Chapter 3

Compatibility Studies of PS/NBR, SAN/NBR & ABS/NBR Binary Systems

The results of this chapter have been published in:

Polymer, 1998, 39, 6235.
The mechanical, thermal, rheological and other properties of a polymer blend depend strongly on its state of miscibility.\textsuperscript{1}

The compatibility of polymer blends is calculated theoretically as well as estimated experimentally by dynamic, mechanical, thermal, electron-microscopy, neutron and light-scattering, spectroscopic and viscometric techniques.\textsuperscript{1,2} Owing to its simplicity, viscometry is an attractive and a very useful method for studying the compatibility of polymer blends. Additional advantage like need of no sophisticated equipments and no effect of crystallinity or morphological states of polymer blends on the results,\textsuperscript{3} make the viscosity method a suitable one for characterising polymer mixtures. Also, the retarded diffusion of polymers in the solid state makes it difficult to attain a condition of true thermodynamic equilibrium, and so behaviour of polymer mixture in solution is the best method to assess the miscibility.\textsuperscript{4}

Several authors have attempted the estimation of compatibility of different pairs of polymers based on dilute solution viscosity for ternary polymer/polymer/solvent system. These include the studies of Mikhailov and Zeilkman\textsuperscript{5}, Bohmer and Florian,\textsuperscript{6} Feldman and Rusu,\textsuperscript{7} Krigbaum and Wall,\textsuperscript{8} and Catsiff and Hewett.\textsuperscript{9} The compatibility of polycarbonate (PC) and poly(hexamethylene sebacate) (PHMS) blends has been characterised by viscosity technique using the Krigbaum and Wall parameter, \(\Delta b\), by Shih and Beatty.\textsuperscript{10} The values of \(\Delta b\) for PC/PHMS mixtures were negative and therefore they concluded that these blends were not thermodynamically compatible under equilibrium conditions. Using \(T_g\) of the blend as a measure of bulk solid-state compatibility, a correlation was obtained with the Krigbaum and Wall parameter \(\Delta b\). The versatility of viscometric technique is not affected by the choice of solvent, as shown by Kulshreshta et al.\textsuperscript{11} Lizymol et al.\textsuperscript{12} have reported that for the three binary systems, poly(vinyl chloride)/poly(ethylene vinyl acetate) PVC/EVA, PVC/SAN and
EVA/SAN, the Krigbaum and Wall model modified by Williamson and Wright was more applicable than the Catsiff and Hewett model. The compatibility in the solution state was correlated to that in the solid state for these blends, and was found to be in good agreement.\textsuperscript{13-17}

The present work discusses in detail our investigation into the compatibility of the three binary polymer blends of NBR/PS, NBR/SAN and NBR/ABS. Our attempt has been to extend the most applicable viscometric theories to these three polymer blend systems which exhibit different levels of compatibility.


3.1.1. Determination of Solubility Parameter

The application of solubility parameter theory to predict the miscibility of polymer blends has been widely reported.\textsuperscript{12,18,19} In the search for new miscible polymer blend systems, the first rule of thumb is to minimise $\chi_{\rho-p}$, which in turn, necessitates looking for closely matched solubility parameters.\textsuperscript{20,21} In contrast to low molecular weight compounds, where solubility parameters can be directly calculated from heat of vaporization measurements, polymer solubility parameters have to be determined indirectly, either by experiment (eg., swelling measurements of a slightly cross linked polymer in a series of solvents of known solubility parameters),\textsuperscript{22} or, by calculation from molar attraction constants.\textsuperscript{23-25} It has been found that the molar attraction constants give varying range of solubility parameters depending upon which set of molar attraction constants and molar volume is used, for a given polymer.\textsuperscript{26} The discrepancies are particularly acute for polymers containing small repeat units.
Table 3.1: Intrinsic viscosities (dl/g) of the polymers in various solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>NBR</th>
<th>PS</th>
<th>SAN</th>
<th>ABS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene (8.9)</td>
<td>2.509*</td>
<td>0.383</td>
<td>0.143</td>
<td>0.421</td>
</tr>
<tr>
<td>Vinyl Acetate (9.0)</td>
<td>n.d</td>
<td>n.d</td>
<td>0.448</td>
<td>0.512</td>
</tr>
<tr>
<td>Tetrahydrofuran (9.1)</td>
<td>0.315</td>
<td>0.524</td>
<td>0.730*</td>
<td>0.583</td>
</tr>
<tr>
<td>Trichloroethylene (9.2)</td>
<td>n.d</td>
<td>n.d</td>
<td>0.719</td>
<td>0.597*</td>
</tr>
<tr>
<td>Chloroform (9.3)</td>
<td>1.663</td>
<td>0.769*</td>
<td>0.712</td>
<td>0.571</td>
</tr>
<tr>
<td>Cyclohexanone (9.9)</td>
<td>0.494</td>
<td>0.112</td>
<td>0.209</td>
<td>0.108</td>
</tr>
</tbody>
</table>

* The highest $[\eta]$ value among the various polymer/solvent system.

# The solubility parameter (cal$^{1/2}$/cm$^{3/2}$) of the solvent are given in bracket.

n.d - not measured.

