ml$^{-1}$ depending on the AN content of NBR. Thus, the two polymers are fairly compatible and show increased compatibility with increase in AN content of NBR.

**(Keywords: compatibility; inverse gas chromatography; thermodynamic interaction parameter; solubility parameter; glass transition temperature)**

## INTRODUCTION

Miscible blends of polymers are rare[1]. This is because of the poor combinatorial entropy of mixing due to the high molecular weights of polymers. Miscibility in polymer–polymer mixtures has been the subject of considerable discussion and debate in the literature[2].

Miscibility is best understood in thermodynamic terms. Until recently there were a very limited number of techniques for critically and unambiguously examining the thermodynamics of polymer–polymer blends.

The molecular probe technique of gas–liquid chromatography, generally known as inverse gas chromatography (i.g.c.), reveals information about the polymeric stationary phase[3–5]. Recently, this method has proved popular because of its speed and convenience in providing thermodynamic data for concentrated polymer solutions[6–8].

I.g.c. was first applied to estimate the thermodynamics of solvent–homopolymer interaction. Deshpande *et al.* have extended this technique for the determination of thermodynamic interaction between components of a mixture of a polymer and a non-polymeric compound[9]. Su *et al.* used this technique to measure the interaction parameter of poly(vinyl chloride) (PVC) and dioctyl phthalate as plasticizer to predict their compatibility[10]. Later, this study was successfully utilized to measure the compatibility of polymer blends. Some of the important blends studied were oligomeric polystyrene with poly(vinyl methyl ether)[11] and poly(n-butyl methacrylate)[12,13], poly(methyl methacrylate) with poly(vinylidene fluoride)[14], PVC with poly(caprolactone), chlorinated polyethylene, acrylates and methacrylates[3,15,16], chlorinated polyethylene with ethylene vinyl acetate copolymers[17,18], and poly(dimethylsiloxane) with tetracosane, dioctyl phthalate[9,19] and styrene–dimethylsiloxane block copolymers[20]. The various blends studied have been reviewed by Mandal *et al.*[21] and Barashkov *et al.*[1].

From the above it can be seen that there has been no study on the compatibility of plastomers and elastomers using i.g.c. Such systems, particularly the PVC and nitrile rubber (NBR) blend, have immense technological importance[22,23]. The polymer industry has been using PVC/NBR blends to achieve balances of properties, not possible with either of the polymers alone. The main advantages of the addition of PVC to an NBR stock are resistance to ozone and weathering, better gloss of extrudates and mouldings, bright colours, high abrasion resistance, fuel/oil resistance and creep resistance. In addition, optimum blending of NBR improves the toughness of PVC resin[22]. The PVC/NBR blend has been examined with the help of various analytical methods such as scanning electron microscopy[24], mechanical methods[25], wide-angle X-ray diffraction[26] and pulsed n.m.r.[27]. Such experiments by Nielson[28], Takayanagi *et al.*[29], Bohn[30] and Fukumori *et al.*[27] revealed a considerable degree of compatibility in the PVC/NBR blend system. It was, therefore, thought worthwhile to study the compatibility of this system by measuring the interaction parameters using i.g.c.

We report in this paper the results of i.g.c. measurements on PVC and NBR as constituents of binary stationary phases with various probes of different polarities. The results are discussed on the basis of Flory–Huggins thermodynamic interaction parameters, such as $\chi_{12}$, $\chi_{13}$ and $\chi'_{23}$, measuring the respective interactions between

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the solvent probe and PVC and NBR and that between PVC and NBR normalized to probe size.

Several authors have observed that the interaction parameter values obtained by i.g.c. are probe dependent. Consequently, an average value was used to estimate compatibility[10–21]. Munk *et al.*[31,32] have, however, criticized this approach and have used a different technique. In the present paper, the evaluation of the interaction parameter ($B_{23}$) using the analytical form of Munk has been applied to estimate compatibility.

## EXPERIMENTAL

PVC grade 613 (Calico Plastics, Bombay, India) was used without purification. The molecular weight ($\bar{M}_n$) and polydispersity ($\bar{M}_w/\bar{M}_n$), as determined by g.p.c., were 98 000 and 1.65, respectively, and the glass transition temperature ($T_g$) measured by d.s.c. was 76.3°C. The d.s.c. measurements were carried out in a nitrogen atmosphere (flow rate 40 ml min$^{-1}$) at a heating rate of 10°C min$^{-1}$ using a DuPont instrument with 910 module.

