Chapter 7

Compatibilisation of Heterogeneous
PS/NBR blends by the Addition of
SAN and ABS Copolymers

Part of this chapter have been communicated for publication in:
As discussed in chapter 4, PS/NBR blends show negative deviation in their mechanical properties from the additive contribution of each component, suggesting poor interfacial adhesion. In this chapter, the effect of styrene-acrylonitrile copolymer (SAN) and acrylonitrile-butadiene-styrene terpolymer (ABS) as potential compatibilisers for PS/NBR blends are discussed. The influence of compatibilisation on the morphology, mechanical, processing and thermal properties is discussed in this chapter.

7.1. Compatibilisation using SAN copolymer

As discussed in chapter 3, a favourable intermolecular interaction between SAN-PS and SAN-NBR pair, imparting compatibility to the respective blends due to their structural similarity is expected. Hence, SAN is a logical choice as a compatibiliser in PS/NBR blends. The schematic mechanism of the interfacial activity of the copolymer is depicted in Fig. 7.1. Due to the close affinity of the respective phases, styrene-segments of the copolymer may diffuse into the PS-phase, while the acrylonitrile segments diffuse into the NBR-phase. Localisation of the copolymer at the interface is increasingly favoured. This will facilitate the effective dissipation of stress from the matrix phase to dispersed phase, thereby, increasing the interfacial strength of PS/NBR blends.

The densities of different SAN compatibilised PS/NBR blends are shown in Fig. 7.2. The incorporation of SAN marginally increases the density of the respective PS/NBR blend. The positive deviation of density from the additive contribution of respective components is caused due to the increased interfacial adhesion and consequent packing densification of the compatibilised compositions.
COMPATIBILITY USING SAN IN NBR/PS BLENDS

Fig. 7.1: Schematic mechanism illustrating the interfacial activity of SAN copolymer in PS/NBR blends.
Fig. 7.2: Variation of density with SAN concentration in PS/NBR blends (prepared by melt-mixing).

7.1.1. Morphology

Solution-casting technique was used to prepare samples specifically for morphological studies due to the ease of preparing the samples and subsequent optical-microscopic analysis. Heterogeneous PS/NBR blends are grossly incompatible. The homogeneity of the system was improved by the addition of styrene-acrylonitrile copolymer. The optical micrographs of PS$_{30}$, PS$_{50}$ and PS$_{70}$ blends with 5 wt.% of SAN are shown in Figs. 7.3 – 7.5, respectively. The morphologies of the compatibilised blends may be compared with the optical micrograph of the respective uncompatibilised blend, in Fig. 4.7 (in chapter 4). In the virgin PS$_{30}$ blend, PS phase is dispersed as
Figure 7.3: Optical micrographs of PS/NBR 30/70 blend with 2 wt.% SAN.

Figure 7.4: Optical micrographs of PS/NBR 50/50 blend with 2 wt.% SAN.

Figure 7.5: Optical micrographs of PS/NBR 70/30 blend with 2 wt.% SAN.
spherical domains of about 16 μm in diameter in the NBR matrix. Addition of 5 wt.% of SAN in PS30 blend reduced the domain size to 6 μm. In case of PS50 blend, addition of 5 wt.% SAN reduced the dispersed domain size from 22 μm to 0.7 μm. In the PS70 blend too, the dispersed domain size reduction was very effective from 46 μm to 1 μm on addition of 5 wt.% SAN.

A quantitative assessment of the compatibilising effect of SAN in PS/NBR blends is made by measuring the diameter of about 400 domains in them. In Fig. 7.6 the average size of the dispersed phase is plotted as a function of the weight percentage of SAN copolymer. The average domain size decreases with increasing concentration of the compatibiliser and finally gets leveled-off at higher concentrations. This leveling-point can be considered as the so-called critical micelle concentration (CMC) of the copolymer at which micelles are formed. The micelle formation is highly undesirable in polymer blends.