Table 3.2. Solubility parameter of polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>NBR</th>
<th>PS</th>
<th>SAN</th>
<th>ABS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility parameter $\delta$ (cal cm$^{3/2}$)</td>
<td>8.9</td>
<td>9.3</td>
<td>9.1</td>
<td>9.2</td>
</tr>
</tbody>
</table>

The solubility parameter of polymers, required in our work were calculated by measuring the intrinsic viscosities in a series of solvents. The $\delta_p$ values are derived from the solubility parameter values of the solvents, corresponding to the maximum viscosity shown by the polymer in that solvent. Six solvents spanning a solubility parameter range of 8.9 - 9.9 (cal cm$^{-3}$)$^{0.5}$ were used, and the corresponding viscosities are reported in Table 3.1. The solubility parameter of the polymers so obtained, are tabulated in Table 3.2.
3.1.2. Polymer - Polymer Interaction in the Blends

The free energy of mixing for a polymer A- polymer B system is defined by the relationship: \(^ {20,27}\)

\[
\frac{\Delta G_m}{RT} = \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B + \phi_A \phi_B \chi + \frac{\Delta G_H}{RT} \quad \ldots \quad (3.1)
\]

where \(\phi_A\) and \(\phi_B\), and \(N_A\) and \(N_B\), are the volume fractions and degree of polymerisation of A and B, respectively; \(\chi\) is the polymer-polymer interaction parameter. Here, \(\chi\) is restricted to values that are \(\geq 0\). Hence, the \(\phi_A \phi_B \chi\) term is generally unfavourable to mixing, reflecting only the contribution of physical forces. The \(\Delta G_H / RT\) term, on the other hand, represents favourable contributions to the change in the free energy of mixing, arising from the presence of specific intermolecular interactions and it assumes values that are \(\leq 0\).

According to Eq. (3.1), in the absence of favourable intermolecular interactions (i.e., when \(\Delta G_H / RT = 0\)), molecular mixing of two high molecular weight polymers can only occur when \(\chi\) is very close to zero.

The interaction parameter between the polymers is related to the Hildebrand solubility parameter of the two polymers using the expression: \(^ {14,28-10}\)

\[
\chi = \frac{V_r}{RT} \left[ \delta_A - \delta_B \right]^2 \quad \ldots \quad (3.2)
\]

Assuming a reference volume, \(V_r = 100 \text{ cm}^3 \text{ mol}^{-1}\), a critical value of the solubility parameter difference, \(\Delta \delta_{\text{crit}}\), was calculated. For the simple case, when \(N_A = N_B = 1000\), the difference in the solubility parameter must be less than about \(0.1(\text{cal/cm}^3)^{0.5}\) in order to ensure molecular mixing. \(^ {18}\) Table 3.3 gives the polymer-polymer interaction parameter of all the three blend systems studied here. The \(\chi_{\text{PS/NBR}}\) is
Table 3.3: Interaction parameters of the polymer (1) - polymer (2) systems

<table>
<thead>
<tr>
<th>System</th>
<th>Polymer as component I</th>
<th>Molar vol. of component I</th>
<th>Interaction parameter (( \chi ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBR/PS</td>
<td>NBR</td>
<td>78.6</td>
<td>0.021</td>
</tr>
<tr>
<td></td>
<td>PS</td>
<td>129.2</td>
<td>0.034</td>
</tr>
<tr>
<td>NBR/SAN</td>
<td>NBR</td>
<td>78.6</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>SAN</td>
<td>104.2</td>
<td>0.007</td>
</tr>
<tr>
<td>NBR/ABS</td>
<td>NBR</td>
<td>78.6</td>
<td>0.012</td>
</tr>
<tr>
<td></td>
<td>ABS</td>
<td>55.4</td>
<td>0.008</td>
</tr>
</tbody>
</table>

# Molar volume of monomer unit was taken as reference volume.

0.021, which is evidently high enough to manifest in the immiscibility of the system. The appreciably low value of \( \chi_{SAN/NBR} \) and \( \chi_{ABS/NBR} \) indicates strong polymer-polymer interactions in these systems.

Krause\(^{27}\) has discussed the limits of the values of \( \chi \). A critical value of the polymer-polymer interaction parameter (\( \chi_{crit} \)), which sets the upper limit for miscibility across the entire composition range, may be determined using the expression:\(^{27,31,32}\)

\[
\frac{\delta^2 \left[ \Delta G_m/RT \right]}{\delta \phi_A^2} = \frac{\delta^3 \left[ \Delta G_m/RT \right]}{\delta \phi_A^3} = 0 \quad \text{..... (3.3)}
\]

This leads to

\[
\chi_{crit} = \frac{1}{2} \left[ \frac{1}{N_A^{0.5}} + \frac{1}{N_B^{0.5}} \right]^2 \quad \text{..... (3.4)}
\]

It is important to note that Eqs.(3.1)-(3.4) are expressed in terms of a reference volume \( V_r \) that stems from the notion of the volume of a lattice element.\(^{31}\) Thus, the degree of polymerisation (\( N_i \)) in Eq (3.4) is defined as,

\[
N_A = \frac{V_A}{V_r} \quad \text{and} \quad N_B = \frac{V_B}{V_r} \quad \text{.....(3.5)}
\]
where $V_i$ is the molar volume of polymer component $i$. Since, $N_A$ and $N_B$ can only be identified as such when the molar volumes of the monomers comprising polymers $A$ and $B$ are identical, $V_r$ is taken to be this value. In the present work, $\chi$ and $\chi_{crit}$ values have been calculated, assuming $V_r = 100$ cm$^3$mol$^{-1}$. For a generalised case of a blend in which $N_A = N_B = 1000$, the value of $\chi$ needs to be less than 0.002 in order to facilitate molecular mixing.