NBR samples, Perbunan N2807 and Perbunan N3307, with 28% and 34% acrylonitrile (AN), respectively, were received from Bayer (India) Ltd, Bombay, India. They are subsequently referred to as NBR-28 and NBR-34. Both the NBR samples had the same $\bar{M}_n$ ($1.1 \times 10^5$, by g.p.c.). The $\bar{M}_w/\bar{M}_n$ values for NBR-28 and NBR-34 were 1.00 and 1.04, respectively.

The solvents were of analytical grade. An Aimil Nucon 5700 (Nucon Engineers, India) dual column gas chromatograph with a thermal conductivity detector was used. The temperature was measured using a standard thermometer with an accuracy of 0.5°C. The solid support was chromosorb WAW (dimethyl chlorosilane (DMCS) treated). Both the polymers were soluble in methylene dichloride and their mixture in any ratio produced a clear solution. The polymer or its mixture was coated on the solid support by the soaking method of Al-Saigh and Munk[31]. The requisite quantity of polymer or its mixture was dissolved in methylene dichloride. A small portion of the solution was then poured over a pile of solid support on a watch glass, just to wet the solid completely. The wetted solid was dried by stirring. This procedure was repeated several times till all the solution (including rinsing of the sample tube) had been used. The coated solid was finally air and vacuum dried. There was thus negligible loss of polymer due to its sticking to the surface of the vessel. The polymer loading on solid support was ~10% and was cross-checked by calcination. The coated solid was packed in 2.5 m × 3 mm i.d. stainless steel columns. The columns were conditioned at 80°C for ~4 h.

The inlet column pressure was measured by a mercury manometer near the inlet. The column outlet pressure was taken as atmospheric. Ultra-pure hydrogen was used as the carrier gas. The flow of the carrier gas was 6.5–7.5 ml s$^{-1}$. The quantity of solvent (probe) injected varied from 0.01 to 0.1 $\mu$l. Other experimental details and the method of calculating the retention volume ($V_R$) have been described previously[33]. The corrected $V_R$ of the probe was calculated using the method of Newman and Prausnitz[34]. In order to eliminate the contribution of the solid support, $V_R$ was calculated at the outset using a column containing blank support only. The weight of material packed in each polymer-coated support column was such that the weight of solid support always remained the same as that in the blank support column. The $V_R$ of the solid support was then subtracted from the $V_R$ of the polymer-coated column and the corrected specific retention volume ($V_g$) determined. The limit of accuracy was ±0.5%.

Besides pure PVC and NBR-28 and NBR-34, blends containing 25, 50 and 75% PVC were used. The total polymer content in each column was ~0.25 g and in the solid support 2.5 g. The probes used were of diverse polarity and included n-octane, n-nonane, n-decane, benzene, toluene, *o*-xylene, butyl acetate (BA), tetrahydrofuran (THF), methyl ethyl ketone (MEK), ethylene dichloride (EDC), dioxane and cyclohexanone.

The experiments were carried out at 130°C. This temperature was chosen because temperatures 50–60°C above the $T_g$ were required. This temperature has been used by many authors for PVC using the i.g.c. technique[10,15]. PVC is essentially amorphous and in our calculation we have assumed PVC to be totally amorphous. The solvent probe interacts only with the amorphous region of the polymer. A correction for percentage crystallinity would lower the values of $\chi_{12}$ and $\chi'_{23}$ further.

The $T_g$ values of the pure polymers and their blends were determined from plots of log $V_g$ *versus* $1/T$ using n-octane as the probe[33,35].