Let us look at PS50 blend in detail. The domain size of uncompatibilised blend is 27.5 μm, indicating the gross incompatibility. Addition of only 1 wt.% SAN reduces the domain size to 1.1 μm, i.e., a reduction of 96%. Further addition corresponding to 2 and 5 wt.% SAN caused a reduction of 28% and 10%, respectively. Addition of compatibiliser beyond 5 wt.% does not affect any more change in the domain size. The PS30 and PS70 compatibilised series also show similar trends. The interfaces of all blends seem to be saturated at a SAN concentration of about 2%, and no further reduction in domain size was noted at larger amounts. The saturation effect and the general features of the curves in Fig. 7.6 has been reported by others and can be explained by a theory derived by Taylor.\(^3\,^4\) For a Newtonian dispersed system in shear flow,

\[
W_c = \frac{\eta_m D_n \gamma}{2 \gamma_{12}} \quad \text{....(7.1)}
\]

where \(W_c\) is the critical weber number, \(\eta_m\) is the matrix viscosity, \(\dot{\gamma}\) is the shear rate, \(\gamma_{12}\) is interfacial tension and \(D_n\) is the number average diameter of
the dispersed phase. There is a critical value of $W_s$ below which no particle deformation occurs, and at this point, the compatibiliser occupies the maximum interfacial area. The final domain size will be determined by a balance of shear forces causing domain break-up, and interfacial tension working against deformation and domain break-up. Thus, addition of compatibiliser beyond the saturation concentration will not result in any further decrease in $D_n$.

The equilibrium concentration at which the domain size leveled-off is considered as the 'critical micelle concentration'. There are numerous published reports on the interfacial saturation by the addition of compatibiliser in heterogeneous blends.\textsuperscript{5-8} The pioneering work of Noolandi and Hong predicted that micellar aggregation of the copolymer takes place at the interface of the blend beyond a critical concentration of the copolymer (CMC). According to Noolandi and Hong,\textsuperscript{5,6} the compatibiliser added to a heterogeneous blend locates at the interface and reduces the interfacial energy by broadening the interfacial area. The consequent reduction in interfacial
tension (Δγ) in a heterogeneous binary blend A/B upon the addition of a copolymer A-b-B is given by

\[ Δγ = dφ_c \left[ \frac{1}{2} \chi + \frac{1}{Z_c} \right] - \frac{1}{Z_c} \exp \left( Z_c \chi / 2 \right) \]  

(7.2)

Where 'd' is the width at half height of copolymer profile reduced by Kuhn statistical segment length, χ is the Flory Huggins interaction parameter between the A and B segment of the AB copolymer, \( Z_c \) is the degree of the polymerisation of the copolymer. The theory predicts the proportionality of interfacial tension reduction (Δγ) to copolymer volume fraction (φ_c), until the system reaches CMC. However beyond CMC, Δγ levels-off with φ_c. Since interfacial tension reduction is directly proportional to particle size reduction (Δd), it can be substituted for Δγ in Eq. 7.2, and CMC can be determined. 

Our present work also suggests that there is a critical concentration of the copolymer (i.e. CMC) required to saturate the PS/NBR blend interface. The addition of the compatibiliser beyond this concentration (i.e., CMC) leads to undesirable micelle formation, which very often reduces the total performance of the blend system. The plot of Δd versus φ_c is given in Fig. 7.7. It can be seen that at low concentration of the compatibiliser, Δd increases linearly with SAN concentration; and at high loadings, Δd levels-off, as indicated by Noolandi and Hong. The percentage of SAN required to saturate the interface (CMC) was determined, as shown in the Fig. 7.7. Thus, as observed from solution-casted blends, 1.1 - 1.35 wt.% of SAN is sufficient to effectively emulsify the heterogeneous PS/NBR system. It may be noted that conventionally employed blending methods are not expected to attain the same level of dispersion and orientation as in solution blending method. Unlike melt-mixing, solution-mixing results in molecular mixing. Hence, the corresponding melt-mixed blends may possess fractionally greater CMC than the solution prepared ones.
Tang and Huang proposed an equation where the average radius ($R$) of the dispersed phase is given by\(^1\)

$$R = (R_0 - R_S) e^{KC} + R_S \quad \ldots \quad (7.3)$$

where $R_0$ and $R_S$ are the average radii of dispersed domains at compatibiliser concentration zero and at saturation, respectively and $C$ is the concentration of the compatibiliser. The equation is based on the assumption that the change in the interfacial tension with the concentration of compatibiliser is given by

$$- \frac{d\gamma}{dC} = K(\gamma - \gamma_S) \quad \ldots \quad (7.4)$$
Concentration of SAN (wt.%) | K
---|---
0.50 | 1.110
0.75 | 1.359
1.00 | 3.704
2.00 | 2.787
5.00 | 1.392
10.0 | 0.627

where 'γ' is the interfacial tension at a compatibiliser concentration 'C', 'γ_s' is the interfacial tension at the saturation concentration and 'K' is a constant. The changes of average radii of domains with compatibiliser concentration were fitted to Eq.7.3. The fitted parameters for R_n are given in Table 7.1. The constant K can be expected to increase with the level of compatibilisation and decrease with the degree of compatibiliser self-association in the blend.16,11