The closer the match of the two hydrogen bonded solubility parameters and greater the relative strength of intermolecular interactions between the polymeric components of the blend, the greater the probability of its miscibility. This is summarised in Table 3.4 in terms of critical values of $\chi$ and the solubility parameter difference, $\Delta\delta_{crit}$ for the blends. Also, the greater the difference between the values of polymer-polymer interaction parameter $\chi_{p-p}$ and the critical values predicted for upper limit of miscibility to occur $\chi_{crit}$, the smaller the range in which the polymers would be compatible. The tendency of the system to be miscible is proportionally diminished. The PS-NBR pair shows a significantly large difference between their $\chi$ and $\chi_{crit}$ values, indicating the

<table>
<thead>
<tr>
<th>Blend system</th>
<th>Degree of polymerisation</th>
<th>Value of solubility param. diff, $\Delta\delta$ (cal cm$^{-3}$)$^{0.5}$</th>
<th>Critical value of interaction param. $\chi_{crit}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBR/PS</td>
<td>1481 1041</td>
<td>0.4</td>
<td>0.002</td>
</tr>
<tr>
<td>NBR/SAN</td>
<td>1481 1435</td>
<td>0.2</td>
<td>0.001</td>
</tr>
<tr>
<td>NBR/ABS</td>
<td>1481 543</td>
<td>0.3</td>
<td>0.002</td>
</tr>
</tbody>
</table>

* $N_i = V_i/V_r$, where $V_i$ is the molar volume of polymer component $i$ and $V_r$ is taken as 100 cm$^3$mol$^{-1}$. 
immiscibility of the system. However, the relatively low difference in $\chi$ and $\chi_{\text{crit}}$ values of SAN-NBR and ABS-NBR suggests that these systems may tend to be miscible in a narrow range of compositional variation, in their solid state.

Schneier\textsuperscript{14} has calculated the heat of mixing as a measure of polymer-polymer compatibility. The heat of mixing ($\Delta H_{\text{mix}}$) for a two-component blend system was calculated using the expression:\textsuperscript{34,35}

$$\Delta H_{\text{mix}} = \{ x_1 M_1 \rho_1 (\delta_2 - \delta_1)^2 \left[ \frac{x_2}{(1-x_3) M_2 \rho_2 + (1-x_1) M_1 \rho_1} \right] \}^{1/2} \quad \text{...(3.6)}$$

where $x$, $\rho$ and $M$ are the weight fraction of polymer, density of the polymer and the molecular weight of monomer unit, respectively. The $(\delta_2 - \delta_1)$ represents the difference in solubility parameter between the two polymer components. Schneier\textsuperscript{34} in his studies noted that, for the compatible polymer pairs listed by Bohn,\textsuperscript{35} $10 \times 10^{-3}$ cal/mol marks the upper limit of compatibility in the solid state. Eq.(3.6) has been widely used to assess the degree of compatibility in blends.\textsuperscript{1}

The variation of $\Delta H_{\text{mix}}$ (calculated using Eq.3.6) of the three binary blends with compositional variation are presented in Fig.3.1. The heat of mixing of PS/NBR blends at almost all compositions except those with NBR content higher than 60 wt.%, are found to be between $14.56 \times 10^{-3}$ to $11.66 \times 10^{-3}$ cal/mol, i.e., above the value considered to be the upper limit of compatibility. The heat of mixing of SAN/NBR blends are found to be quite below the limit of compatibility at all compositions. Thus, a favourable $\Delta H_{\text{mix}}$ leads the NBR/SAN blends toward compatibility. In ABS/NBR, some degree of compatibility is indicated when the proportion of NBR is higher than 60 wt.% in the blend. Thus, the PS/NBR blends seem to be largely incompatible.
As explained earlier, the terms 'miscibility' and 'compatibility' have been used intermitantly in the text, with distinct meanings. Compatibility is a technological term, which does not require mixing of polymers at molecular scale. A compatible system possess strong interactions between the two polymer components but the two hetero-phases preserve the identities at their molecular level. Thus, a
compatible blend, most often, retains the properties of their individual components. However, miscibility is a strictly thermodynamic term. It implies that the state of mixing of the two polymers in the blend is at the molecular level and the resulting $\Delta G_{\text{mix}}$ is always negative.

3.1.3. Spectroscopic Evidence for Polymer-Polymer Interaction in the Blends

FTIR spectroscopy has been used as a potential tool for the investigation of the mutual interactions of various polymers.$^{38-40}$ The presence of favourable intermolecular interactions effectively increases the magnitude of $\chi_{\text{crit}}$ and permits the tolerance of a greater difference in the non-hydrogen bonding solubility parameters of the two polymers.$^{18}$ For very weak or 'repulsive interactions', values of $\chi < 10^{-3}$ are necessary for miscible blend systems, which correspond to values of $\Delta \delta < 0.1$ (cal cm$^{-3}$)$^{0.5}$. However, if certain functional groups contribute to intermediate strength favourable interactions, values of $\chi$ upto 0.1 may be tolerated, corresponding to an upper $\Delta \delta$ value close to 1 (cal cm$^{-3}$)$^{0.5}$. When strong interactions are involved, values of $\chi$ greater than 0.1 can be tolerated and miscible blends are possible even when the $\Delta \delta$ exceeds 1(cal/cm$^{-3}$)$^{0.5}$. The FTIR spectra of NBR, PS, SAN, and ABS are shown in Figures (3.2)-(3.5). Monitoring the -C=N stretching frequency of NBR provides an easy approach for studying this aspect for NBR based blend systems.