## DATA REDUCTION

### *Interaction parameters*

From the Flory–Huggins treatment of solution thermodynamics[36,37], the interaction parameter $\chi_{1i}$ between the solvent and polymer was calculated from the following equation[6,9]:

$$\chi_{1i} = \frac{\ln 273.15 R v_{i\mathrm{sp}}}{P_1^\circ V_g^\circ V_1} - \frac{P_1^\circ (B_{11} - V_1)}{RT} - \left(1 - \frac{V_1}{V_2}\right)\phi_2 \quad (1)$$

From Scott's ternary solution treatment[38] of the Flory–Huggins theory, the overall interaction parameter between the probe (1) and the binary stationary polymer phase (2–3) was calculated using:

$$\chi_{1(23)} = \frac{\ln 273.15 R(w_2 v_{2\mathrm{sp}} + w_3 v_{3\mathrm{sp}})}{P_1^\circ V_{g23}^\circ V_1} - \frac{P_1^\circ (B_{11} - V_1)}{RT} - 1$$
$$= \left(\frac{\chi_{12}}{V_1}\phi_2 + \frac{\chi_{13}}{V_1}\phi_3 - \frac{\chi_{23}}{V_2}\phi_2\phi_3\right)V_1 \quad (2)$$

$$\chi'_{23} = \frac{\chi_{23}V_1}{V_2} = \frac{\chi_{12}}{\phi_3} + \frac{\chi_{13}}{\phi_2} - \frac{\chi_{1(23)}}{\phi_2\phi_3} \quad (3)$$

where $w_i$, $\phi_i$ and $v_{i\mathrm{sp}}$ represent the weight fraction, volume fraction and specific volume of the respective polymer. $B_{11}$, $P_1^\circ$ and $V_1$ are the second virial coefficient, the vapour pressure and the molar volume of the solvent, respectively, at the column temperature. The densities and the above parameters of the desired components were calculated or obtained from the literature[34,38–45]. The calculation of $\chi'_{23}$ represents the polymer–polymer interaction parameter normalized to the size of the probe, and $\chi_{23}$ is based on the size of a polymer molecule. The interaction parameter $B_{23}$, as expressed by equation (4), has also been evaluated:

$$B_{23} = \frac{RT\chi'_{23}}{V_1} \quad (4)$$

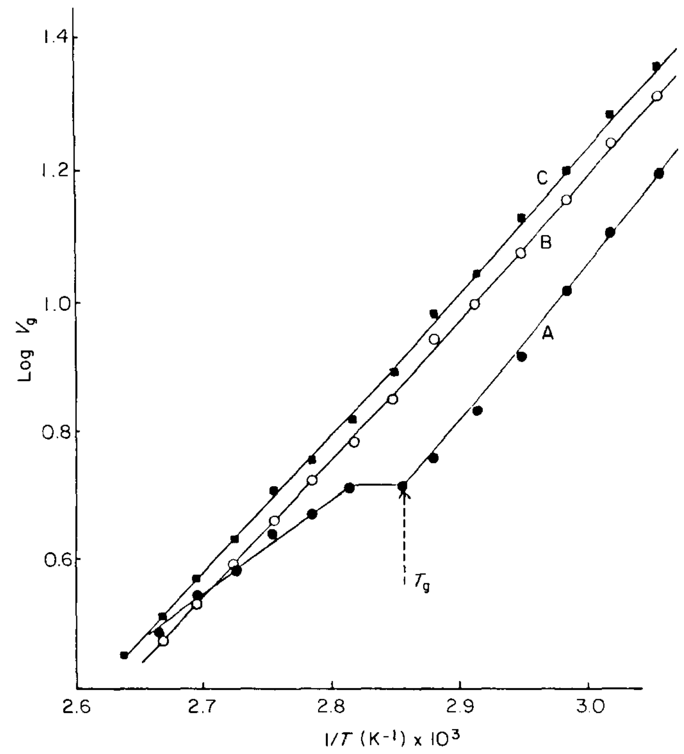

**Figure 1** Retention diagram for n-octane as molecular probe with: (A) PVC; (B) 50:50 PVC/NBR-34; (C) 50:50 PVC/NBR-28

*Solubility parameter*

The solubility parameter ($\delta$) was determined from the relation obtained by combining the Hildebrand–Scatchard solution theory[46] with Flory's theory[47,48] giving the following equation:

$$\left(\frac{\delta_1^2}{RT}-\frac{\chi}{V_1}\right)=\left(\frac{2\delta_2}{RT}\right)\delta_1-\left(\frac{\delta_2^2}{RT}+\frac{\chi_s}{V_1}\right) \qquad (5)$$

where $\delta_1$ and $\delta_2$ are the solubility parameters of the probe and polymer, respectively, and $\chi_s$ is the excess entropy term for the polymer.