**Domain size distributions**

The addition of SAN not only reduces the domain size but also narrows the size distribution in PS/NBR blends. The domain size distributions of uncompatibilised and compatibilised PS/NBR blends (prepared by solution casting) are shown in Fig. 7.8. The polydispersity index (PDI) values of the blends are given in Table 7.2. The uncompatibilised blends contained a significantly higher percentage of large domains formed through coalescence, than the compatibilised ones. On the addition of SAN, the distribution curve has narrowed down. The incorporation of 2 wt.% SAN results in a very narrow and uniform distribution of the dispersed phase. As the concentration of SAN is increased, the PDI values decrease. The PDI values for PS_{50} blends with 2, 5 and 10 wt.% SAN were nearly identical, presumably due to the saturation at the 2 wt.% level.
Fig. 7.8: Plot showing the size distribution of the dispersed domains in PS/NBR blends, compatibilised with SAN copolymer

Table 7.2: Effect of the addition of SAN on the polydispersity index (PDI) values of PS/NBR blends*

<table>
<thead>
<tr>
<th>SAN concentration in the blend (wt %)</th>
<th>PS30 blend</th>
<th>PS50 blend</th>
<th>PS70 blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.15</td>
<td>1.20</td>
<td>1.10</td>
</tr>
<tr>
<td>1</td>
<td>1.10</td>
<td>1.04</td>
<td>1.09</td>
</tr>
<tr>
<td>2</td>
<td>1.01</td>
<td>1.01</td>
<td>1.02</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>1.01</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>1.03</td>
<td>-</td>
</tr>
</tbody>
</table>

*prepared by solution-casting technique
It has been reported in literature\textsuperscript{3,4,12} that the role of a compatibiliser is to lower the interfacial tension and to suppress the coalescence process. The phenomenon of coalescence or aggregation of domains was not noticed in optimally compatibilised blends, as evident from the very small PDI values. Thus, when two domains collide during mixing or processing, a stabilising copolymer layer between the aggregated domains may inhibit coalescence.

7.1.2. Brabender torque rheometry

The various SAN incorporated PS/NBR blends showed similar processing profiles during their melt-mixing, except the torque developed towards the end of the melt-mixing process. Fig. 7.9 illustrates the plot of the steady torque developed during the end of melt-mixing versus SAN concentration for the blends. As discussed in chapter 4, the uncompatibilised blends showed steady torque values which were significantly lower than the

![Steady torque values as a function of the compatibiliser (SAN) content in PS/NBR blends](image)

Fig. 7.9: Steady torque values as a function of the compatibiliser (SAN) content in PS/NBR blends
values based on additivity, due to their incompatible nature. The compatibilised blends show a higher steady torque than the uncompatibilised ones, due to the emulsifying action of SAN at the interfaces and the possible occurrence of micelle formation. The PS_{30} and PS_{50} compatibilised blends show high melting torque due to the continuous nature of the high viscous NBR phase.

7.1.3. Morphology of the melt-mixed blends

Fig. 7.10 shows the scanning electron micrographs of the cryogenically fractured surface of PS_{50} composition and those compatibilised with 2 and 10 wt.\% SAN, respectively. In these blends, the PS-phase has been etched with cyclohexane, and hence the holes indicate the extracted phase. The uncompatibilised PS_{50} blend shows a co-continuous phase morphology (Fig. 4.6b, Chapter 4). In this blend, both the PS and NBR components tend to form the continuous phase. The phase co-continuity of PS_{50} blend is retained on addition of SAN copolymer in it. The morphology of the compatibilised blends shows that the addition of the copolymer results in a considerable reduction in the phase heterogeneity. The dimensions of the PS and NBR phases in the compatibilised blend are reduced considerably. Also, the blends attain a more uniform distribution of the PS and NBR components on compatibilisation.