The FTIR spectrum of NBR showed a sharp and intense peak at 2229 cm$^{-1}$, corresponding to the absorption frequency of the -CN group. However, in the spectrum of PS$_{50}$ blend, the -CN peak shifts to 2233 cm$^{-1}$ (Fig.3.6). This shift of about 4 cm$^{-1}$ towards the higher energy region is due to the possible interactions involving the NBR and PS molecules. In pure nitrile rubber system, there would be cohesive interactions between the macromolecular chains. Owing to the strongly electron withdrawing nature of the nitrile group, the nitrogen atom of
Figure 3.2: FTIR spectrum of NBR

Figure 3.3: FTIR spectrum of PS
Figure 3.4: FTIR spectrum of SAN

Figure 3.5: FTIR spectrum of ABS
the -CN group would show an appreciable tendency to have hydrogen-bond like interactions with the appropriately placed hydrogen atoms. In pure NBR, this is operative with the \( \alpha \)-hydrogen atoms of nearby macromolecular chains. However, in PS\(_{50} \) blend, the probability of two NBR strands being in close proximity is less than in pure NBR. In the former case, the NBR chains would be inter-spaced with PS units. Hence the interaction between the -CN groups of a NBR chain and the \( \alpha \)-hydrogen atom of neighbouring NBR chain is less operative. Consequently, the effective strength of the -C=N bond would increase. This is reflected in the shift of the \( \bar{\nu}_{\text{CN}} \) of PS\(_{50} \) blend towards the higher energy region. Similarly, the \( \bar{\nu}_{\text{CN}} \) for the PS\(_{30} \) and PS\(_{70} \) systems were found to be 2236 cm\(^{-1} \). The enlarged regions of the FTIR spectra of NBR/PS blends showing the -CN absorption peak is shown in Fig. 3.6.

However, the \( \bar{\nu}_{\text{CN}} \) of SAN\(_{50} \) blend is found to be 2222 cm\(^{-1} \). The corresponding \( \bar{\nu}_{\text{CN}} \) absorption frequencies of pure NBR and pure SAN were both found to be 2229 cm\(^{-1} \). The shift of the \( \bar{\nu}_{\text{CN}} \) of SAN\(_{50} \) blends towards the lower energy region is due to the presence of acrylonitrile segments in SAN molecules as well. In contrast to the PS/NBR blends, in the case of SAN/NBR blends the presence of SAN molecules in the matrix promotes hydrogen-bonding between the nitrogen atom of the -CN group and the hydrogen atom of either the NBR or SAN molecules. This would decrease the effective strength of the -C=N bond. Hence SAN\(_{50} \) blend shows the \( \bar{\nu}_{\text{CN}} \) at a lower energy region. The \( \bar{\nu}_{\text{CN}} \) of SAN\(_{30} \) and SAN\(_{70} \) blends also showed a similar shift, with the corresponding values at 2226 cm\(^{-1} \) and 2227 cm\(^{-1} \) respectively. The FTIR spectra of SAN/NBR blends are shown in Fig. 3.7. The trend in the shift of \( \bar{\nu}_{\text{CN}} \) of ABS/NBR blends are similar to the SAN/NBR blends discussed earlier. The FTIR spectra of ABS/NBR blends are shown in Fig. 3.8. The \( \bar{\nu}_{\text{CN}} \) of ABS was found to be 2229 cm\(^{-1} \). However, the ABS\(_{30} \), ABS\(_{50} \) and ABS\(_{70} \) blends have the \( \bar{\nu}_{\text{CN}} \) at 2208 cm\(^{-1} \), 2211 cm\(^{-1} \) and 2212 cm\(^{-1} \), respectively. This
Figure 3.6: FTIR spectra of PS/NBR blends (enlarged part).

(a-PS70, b-PS50, c-PS30).

Figure 3.7: FTIR spectra of SAN/NBR blends (enlarged part).

(a-SAN70, b-SAN50, c-SAN30).
implies that, as in SAN/NBR blends, the ABS molecules increase the hydrogen bonding in ABS/NBR blends. Among the three blend systems studied here, there appears to be a predominant effect of steric hindrance caused due to the increasing concentration of the aromatic moiety, on the interaction between the nitrile segments. The aromatic content of the three blends decrease in the order PS/NBR > SAN/NBR > ABS/NBR, and consequently the intermolecular interaction involving the nitrile segments would be maximum in NBR/PS blends, and the least in ABS/NBR blends. For example, the 50/50 compositions of PS/NBR, SAN/NBR and ABS/NBR blends showed the $\tilde{\nu}_{\text{CN}}$ at 2233 cm$^{-1}$, 2222 cm$^{-1}$ and 2211 cm$^{-1}$, respectively. The attractive interacting nature, and hence the resulting compatible nature of SAN/NBR and ABS/NBR blends are due to the identical structural aspects of their respective components.
3.2. Compatibility of the NBR Based Blends in Solution

Unlike in solid state, the polymer-polymer interaction parameter \( \chi_{23} \) in blends as a tool to predict miscibility in solution has an obvious limitation. This is because, with increasing concentration of the diluent, the contribution of \( \Delta G_H/RT \) towards \( \chi \) decreases (Eq.3.1). Further, according to Robard and Patterson\(^{32,33} \), phase equilibrium in ternary systems containing two polymers (components 2 and 3) and a solvent (component 1) depend not only on \( \chi_{23} \) but also on any difference in strength of the polymer-solvent interactions, i.e., on

\[
|\Delta \chi| = |\chi_{12} - \chi_{13}| \quad \cdots \quad (3.7)
\]

Due to this ‘\( |\Delta \chi| \) effect’, phase separation is predicted even when the polymers are compatible, provided that \( |\Delta \chi| \) is sufficiently large. Thus, blend-solvent systems are expected to be either clear or cloudy depending on whether the solvents give small or large values of \( |\Delta \chi| \).\(^{12,33} \)