Based on the regression analysis, $\delta_2$ was evaluated from the slope of a plot of $\left(\frac{\delta_1^2}{RT}-\frac{\chi}{V_1}\right)$ *versus* $\delta_1$, assuming $\delta_2$ to be constant for all probes.

The $\delta_1$ values for the volatile probes were determined from the calculated data of the heat of vaporization of the probe[43,48].

## RESULTS AND DISCUSSION

*Glass transition temperature*

The $T_g$ of pure PVC, as estimated from the point of inflection in the log $V_g$ *versus* $1/T$ plot, was 77°C. The i.g.c.-estimated $T_g$ agrees well with that estimated for PVC by d.s.c. (76.3°C, see *Figure 1*) and that reported in the literature[49]. In the case of PVC/NBR blends, the inflection was much less marked and the curves were similar. For pure NBR the plots were, however, linear as was expected since the experiments were carried out above the ambient temperature. No significant information regarding compatibility of the blends could be obtained from the $T_g$ data. Typical log $V_g$ *versus* $1/T$ plots of 50:50 PVC/NBR-28 and 50:50 PVC/NBR-34 are given in *Figure 1* together with that of pure PVC. The $T_{g23}$ of the blends was evaluated from theory using the Flory–Fox relationship[50,51] as well as from experiment using d.s.c. The Fox relationship is expressed by:

$$\frac{1}{T_{g23}}=\frac{W_2}{T_{g2}}+\frac{W_3}{T_{g3}} \qquad (6)$$

*Table 1* shows the $T_g$ values of the polymers and their blends. It appears from *Table 1* that the Flory–Fox relationship for glass transition is also generally applicable to PVC/NBR systems.

*Specific retention volume*

The specific retention volume ($V_g^\circ$) has been measured for a number of probes in pure and mixed stationary phases containing PVC and NBR.

A qualitative method of measuring the interaction between the components of the blend has been used by DiPaola-Baranyi *et al.* using the following expression[12–14]:

$$V_{g23}^\circ=w_2V_{g2}^\circ+w_3V_{g3}^\circ \qquad (7)$$

where $w_i$ refers to the weight fraction of each polymer in the blend. A negative deviation from linearity has been interpreted as highly interacting[14,32] because if two polymers interact with one another then it will reduce the ability of the blend to interact with the solvent, and hence the retention volume for the blend will be smaller than the weight average of the retention volumes for the two polymers at the corresponding composition[21]. In our experiment such deviations generally decrease with increasing proportion of NBR in the blend (*Table 2*). Thus, in the present study, the estimated deviation of

**Table 1** Glass transition temperatures of the polymers and their blends

| | $T_g$ | |
|---|---|---|
| | Theoretical[a] | Experimental[b] |
| PVC | | 76.3 |
| NBR-34 | | −23.1 |
| NBR-28 | | −29.8 |
| 75:25 PVC/NBR-34 | 43.9 | 45.0 |
| 50:50 PVC/NBR-34 | 18.8 | 20.7 |
| 25:75 PVC/NBR-34 | −3.5 | −4.0 |
| 75:25 PVC/NBR-28 | 42.0 | 41.1 |
| 50:50 PVC/NBR-28 | 13.5 | 8.8 |
| 25:75 PVC/NBR-28 | −9.6 | −5.0 |

[a] From the Flory–Fox relationship
[b] From d.s.c.