7.1.4. Tensile Properties

The variation of Young’s modulus with SAN concentration in PS_{30}, PS_{50} and PS_{70} blends is shown in Fig. 7.11. Addition of SAN in PS/NBR system improves the tensile modulus of the blends. The increase in tensile modulus with the addition of SAN is due to the enhancement in interfacial adhesion between NBR and PS phases. For PS_{70} and PS_{50} blends, the highest tensile modulus is obtained at 5 wt.\% SAN concentration, while the lowest value is obtained for the uncompatibilised blends. For instance, the addition of 5 wt.\% SAN in PS_{70} brings about an increase of 400 MPa in the blend modulus. The modulus of PS_{30} does not show any considerable improvement on addition of SAN. This may be due to the fact that SAN molecules are not
Figure 7.10: Scanning electron micrographs of melt-mixed PS/NBR blends compatibilised with SAN; (a) PS50 SAN 2wt.%, (b) PS50 SAN 10wt.%. 
able to reach the interface on account of the high viscosity of the NBR matrix. Addition of SAN in PS$_{70}$ blend brings about a higher increase in modulus compared to PS$_{50}$ and PS$_{70}$ blends. Thus, the tensile modulus improvement is more in the case of PS-rich blends. The effectiveness of SAN in improving the modulus is higher in blends in which PS forms the continuous phase.

The variation of stress-at-break ($\sigma_b$) of PS$_{30}$, PS$_{50}$ and PS$_{70}$ blends with the concentration of SAN is shown in Fig. 7.12. By the addition of the compatibiliser, the interfacial condition of the blend is improved, and thereby the tensile strength also increases. In PS$_{70}$ blends, the stress-at-break shows a maximum at 2 wt.% SAN concentration. Addition of SAN beyond 2 wt.% does not appreciably alter the $\sigma_b$ values. In case of PS$_{50}$ also, the blend with 2 wt.% SAN showed the highest strength, and, thereafter showed a leveling-off behaviour. The PS$_{30}$ blends showed only a marginal increase with the SAN concentration. The tensile strength improvement is more in the case of
PS70 system. A leveling-off in tensile strength can be observed at 5 wt.% SAN concentration in the blends. The leveling-off of \( \sigma_b \) values at 5 wt.% SAN can be correlated with the saturation of SAN molecules at the PS/NBR interface.

The effect of SAN concentration on the break-strain % of PS/NBR blends is shown in Fig. 7.13. In all the three blends, the compatibilised compositions are more ductile than the uncompatibilised ones. For example, the uncompatibilised PS70 shows low break-strain % (9.8%). Addition of 5wt.% SAN in the blend increases the break-strain % to 16%. The blends exhibit an increase in break-strain % with SAN concentration. It can be seen that the break-strain% increases and reaches a leveling-off at 5wt.% SAN concentration. The increase in ductility of PS/NBR blends with compatibilisation is due to the improved interfacial adhesion. An improvement in elongation-at-break on compatibilisation of polymer blends has been reported in literature.\textsuperscript{13,14}
7.1.5. Tear properties and Hardness

Tear strength of PS/NBR blends as a function of SAN concentration is shown in Fig. 7.14. The blends exhibit an increase in tear strength with SAN concentration. The change in tear strength of the blends can be explained in terms of the change in morphology with compatibilisation. With increasing concentration of SAN in the blend, the average domain size decreases and the number of deformable particles per unit area increases proportionally. The highly deformable particles in the compatibilised systems are able to elongate to the high strain-levels and obstruct the advancing tear front more effectively. The tear strength of blends are considerably higher when the NBR particles comprise the dispersed phase (i.e. PS ≥ 50wt.%). As in the case of tensile properties, the leveling-off observed in tear strength at 5wt.% SAN is also due to the interfacial saturation.
Although, hardness is a surface property, the compatibilising effect of SAN shows an increase in Shore hardness of PS/NBR blends (Fig. 7.15). Perhaps, the particle size reduction and accompanying packing densification contributes to the enhanced hardness.