All the polymer pairs studied here gave clear solutions when mixed with the respective solvents. The solvent concentration in the blend solution was in the dilute solution regime (0.5% w/v). Table 3.5 presents the \( \chi_{12} \) and \( \chi_{13} \) values for the various polymer-polymer-solvent systems, as calculated using Eq.(3.2). The \( |\Delta \chi| \) values of all the systems are quite low. It is evident from the low \( |\Delta \chi| \) values that it would not be a cause to manifest in the incompatibility of the otherwise compatible NBR-SAN-solvent and NBR-ABS-solvent systems. However, for cyclohexanone systems, where the \( |\Delta \chi| \) values are relatively larger, immiscibility in solution for all the polymer pairs is predicted.
Table 3.5. Interaction parameter for Solvent(1)-Polymer(2)-polymer(3) systems at 30°C.

<table>
<thead>
<tr>
<th>Solvent (1) - PS (2) - NBR (3) ternary system</th>
<th>Toluene</th>
<th>Dichloro-Ethylene</th>
<th>THF</th>
<th>Trichloro-Ethylene</th>
<th>CHCl₃</th>
<th>Cyclohexanone</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \chi_{12} )</td>
<td>0.030</td>
<td>0.011</td>
<td>0.005</td>
<td>0.002</td>
<td>0.005</td>
<td>0.07</td>
</tr>
<tr>
<td>( \chi_{13} )</td>
<td>0</td>
<td>0.001</td>
<td>0.005</td>
<td>0.013</td>
<td>0.021</td>
<td>0.201</td>
</tr>
<tr>
<td>( \Delta \chi )</td>
<td>0.030</td>
<td>0.011</td>
<td>0</td>
<td>0.011</td>
<td>0.021</td>
<td>0.131</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solvent (1) - SAN (2) - NBR (3) ternary system</th>
<th>Toluene</th>
<th>Dichloro-Ethylene</th>
<th>THF</th>
<th>Trichloro-Ethylene</th>
<th>CHCl₃</th>
<th>Cyclohexanone</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \chi_{12} )</td>
<td>0.007</td>
<td>0.001</td>
<td>0</td>
<td>0.001</td>
<td>0.005</td>
<td>0.128</td>
</tr>
<tr>
<td>( \chi_{13} )</td>
<td>0</td>
<td>0.001</td>
<td>0.005</td>
<td>0.013</td>
<td>0.021</td>
<td>0.201</td>
</tr>
<tr>
<td>( \Delta \chi )</td>
<td>0.007</td>
<td>0</td>
<td>0.005</td>
<td>0.012</td>
<td>0.016</td>
<td>0.073</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solvent (1) - ABS (2) - NBR (3) ternary system</th>
<th>Toluene</th>
<th>Dichloro-Ethylene</th>
<th>THF</th>
<th>Trichloro-Ethylene</th>
<th>CHCl₃</th>
<th>Cyclohexanone</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \chi_{12} )</td>
<td>0.015</td>
<td>0.005</td>
<td>0.002</td>
<td>0</td>
<td>0.002</td>
<td>0.098</td>
</tr>
<tr>
<td>( \chi_{13} )</td>
<td>0</td>
<td>0.001</td>
<td>0.005</td>
<td>0.013</td>
<td>0.021</td>
<td>0.201</td>
</tr>
<tr>
<td>( \Delta \chi )</td>
<td>0.015</td>
<td>0.004</td>
<td>0.003</td>
<td>0.013</td>
<td>0.019</td>
<td>0.103</td>
</tr>
</tbody>
</table>

The measure of interaction between the polymer segments and the solvent in a polymer blend-solvent system is the blend-solvent interaction parameter \( \chi_{b-s} \).\(^{11-13} \) The blend-solvent interaction parameter has been calculated in the present work using Eq.(3.2), where \( \delta_{A} \) and \( \delta_{B} \) represent the solubility parameter of solvent and polymer blend, respectively. The solubility parameter of blends was calculated using the values of individual components,\(^{11-13,43} \)

\[
\delta_{B} = w_{1}\delta_{1} + w_{2}\delta_{2} \quad \text{.....(3.8)}
\]

where \( w \) and \( \delta \) are the weight fraction and solubility parameter, respectively, of the polymer components.
An estimate of blend-solvent interaction parameter using Eqs. (3.2) and (3.8), is shown graphically for five solvents of varying solubility parameters 8.9-9.9 (cal cm$^{-3}$)$^{0.5}$ (Fig. 3.9). It may be noted that the $\chi$ values have been calculated using the molar volume of respective solvents, since it has been assumed that the polymer segments occupy the lattice site of the solvent molecules. Generally, $\chi \leq 0.002$ is taken as the upper critical limit for miscibility to occur in blends. The lower the value of $\chi$, the higher is the expected degree of miscibility. Hence, among the different solvent-PS-NBR systems studied here, only THF-PS-NBR is expected to exhibit miscibility throughout the PS/NBR ratio. The blend-solvent interaction parameter of SAN-NBR in various solvents suggests miscibility of the blends to occur in THF and dichloroethylene, and to a lesser extent in toluene (Fig. 3.10). Similarly for solvent-ABS-NBR systems, when THF and dichloroethylene are the solvents, partial miscibility is predicted for the polymers in solution (Fig. 3.11).