**Table 2** Percentage deviation from the theoretical $V_{g23}^\circ$ based on equation (7) at 130°C

| | PVC/NBR-28 | | | PVC/NBR-34 | | |
|---|---|---|---|---|---|---|
| Probe | 75:25 | 50:50 | 25:75 | 75:25 | 50:50 | 25:75 |
| Octane | 29.2 | 17.0 | 11.6 | 31.2 | 20.0 | 12.7 |
| Nonane | 51.5 | 39.4 | 31.6 | 13.7 | 9.0 | 8.7 |
| Decane | 20.1 | 15.7 | 10.9 | 11.6 | 4.4 | 3.9 |
| Benzene | 10.0 | 7.7 | 3.4 | 13.4 | 9.3 | 3.3 |
| Toluene | 10.4 | 8.8 | 4.7 | 4.9 | 8.1 | 3.7 |
| *o*-Xylene | 12.8 | 10.8 | 7.9 | 6.8 | 9.9 | 3.4 |
| EDC | 6.9 | 5.0 | 2.9 | 3.3 | 2.0 | 0.004 |
| THF | 6.1 | 5.6 | 3.1 | 5.0 | 1.3 | 2.9 |
| MEK | 14.8 | 9.2 | 7.8 | 3.4 | 2.7 | 0.002 |
| BA | 9.1 | 7.4 | 1.5 | 5.7 | 8.7 | 3.7 |
| Dioxane | 0.007 | −1.1 | −2.5 | 1.17 | 0.007 | 0.001 |
| Cyclohexanone | 5.2 | 4.1 | 1.2 | 1.27 | −0.31 | −0.33 |

**Table 3** Thermodynamic interaction parameter ($\chi_{1i}$) for solvent and single polymer systems at 130°C

| | $\chi_{12}$ | $\chi_{13}$ | | $\lvert\Delta\chi\rvert = \lvert\chi_{12}-\chi_{13}\rvert$ | |
|---|---|---|---|---|---|
| Probe | PVC | NBR-28 | NBR-34 | NBR-28 | NBR-34 |
| n-Octane | 1.45<br>(1.55)[a] | 0.77 | 1.05 | 0.68 | 0.40 |
| n-Nonane | 1.52<br>(1.61)[a] | 0.89 | 1.06 | 0.63 | 0.46 |
| n-Decane | 1.56<br>(1.64)[a] | 0.91 | 1.20 | 0.65 | 0.36 |
| Benzene | 0.13 | −0.12 | −0.10 | 0.25 | 0.23 |
| Toluene | 0.12 | −0.13 | −0.07 | 0.25 | 0.19 |
| *o*-Xylene | 0.11 | −0.10 | −0.07 | 0.21 | 0.18 |
| EDC | −0.68 | −0.93 | −0.93 | 0.25 | 0.25 |
| THF | −0.10 | −0.11 | −0.08 | 0.01 | 0.02 |
| MEK | 0.06 | 0.15 | −0.06 | 0.09 | 0.00 |
| BA | 0.20 | 0.07 | 0.19 | 0.13 | 0.01 |
| Dioxane | −0.07 | −0.02 | −0.07 | 0.05 | 0.00 |
| Cyclohexanone | −0.28 | −0.14 | −0.19 | 0.14 | 0.09 |

[a] Values in parentheses are obtained from ref. 10

**Table 4** Polymer–polymer thermodynamic interaction parameters ($\chi'_{23}$ and $B_{23}$) at 130°C for different polymer blend ratios (w/w)

| | $\chi'_{23}$ of PVC/NBR-28 | | | | |
|---|---|---|---|---|---|
| Probe | 75:25 | 50:50 | 25:75 | $\chi'_{23}$[a] | $B_{23}$ (cal ml$^{-1}$) |
| n-Octane | 1.09 | 0.71 | 0.82 | 0.87 | 3.70 |
| n-Nonane | 1.59 | 1.32 | 1.01 | 1.31 | 5.09 |
| n-Decane | 1.04 | 0.81 | 0.89 | 0.91 | 3.28 |
| Benzene | 0.46 | 0.34 | 0.25 | 0.35 | 2.72 |
| Toluene | 0.47 | 0.38 | 0.34 | 0.39 | 2.61 |
| *o*-Xylene | 0.56 | 0.45 | 0.54 | 0.52 | 3.03 |
| EDC | 0.30 | 0.19 | 0.13 | 0.21 | 1.65 |
| THF | 0.26 | 0.23 | 0.21 | 0.23 | 1.96 |
| MEK | 0.77 | 0.63 | 0.53 | 0.64 | 4.86 |
| BA | 0.40 | 0.31 | 0.11 | 0.27 | 1.43 |
| Dioxane | 0.07 | 0.04 | 0.02 | 0.04 | 0.35 |
| Cyclohexanone | 0.23 | 0.18 | 0.08 | 0.16 | 1.11 |

[a] Averaged over all blend compositions

$V_g^\circ$ appears to indicate qualitatively the composition dependency of the compatibility of the blend (*Table 2*).