7.1.6. Impact properties

The effect of the compatibiliser concentration on the impact properties was examined at three different PS/NBR ratios (Fig. 7.16). The uncompatibilised PS$_{30}$ is, as such tough, having an impact strength of 514 Jm$^{-1}$. The incorporation of just 1 wt.% SAN drastically increases the impact strength to 794 Jm$^{-1}$. Increasing the compatibiliser concentration beyond 2 wt.% results in a plateau effect. The PS$_{50}$ blends also show a similar behaviour as that of PS$_{30}$ blends. Since PS matrix (without rubber) is very brittle, the PS$_{70}$ blend expectedly shows poor impact toughness. Addition of SAN increases the toughness of the brittle blend by a factor of 3 to 5. This is a significant improvement, with the brittle blend exhibiting considerable toughness at an optimum concentration of 2 wt.% SAN. Both large particle-size and weak adhesion appear to have caused the deterioration in impact properties and resulting brittleness of uncompatibilised PS$_{70}$. On the other hand, the compatibilised PS$_{50}$ and PS$_{30}$ blends have notched impact
Fig. 7.15: Shore hardness as a function of SAN concentration in PS/NBR blends

Fig. 7.16: Notched Izod impact strength as a function of SAN concentration in PS/NBR blends
toughness of $806 \sim 1072 \text{ Jm}^{-1}$ with an improvement of 71% over the corresponding uncompatibilised blends, and they are transformed to super tough materials in impact. The impact results indicate the importance of a critical SAN concentration for toughening of PS/NBR blends. It may be added that strong adhesion, brought about by a compatibiliser, is not a sufficient condition for toughening of rubber-plastic blends. The particle size must also be smaller than the critical size to achieve a tough behaviour.\textsuperscript{14} As discussed earlier, the optimum particle size was obtained at 2 wt.% SAN concentration in the blends, and this was found to be sufficient to effectively saturate the PS/NBR interface. The effect of increasing the concentration of SAN beyond 2-5 wt.% would only be to force away a portion of it away from the blend interface, to form micellar aggregates in the matrix. It is expected that such a situation would lead to an increased effective viscosity of the matrix. Thus, the incorporation of SAN above 5 wt.% in PS/NBR does not improve the impact strength any further. Majumdar et al.\textsuperscript{15,16} reported similar result on addition of imidized acrylic compatibiliser beyond 10 wt.% in nylon-6/ABS system.

The rebound resilience of PS/NBR blends on compatibilisation with SAN shows similar behaviour as impact strength (Fig. 7.17).
7.1.7. Effect of PS/NBR ratio on the mechanical properties

The PS/NBR systems present two extremes in properties, depending on whether the major component is plastic or rubber. When the blend is grossly PS-rich, we have strong ultimate properties but poor ductility. On the other extreme, the elastomeric NBR-rich blend has excellent elongational properties at the expense of ultimate strength. This section explores the minimum rubber concentration necessary for achieving a super-tough compatibilised blend, remaining reasonably ductile and mechanically strong. For this purpose, the SAN concentration is kept constant, while the PS content is varied.

The stress-strain behaviour of the compatibilised PS/NBR blends can be analyzed from Fig. 7.18. The PS50 blend shows elastic and inelastic regions. The PS50 blend shows yielding and necking behaviour, before failure occurs. In case of PS30, the modulus of the compatibilised blend is improved vastly relative to the uncompatibilised one. The PS70 blends show remarkable stiffness due to the presence of PS matrix. The higher tensile strength and modulus of PS70 and PS50 blends in comparison to PS30 blends is due to the continuous nature of PS phase and smaller particle sizes.

Fig. 7.19 shows the Izod impact strength (notched) of PS/NBR blends, compatibilised as well as uncompatibilised. There is a precipitous drop in the impact strength as the NBR concentration is decreased from 50 to 30%, corresponding to the critical NBR concentration for toughening of PS/NBR blends. The superior impact toughness of PS50 blends is associated with the co-continuous phase morphology in PS50 blends, where NBR and PS tend to form the continuous phase. The intrinsic morphology of the compatibilised blend showed better interfacial adhesion between the phases. All the compatibilised blends, including PS70, have impact strength in the range 553-864 Jm⁻¹. It is evident that super-tough materials can be achieved over a broad range of PS/NBR ratios, by addition of SAN copolymer. It is clear from Fig. 7.19 that 2 wt.% is the optimum concentration of SAN to
Fig. 7.18: Stress-strain plots of PS/NBR blends, with and without the addition of SAN.

Fig. 7.19: Effect of PS/NBR ratio on the Izod impact strength of compatibilised blends.
effectively improve the impact toughness of PS/NBR blends. The highest impact toughness of 2 wt.% SAN compatibilised blends is in agreement with the variation of the dispersed domain size. As discussed earlier, the blends containing 2 wt % SAN exhibits a more uniform phase distribution and lesser phase heterogeneity than the uncompatibilised blend.