![Blend-solvent interaction parameter of PS/NBR blends in various solvents](image)
Figure 3.10: Blend-solvent interaction parameter of SAN/NBR blends in various solvents

Figure 3.11: Blend-solvent interaction parameter of ABS/NBR blends in various solvents
Chloroform was taken as the solvent to study the behaviour of the blends in a good solvent, and to understand the competing interactions. The choice of chloroform for this purpose was dictated by the obvious advantages of using it as a mutual solvent for the blend preparation (solution casting). The polymer-polymer interaction parameter ($\chi_{23}$) has been discussed already, and is presented in Table 3.3. The $\chi_{b-s}$ values of the three different ternary systems with chloroform as the solvent is given in Table 3.6. It is evident that, $\chi_{23} > \chi_{b-s}$ for CHCl$_3$/PS/NBR systems, while $\chi_{23} < \chi_{b-s}$ for CHCl$_3$/SAN/NBR systems. Thus, assuming that the dilution of the blend solution with solvent would not affect considerable change in inherent interactions, the following implications can be gauged: The strength of polymer(2) - polymer(3) interaction is greater than blend-solvent(1) interaction for CHCl$_3$/SAN/NBR and CHCl$_3$/ABS/NBR systems. It has been reported that, when the polymer-polymer interaction is stronger than blend-solvent interaction in a blend solution, it results in strong intermolecular attraction.$^{33,43,44}$ Hence, CHCl$_3$/PS/NBR system seems to be incompatible while CHCl$_3$/SAN/NBR and CHCl$_3$/ABS/NBR systems seem to be compatible.
These results also imply that there are strong polymer-polymer interactions existing in SAN/NBR and ABS/NBR systems. This is in agreement with the spectroscopic results discussed earlier.

3.2.1. Dilute Solution Viscosity Theories for Compatibility Studies of Polymer Blends

Earlier studies indicate that the interaction in binary polymer systems can be analysed accurately by its viscosity behaviour. For this purpose, different theoretical approach has been formulated with reference to an ideal binary polymer system.

A completely empirical equation for predicting the ideal behaviour of mixed solutions based on the additivity concept was developed by Catsiff and Hewett. According to Catsiff and Hewett,\textsuperscript{9}

\[ \eta_{sp,m} = \frac{[C_1 (\eta_{sp,1}) + C_2 (\eta_{sp,2})]}{C} \] \hspace{1cm} (3.9)

where \( \eta_{sp,m} \) is the specific viscosity of the mixed polymer solution, \( \eta_{sp,1} \) and \( \eta_{sp,2} \) are the specific viscosities of polymer components 1 and 2, respectively at a concentration of \( C = C_1 + C_2 \), and \( C_1 \) and \( C_2 \) are concentrations of components 1 and 2 respectively. Using the above equation, Catsiff showed that a higher apparent specific viscosity shown by the mixed polymer solution than the expected ideal \( \eta_{sp,m} \) value may give a measure of the attractive interactions in the system.

However, the classical Huggins\textsuperscript{45} equation expresses the specific viscosity, \( \eta_{sp} \) of a single polymer solution as a function of the
concentration \( C \), i.e.,

\[
\frac{\eta_p}{C} = [\eta] + K_h[\eta]^2 C
\]  

\( \text{(3.10)} \)

where \([\eta]\) is the intrinsic viscosity. The term \( K_h[\eta]^2 \) is termed the specific interaction coefficient \( 'b' \), arising from the polymer interactions at infinite concentrations. A Huggin's plot of \( (\eta_p/C) \) versus \( C \) of the polymer solution should yield a straight line with intercept and gradient equal to \([\eta]\) and \( 'b' \) respectively. Krigbaum and Wall\(^8\) have adapted the Huggin's equation for an ideal polymer-polymer mixed solution as,

\[
\eta_{sp,m} = [\eta_1]C_1 + [\eta_2]C_2 + b_{11}C_1^2 + b_{22}C_2^2 + 2b_{12}C_1C_2
\]  

\( \text{(3.11)} \)

where \([\eta_1]\) and \([\eta_2]\) are intrinsic viscosities of polymer components 1 and 2 respectively; \( C_1 \) and \( C_2 \) are concentration of the respective components in the mixed polymer solution, and \( b_{12} \) is the interaction coefficient for the mixture of components 1 and 2.

The interaction coefficient between the two polymers \( b_{12} \) in a polymer blend, according to Williamson and Wright\(^{17}\), can be calculated theoretically as,

\[
b_{12} = \frac{(b_{11} + b_{22})}{2}
\]  

\( \text{(3.12)} \)

According to Krigbaum and Wall, information on the interaction between polymer molecules 1 and 2 should be obtainable from a comparison of experimental \( b_{12} \) and the theoretical \( (b_{12})^* \) values. The experimental \( b_{12} \) values are obtained from Eq.(3.11) while the theoretical \( (b_{12})^* \) is computed using Eq.(3.12). The compatibility of
polymer mixture can be characterised by a parameter $\Delta b$ (hereafter referred to as the Krigbaum and Wall parameter) which is given by,

$$\Delta b = b_{12\text{exp}} - b_{12\text{theor}} \quad \text{(3.13)}$$

Negative values of $\Delta b$ are found for solutions of systems containing incompatible polymers, while positive values of $\Delta b$ refer to attractive interaction and compatibility.

An alternative definition of ideal solution behaviour may be obtained by considering the intrinsic viscosities of the mixed polymer solution, derived from equation,

$$[\eta_{\text{sp,m}}/C]_{\infty} = [\eta_1](C_1/C)_{\infty} + [\eta_2](C_2/C)_{\infty} \quad \text{(3.14)}$$

Here also, if the apparent intrinsic viscosity of the blend determined experimentally is greater than the ideal value (obtained from Eq.3.14), the system indicates strong attractive interaction between the two polymers.