### *Solvent–polymer interaction*

*Table 3* presents the interaction parameters $\chi_{12}$ (probe PVC), $\chi_{13}$ (probe NBR) and $|\Delta\chi| = |\chi_{12}-\chi_{13}|$. From *Table 3* it appears that the relative order of interaction between the various probes and either of the nitrile rubbers remains more or less unaltered. According to Patterson[52] the compatibility of polymers in solution should reflect not only the interaction between the polymers themselves, i.e. $\chi'_{23}$, but also any difference between the interaction of the polymers with the solvent as represented by $\Delta\chi = |\chi_{12}-\chi_{13}|$. Moreover, the interaction parameter $\chi_{1i}$ is related to the solubility parameters[2,3,53] by the equation:

$$\chi_{1i} = \frac{V}{RT}(\delta_1 - \delta_i)^2 \tag{8}$$

A lower value of $\Delta\delta = (\delta_1 - \delta_i)$ is favourable for compatibility[53,54]. *Table 3* indicates that the $\Delta\chi$ value in the case of NBR-34 is lower than that of NBR-28 indicating a greater tendency for compatibility of PVC with NBR-34 than with NBR-28 in solution.

### *PVC–NBR interaction*

The $\chi'_{23}$ values of the polymers and their blends are given in *Tables 4* and *5*. It is apparent that the interaction parameter is highly probe dependent as observed in most studies[1,9–21,31,32,55]. Several authors[10,21] have taken the interaction parameter from the average values corresponding to the probes which interact similarly with both polymers, i.e. for which $|\Delta\chi|$ is low ($\Delta\chi \rightarrow 0$), to adjudge the compatibility. For example, Nandi *et al.* obtained an average $\chi'_{23}$ value of 0.25 for a miscible blend of 75% poly(methyl acrylate) with 25% poly(vinyl acetate)[56]. DiPaola-Baranyi observed a positive $\chi'_{23}$ average value in the range 0.03–0.43 for a miscible blend of low molecular weight polystyrene with poly(n-butyl methacrylate) in different proportions[12,57]; the same author also reported an average $\chi'_{23}$ value of 0.2 for a miscible blend of 25% poly(vinylidene fluoride) with poly(methyl methacrylate)[14]. Tyagi *et al.* reported a similar average $\chi'_{23}$ value for compatible blends of poly(vinyl acetate) and poly(n-butyl methacrylate)[58].

El-Hibri *et al.*[32], however, have evolved another method of selecting the probe for a more accurate evaluation of the interaction parameter to interpret compatibility. It has been argued that the probe which possessed the nearest solubility parameter to that of the blend is the most appropriate and the value of $\chi'_{23}$ obtained from that probe should be used to interpret thermodynamic compatibility[32].

The estimation of the solubility parameter ($\delta_2$) of the stationary phase was done by regression analysis as outlined in the Experimental section. The calculated solubility parameter for the probes ($\delta_1$) at 130°C is shown in *Table 6*. The $\delta_2$ values obtained for the homopolymer, copolymer and their blends are summarized in *Table 7*. The average solubility parameters ($\bar{\delta}_2$) for PVC/NBR-28 and PVC/NBR-34 are 8.35 and 8.60, respectively. In this study, from all the probes, only dioxane ($\delta_1 = 8.21$) and cyclohexanone ($\delta_1 = 8.83$) have similar solubility parameters to those of the blends. Consequently, the solvents for estimating $\chi'_{23}$ for PVC/NBR-28 and PVC/NBR-34 are dioxane and cyclohexanone, respectively.

From *Tables 4* and *5* it can be seen that $\chi'_{23}$ varies from 0.07 to 0.02 for PVC/NBR-28 and from 0.06 to −0.02 for PVC/NBR-34. Since the values are close to zero, the blends may be considered as practically compatible. The increase of compatibility with NBR and