All the ultimate properties, considered here, were vastly improved upon the addition of SAN copolymer in comparison to the virgin blends. The 5 wt.% SAN compatibilised blends, in general, were more ductile, while 2 wt.% SAN compatibilised blends gave better impact toughness.

### 7.1.8. Effect of Mixing Protocol

The sequence of addition of the compatibiliser during mixing has been found to affect the blend properties.\(^{15-22}\) Hence, the sensitivity of PS/NBR blends to the mode of addition of SAN copolymer was examined. Protocol (A) consisted of pre-blending PS with SAN, which was then blended with NBR in a second step. Protocol (B) consisted of first blending PS with NBR, followed by blending the mix with SAN in a second step. The mixes are schematically represented in Fig. 7.20.

It was expected that, owing to the low melt viscosity of PS and SAN, it would form a homogeneous melt. The subsequent melt-mixing of this pre-blend with NBR would result in stronger adhesion between PS/NBR interface. However, mixing as per protocol (B) would inhibit the mobility of the compatibiliser towards the already formed interface and retard the emulsifying phenomenon of the interface.

Table 7.3 summarises the results of the two different mixing protocols on the mechanical properties of the three blends. The blend properties are highly sensitive to the sequence of mixing. The protocol (A) mixed blends
Figure 7.20: Speculative model representing the behaviour of compatibiliser having different mode of mixing.
Table 7.3: Effect of the mode of addition of SAN copolymer during melt-blending on the PS NBR blend properties

<table>
<thead>
<tr>
<th>Mechanical properties</th>
<th>PS_{30} SAN2% blend</th>
<th>PS_{50} SAN2% blend</th>
<th>PS_{70} SAN2% blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's modulus (MPa)</td>
<td>27.8</td>
<td>12.3</td>
<td>109</td>
</tr>
<tr>
<td>Stress-at-break (MPa)</td>
<td>2.1</td>
<td>1.6</td>
<td>7.8</td>
</tr>
<tr>
<td>Break-strain %</td>
<td>133</td>
<td>127</td>
<td>27</td>
</tr>
<tr>
<td>Tear strength (N/mm)</td>
<td>8.9</td>
<td>8.3</td>
<td>42.2</td>
</tr>
<tr>
<td>Notched Izod impact</td>
<td>865</td>
<td>568</td>
<td>936</td>
</tr>
</tbody>
</table>

showed superior tensile properties than those prepared as per protocol (B). The tear strength also showed a similar behaviour. The impact toughness of the blends showed higher values when SAN was incorporated as per protocol (A). The impact strength of the blends prepared with protocol (B) dropped by as much as 31-34 \% for the compatibilised compositions with respect to the protocol (A) mixed blends. The impact strength of blends is greatly dependent upon the capacity of dissipating impact energy through the matrix and the transfer of the internal stress of the continuous phase to the dispersed phase. Hence, the interfacial condition between the phases is very important. Fig. 7.20 shows a speculative model illustrating the effect of mixing-sequence of the compatibilised blends on their properties. The model suggests that mixing as per protocol (A) would locate the compatibiliser at the interface in an efficient manner.

The effect of the mode of compatibiliser addition on the blend properties was higher when the plastic component was the dispersed phase. The mechanical properties of PS_{30} and PS_{50} blends showed
large difference when the mode of compatibiliser addition was changed. But, properties of PS70 blend were less affected by the change in mixing sequence.

The viscosity ratio of NBR with respect to SAN is 1.56 (= $\eta_{NBR}/\eta_{SAN}$) while the viscosity ratio of PS with respect to SAN is 0.69 (= $\eta_{PS}/\eta_{SAN}$). Hence, the mobility of SAN would be affected by the nature of the continuous phase of the blend. Blends in which NBR is the continuous phase, the mobility of the compatibiliser molecule would be lower and its location at the interface would be increasingly difficult.

Willis and Favis$^{22}$ and Asalata et al.$^{18}$ have reported that the two-step mixing is more effective in reducing the dispersed phase size than the one step mixing during compatibilisation. By pre-blending the modifier with the dispersed phase, it was possible to locate the co-polymer at the interface and increase the interaction between the copolymer and the dispersed phase.$^{22}$

In case of PS30 and PS50, by pre-blending SAN with PS (i.e., the dispersed phase in the blend), the amount of copolymer that can diffuse into the interface can be increased and the distance travelled by the copolymer to reach the interface can be minimized. This will lead to the preferential location of the SAN copolymer at the PS/NBR interface during mixing and result in higher interfacial adhesion.