In fact, the basis of viscosity study for assessing the compatibility rests on the following assumption: Repulsive interactions may cause shrinkage of the random coils of polymer molecules. Hence, the viscosity of such a polymer mixture is reduced below the additive value predicted from the viscosities of the pure components in the mixture. If there is attractive interaction, the viscosity increases and the system is compatible, while the converse may suggest incompatibility.
3.2.2. Additivity Concept of Intrinsic Viscosity for Assessing Miscibility

It has been shown that the maximum concentration for validity of Eq. (3.10) is 2.0 g/dl. The highest concentration used in this study was 0.5 g/dl. The intrinsic viscosity of the polymer system \([\eta]\), is obtained from the intercept of the plot of \(\eta_{sp}/C\) versus \(C\), by the method of linear regression and a perfect fit is obtained when \(\gamma^2 = 1\). The data for the various blend systems are given in Table 3.7.

Table 3.7: Observed and calculated intrinsic viscosities of NBR based blends in chloroform as solvent.

<table>
<thead>
<tr>
<th>Polymer system</th>
<th>Corr. coeff. ((\gamma^2))</th>
<th>Intrinsic viscosity (dl/gm)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Observed</td>
<td>Calculated</td>
</tr>
<tr>
<td>NBR</td>
<td>0.99</td>
<td>1.663</td>
<td>-</td>
</tr>
<tr>
<td>PS</td>
<td>1.00</td>
<td>0.769</td>
<td>-</td>
</tr>
<tr>
<td>SAN</td>
<td>0.99</td>
<td>0.712</td>
<td>-</td>
</tr>
<tr>
<td>ABS</td>
<td>0.99</td>
<td>0.571</td>
<td>-</td>
</tr>
<tr>
<td>NBR/PS 30/70</td>
<td>0.99</td>
<td>0.943</td>
<td>1.038</td>
</tr>
<tr>
<td>NBR/PS 50/50</td>
<td>0.99</td>
<td>1.281</td>
<td>1.216</td>
</tr>
<tr>
<td>NBR/PS 70/30</td>
<td>0.99</td>
<td>1.341</td>
<td>1.395</td>
</tr>
<tr>
<td>NBR/SAN 30/70</td>
<td>0.99</td>
<td>0.947</td>
<td>0.998</td>
</tr>
<tr>
<td>NBR/SAN 50/50</td>
<td>1.00</td>
<td>1.221</td>
<td>1.188</td>
</tr>
<tr>
<td>NBR/SAN 70/30</td>
<td>1.00</td>
<td>1.394</td>
<td>1.378</td>
</tr>
<tr>
<td>NBR/ABS 30/70</td>
<td>0.99</td>
<td>0.856</td>
<td>0.899</td>
</tr>
<tr>
<td>NBR/ABS 50/50</td>
<td>0.99</td>
<td>1.065</td>
<td>1.117</td>
</tr>
<tr>
<td>NBR/ABS 70/30</td>
<td>0.99</td>
<td>1.556</td>
<td>1.336</td>
</tr>
</tbody>
</table>

It can be seen that the \(PS_{50}\) system shows a higher intrinsic viscosity value than the value calculated on the assumption of ideal behaviour. But the \(PS_{30}\) and \(PS_{70}\) systems show lower values than the calculated values. According to the assumption that a negative
deviation from ideal solution behaviour means repulsive interactions between the two polymers, it can be concluded that PS$_{30}$ and PS$_{70}$ systems are incompatible, while the PS$_{50}$ composition shows a positive deviation from ideal behaviour, suggesting compatibility.

The observed intrinsic viscosity of SAN$_{70}$ system is slightly lower than the ideal value. However, the SAN$_{30}$ and SAN$_{50}$ blend compositions show a strong positive deviation from ideal behaviour, indicating compatibility in the polymer solution regime. The observed $[\eta]$ value of ABS$_{70}$ and ABS$_{50}$ blends show a slight negative deviation while the ABS$_{30}$ blend shows a positive deviation from the expected ideal value.

3.2.3. Specific Viscosity as given by Catsiff & Hewett's Model

The observed and calculated specific viscosities (according to Eq.3.14) of the various blend systems were determined. The difference between the observed and the calculated values, $\Delta \eta_{sp,m}$, is plotted as a function of blend composition in Fig.3.12. According to Catsiff and Hewett concept,$^9$,$^{17}$ for an ideal blend system, the $\Delta \eta_{sp,m}$ value should be zero throughout.

For the PS$_{70}$ and PS$_{30}$ systems, the $\Delta \eta_{sp,m}$ values are negative, while the PS$_{50}$ blend has a positive $\Delta \eta_{sp,m}$ value. Thus, only the PS$_{50}$ blend system suggests a positively deviating blend (PDB) behaviour, and hence this system can be considered as compatible.

The $\Delta \eta_{sp,m}$ values of SAN$_{30}$ and SAN$_{50}$ blends are positive values, implying miscibility with increasing wt.% of NBR in the blend. But the SAN$_{70}$ blend suggests the behaviour of immiscibility. The NBR/ABS blends show a positive deviation in the case of only the 70/30 composition (i.e., ABS$_{30}$).
The behaviour predicted by the Catsiff model was found to be in agreement with the conclusion drawn from other viscosity theories on polymer blends. Thus the Catsiff and Hewett model is found to be applicable to understand miscibility for all the blend systems studied in our work.