**Table 5** Polymer–polymer thermodynamic interaction parameters ($\chi'_{23}$ and $B_{23}$) at 130°C for different polymer blend ratios (w/w)

| | $\chi'_{23}$ of PVC/NBR-34 | | | | |
|---|---|---|---|---|---|
| Probe | 75:25 | 50:50 | 25:75 | $\chi'_{23}$[a] | $B_{23}$ (cal ml$^{-1}$) |
| n-Octane | 1.00 | 0.84 | 0.76 | 0.87 | 3.67 |
| n-Nonane | 0.20 | 0.40 | 0.35 | 0.32 | 1.23 |
| n-Decane | 0.58 | 0.25 | 0.32 | 0.38 | 1.38 |
| Benzene | 0.61 | 0.39 | 0.24 | 0.41 | 3.22 |
| Toluene | 0.23 | 0.35 | 0.26 | 0.28 | 1.84 |
| *o*-Xylene | 0.31 | 0.41 | 0.24 | 0.32 | 1.88 |
| EDC | 0.18 | 0.12 | 0.06 | 0.12 | 0.96 |
| THF | 0.22 | 0.05 | 0.20 | 0.16 | 1.32 |
| MEK | 0.15 | 0.11 | 0.01 | 0.09 | 0.68 |
| BA | 0.25 | 0.35 | 0.25 | 0.28 | 1.48 |
| Dioxane | 0.05 | 0.03 | 0.01 | 0.03 | 0.25 |
| Cyclohexanone | 0.06 | −0.01 | −0.02 | 0.01 | 0.07 |

[a] Averaged over all blend compositions

**Table 6** Solubility parameter of the probes ($\delta_1$) used to calculate the polymer solubility parameter ($\delta_2$) at 130°C

| Probe | $\delta_1$ (cal$^{1/2}$ cm$^{-3/2}$) | $V_1$ (cm$^3$ mol$^{-1}$) |
|---|---|---|
| n-Octane | 6.16 | 188.26 |
| n-Nonane | 6.34 | 204.85 |
| n-Decane | 6.45 | 221.88 |
| Benzene | 7.47 | 102.46 |
| Toluene | 7.44 | 121.28 |
| *o*-Xylene | 7.71 | 136.02 |
| EDC | 7.08 | 99.90 |
| THF | 7.53 | 95.00 |
| MEK | 7.43 | 105.62 |
| BA | 7.05 | 152.68 |
| Dioxane | 8.21 | 97.63 |
| Cyclohexanone | 8.83 | 117.46 |

**Table 7** Solubility parameter of the polymers and their blends ($\delta_2$, cal$^{1/2}$ cm$^{-3/2}$) at 130°C

| Polymer | $\delta_2$ | PVC/NBR-28 | $\delta_2$ | PVC/NBR-34 | $\delta_2$ |
|---|---|---|---|---|---|
| PVC | 8.70 | 75:25 | 8.47 | 75:25 | 8.69 |
| NBR-34 | 8.51 | 50:50 | 8.33 | 50:50 | 8.59 |
| NBR-28 | 8.22 | 25:75 | 8.22<br>(8.35)[a] | 25:75 | 8.51<br>(8.60)[a] |

[a] Average value in parentheses

AN content is also apparent. This conclusion can also be drawn from the solubility parameter data[2,53,54] presented in *Table 7*. The method of Munk *et al.* thus appears to be more precise since PVC/NBR is a well known commercial blend[2,22,24,59,60].

### *Interaction parameter*

Munk has utilized the term interaction parameter ($B_{23}$) to explain the compatibility phenomenon of polymers[32]. The $B_{23}$ for each probe has been calculated using equation (4) and the average $B_{23}$ values are embodied in *Tables 4* and *5* for PVC/NBR-28 and PVC/NBR-34, respectively. As per the analytical approach of Munk, the apparent $B_{23}$ values in *Tables 4* and *5* can be plotted against the $\delta_1$ values for the 12 probes studied. From such plots, the respective $B_{23}$ values for PVC/NBR-28 and PVC/NBR-34 corresponding to their solubility parameters (i.e. $\bar{\delta}_2 = 8.35$ and 8.60) have been obtained ($-0.1$ and $-1.1$ cal ml$^{-1}$, respectively). These values of intrinsic $B_{23}$ interaction energy for a blend show a moderate level of compatibility between the polymers. This is in agreement with the recent report by Fukumori *et al.*[27].

## CONCLUSIONS

I.g.c. studies on PVC/NBR blends based on the evaluation of the thermodynamic interaction parameters $\chi'_{23}$ and $B_{23}$ suggest that PVC/NBR blends are fairly compatible through weak interaction and the compatibility increases with increase in AN content (at least up to 34% AN) in the NBR.

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