Thus, compared to one-step mixing (Protocol-B), in two-step mixing (Protocol-A), the amount of compatibiliser diffusing into the interface is increased and the distance travelled by the compatibiliser to reach the blend interface is minimized. This leads to better interfacial interaction of the compatibiliser and facilitates the most efficient combination of mechanical properties.
7.1.9. Melt Rheology of Compatibilised Blend

**Melt viscosity, shear stress and shear rate dependence**

Rheometric measurements for the SAN-compatibilised PS$_{50}$ blends were carried out. Plots of $\tau_w$ as a function of $\gamma$ thus obtained are shown in Fig. 7.21. The flow curves of the compatibilised blends are above those of the uncompatibilised one (except PS$_{50}$ SAN 1wt.%). Variation of $\tau_w$ with $\gamma$ is linear on log-log scale, consistent with the power law equation$^{20}$ (Eq. 4.17).

![Fig. 7.21: Plots of shear stress vs. shear rate at 190°C, for PS/NBR blends containing various concentrations of SAN copolymer](image-url)
The flow behaviour index values ($n'$) vary marginally with the concentration of SAN in the blend (Table 7.4). This implies that the melt flow properties of the compatibilised blends is less affected by the level of shear stress than was seen in uncompatibilised PS/NBR blend in Chapter 4.

Variation of shear viscosity with SAN concentration in PS$_{50}$ blends is shown in Fig. 7.22. Addition of 1 wt.% SAN results in a marginal decrease in the shear viscosity of the blend. Further addition of SAN increases the shear viscosity of the blends. At SAN content higher than 2 wt.%, the melt viscosity of the compatibilised blends is higher than those of the uncompatibilised blend. The melt viscosity of the compatibilised blends, at a constant shear stress, show a maximum situated around 2 wt.% SAN content. The melt viscosity then decreases slightly with increasing SAN content. This indicates that 2 wt.% SAN is a critical concentration in SAN-compatibilised PS$_{50}$ blends. Also, as the shear rate increases, the differences in viscosity between the various SAN compatibilised blends narrow down. This is because, as the level of shear rate increases, the structure breaks down and the chances of interaction between the dispersed phase is reduced.

<table>
<thead>
<tr>
<th>Wt.% of SAN in PS$_{50}$ blend</th>
<th>Flow behaviour index ($n'$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.309</td>
</tr>
<tr>
<td>1</td>
<td>0.295</td>
</tr>
<tr>
<td>2</td>
<td>0.288</td>
</tr>
<tr>
<td>5</td>
<td>0.285</td>
</tr>
<tr>
<td>10</td>
<td>0.293</td>
</tr>
</tbody>
</table>

Table 7.4: Flow behaviour index ($n'$) of PS$_{50}$ blends compatibilised with various amount of SAN copolymer, at 190°C.
Fig. 7.22: Shear viscosity as a function of SAN concentration in PS/NBR (50/50) blends, at different shear rates.

The reduction in viscosity at higher shear rate is also due to the decrease in particle size. During extrusion, the dispersed domains are elongated at the entrance of the capillary under the action of shear force, resulting in the deformation and consequent break down of the particles. At low shear rates, the dispersed phase forms a wall structure in the continuous matrix, as was observed by Munstedt and Willis and Favis for rubber-modified plastics. When the shear stress is above a critical value called ‘yield stress’, the structure breaks down and the viscosity decreases.

The compatibilising effect of SAN in PS/NBR blend, when present at the optimum concentration of 2 wt.% effectively decreases the interfacial tension and strengthens the interaction between NBR and PS phases.
The natural affinity of the random copolymer for their respective homopolymer forces the copolymer to stay at the phase boundary and hold the phases together (Fig. 7.1). Beyond the optimum level of 2 wt.% SAN, the excess copolymer tends to migrate away from the interface and form 'micelles' or third phase of itself.