3.2.4. Krigbaum and Wall Parameter, $\Delta b$

The values of $\Delta b$ according to Eq.(3.13) for different total concentration of PS/NBR mixtures are given in Fig.3.13. It is seen that the $\Delta b$ values of PS$_{50}$ blend are positive and exhibit positive deviation from ideal behaviour over almost all dilutions, indicating attractive interaction. The $\Delta b$ values of the PS$_{30}$ blend progressively become
Figure 3.13: Effect of blend composition and concentration on the $\Delta b$ values of the NBR/PS blends.

Figure 3.14: Effect of blend composition and concentration on the $\Delta b$ values of the NBR/SAN blends.
negative with increasing dilution, indicating incompatibility in solution. The $\Delta b$ values of PS$_{70}$ composition steadily become negative with dilution, indicating repulsive interaction after a critical concentration of the polymer blend solution. The decrease in $\Delta b$ values with increasing dilution of the blend solution may be because, the interaction between solvent and polymer increases as the solvent content increases, and ultimately exceeds the polymer-polymer interaction.

The $\Delta b$ values of SAN/NBR blends are shown in Fig. 3.14. The $\Delta b$ values of SAN$_{50}$ and SAN$_{30}$ compositions steadily become increasingly positive with dilution in the polymer solution concentration, implying stronger attractive interaction with dilution. But the $\Delta b$ values of SAN$_{70}$, which is initially positive gradually
decreases and become negative with dilution. The reason for this contradicting behaviour with dilution probably is due to the capability of the individual acrylonitrile chain segments of SAN phase to penetrate into the nitrile rubber phase, since they are chemically identical or vice-versa. As the wt.% of NBR increases in the blend, the concentration of acrylonitrile segments increases, and hence the interaction of the resulting penetration into the other phase increases. Evidently, with increasing dilution of the polymer blend solution, the polymer blend molecules will get disentangled more spaciously, resulting in greater interaction between the structurally similar acrylonitrile segments. However, in the case of SAN$_{70}$ phase, the acrylonitrile concentration is probably not optimum enough to induce greater interaction with dilution.

The $\Delta b$ values of NBR/ABS blends are plotted as a function of concentration in Fig. 3.15. This indicates that with increasing dilution, the ABS$_{70}$ and ABS$_{50}$ compositions steadily show greater negative values suggesting increasing repulsive interactions, while the ABS$_{30}$ blend shows increasing positive values of $\Delta b$ with dilution. Thus, the ABS$_{30}$ blend becomes miscible at higher concentration. In the case of NBR/ABS blends too, the reason for the strange behaviour of $\Delta b$ with dilution cited for NBR/SAN holds good.

3.2.5. Dilute Solution Density Measurements

The concept of miscibility predicted by viscometry has been correlated to the findings of dilute solution density measurements of polymer mixtures. If a system is miscible, the attractive interaction will cause increase in density of the resulting blend. Hence a greater observed density would imply miscibility. However, our intention was to seek a correlation in the dilute solution regime, corresponding to our viscometric findings. Hence the concentration of the polymer mixture solution chosen was 0.25 g/dl. It seems quite natural that the
deviation observed in the density may not be very substantial at this concentration regime. The density was calculated from the density values of individual polymers assuming additive contribution, according to the weight fraction of the components.

Table 3.12 Observed and calculated densities of various NBR-based polymer blend-chloroform solutions.

<table>
<thead>
<tr>
<th>Polymer system</th>
<th>Observed density</th>
<th>Calculated density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(g cm⁻³)</td>
<td>(g cm⁻³)</td>
</tr>
<tr>
<td>NBR</td>
<td>0.980</td>
<td>-</td>
</tr>
<tr>
<td>PS</td>
<td>0.984</td>
<td>-</td>
</tr>
<tr>
<td>SAN</td>
<td>0.989</td>
<td>-</td>
</tr>
<tr>
<td>ABS</td>
<td>0.986</td>
<td>-</td>
</tr>
<tr>
<td>NBR/PS 30/70</td>
<td>0.982</td>
<td>0.983</td>
</tr>
<tr>
<td>NBR/PS 50/50</td>
<td>0.984</td>
<td>0.982</td>
</tr>
<tr>
<td>NBR/PS 70/30</td>
<td>0.980</td>
<td>0.981</td>
</tr>
<tr>
<td>NBR/SAN 30/70</td>
<td>0.986</td>
<td>0.986</td>
</tr>
<tr>
<td>NBR/SAN 50/50</td>
<td>0.986</td>
<td>0.984</td>
</tr>
<tr>
<td>NBR/SAN 70/30</td>
<td>0.983</td>
<td>0.982</td>
</tr>
<tr>
<td>NBR/ABS 30/70</td>
<td>0.985</td>
<td>0.984</td>
</tr>
<tr>
<td>NBR/ABS 50/50</td>
<td>0.983</td>
<td>0.983</td>
</tr>
<tr>
<td>NBR/ABS 70/30</td>
<td>0.982</td>
<td>0.981</td>
</tr>
</tbody>
</table>

"Concentration, 0.25 g dl⁻¹; temperature, 30°C"

The observed and calculated densities (according to the concept of additivity) of the polymer blend solutions are given in Table 3.12. The marginally higher densities of PS₅₀, SANₕ₀, SAN₃₀ and ABS₃₀ blend solutions suggest that these systems are miscible. The miscibility behaviour of the blends are in agreement with our predictions based on viscometric theories.
The state of compatibility in these blends were also confirmed by measuring the glass transition temperature of the blends. The results of this study are discussed in the forthcoming chapters.

References