Incompatible blends are characterized by a sharp interface and poor interactions between the two phases, resulting in interlayer slip between the phases. In contrast, addition of a suitable compatibiliser in such a blend would increase the interfacial adhesion and lessen the slippage at the interface. Thus, the effective viscosity is expected to increase with compatibilisation in blends. Willis and Favis\textsuperscript{22} have reported the increase in viscosity of polymer blends by the addition of compatibiliser. The increase in viscosity of SAN compatibilised PS\textsubscript{50} blends indicate that there is lesser interlayer slippage between the PS/NBR phases as a result of effective compatibilisation

The effect of temperature on the shear viscosity of compatibilised PS\textsubscript{50} blends is shown in Fig. 7.23. The shear viscosity of the blends decreases with temperature. The change in viscosity with temperature is lesser for the compatibilised blends as compared to the uncompatibilised one. More information about the influence of temperature on the viscosity of compatibilised blend is obtained from the flow activation energy, given in Table 7.5.

It may be noted that addition of 2 wt.% of SAN in PS\textsubscript{50} blend gave the best set of morphological and mechanical properties. The SAN-compatibilised PS\textsubscript{50} blends are less sensitive to temperature than the uncompatibilised blend. This is a very important and useful observation, since it increases the tolerance of the compatibilised blend to a higher range of temperature during their processing.
Fig. 7.23: Variation of shear viscosity with SAN concentration and temperature for PS/NBR (50/50) blends. The results obtained at two shear rates are shown.

Table 7.5: Flow activation energy (kcal/mole) of SAN-compatibilised PS$_{50}$ blends at a shear rate of 208 s$^{-1}$.

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<tr>
<th>Wt.% of SAN in PS$_{50}$ blend</th>
<th>Flow activation energy (kcal/mole)</th>
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<tbody>
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</tr>
<tr>
<td>1</td>
<td>3.08</td>
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<td>5</td>
<td>1.79</td>
</tr>
<tr>
<td>10</td>
<td>2.53</td>
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</table>
Die Swell Ratio

The effects of compatibiliser concentration and shear stress on the die swell values of PS$_{50}$ blends are shown in Fig. 7.24. In general, the extrudate swell increases with increase in shear rate. When the material is extruded at a higher shear rate, the residence time of the material in the capillary is lower. Thus, higher amount of elastic energy is stored by the polymer, thereby, increasing the die swell.

The extrudate swell decreases upon the addition of SAN copolymer. The copolymer concentration increases the rigidity and stiffness of the polymer chains. This results in lower mobility of the chain under the influence of applied shear stress. Consequently, the die-swell ratio decreases with compatibilisation.

Fig. 7.24: Plot of Die swell values as a function of shear stress and compatibiliser concentration in PS$_{50}$ blends, when extruded at 190°C
Fig. 7.25: Comparison of the die swell values for the uncompatibilised and compatibilised PS$_{50}$ blend, at various temperatures.

The effect of temperature on the melt-elastic properties was studied by measuring the die-swell ratio of PS$_{50}$ blends at 190, 200 and 210°C as a function of compatibiliser concentration and shear stress. Fig. 7.25 shows the plots of die swell ratio versus shear stress at the three temperatures. In the case of several polymer blends, temperature does not exhibit any effect on the die-swell ratio versus shear stress plots.$^{23-25}$ However, in our study, in the absence of SAN copolymer in the blend, the die-swell values substantially increase with temperature and shear stress. But when 2 wt.% of SAN was incorporated in the blend, the effects of temperature as well as shear stress on the die swell ratio plot were less prominent. This is attributed to the increased rigidity and lower mobility of the macromolecular chains in the
compatibilised blends compared to the uncompatibilised one. Thus, temperature has a lesser effect on the die-swell ratio of compatibilised blends. Similar results were observed for rigid PVC/ENR systems. The change in extrudate behaviour on compatibilisation indicates that the PS particulate hierarchy is diminished when the SAN copolymer is incorporated in the system.

*Principal Normal Stress Difference*

The principal normal stress difference of PS$_{50}$ samples with 0, 1, 2, 5, and 10 wt.% SAN has been studied as a function of shear stress, and is plotted in Fig. 7.26. The principal normal stress difference decreases with the addition of SAN copolymer. The lowered $\tau_{11}-\tau_{22}$ values of the blend on incorporation of SAN can be explained as follows: The compatibilisation of the blend by SAN copolymer results in smaller dispersed phase domains. These smaller domains being less deformable, produce greater resistance to flow. This result in poor elastic recoverability, or, in other words, high $\tau_{11}-\tau_{22}$ values. Thus, the SAN-compatibilised blends show lower melt elasticity than the uncompatibilised blends.

*Elastic Shear Modulus*

The variation of elastic shear modulus with SAN concentration is shown in Fig. 7.27. At a given shear stress, the elastic shear modulus increases with the concentration of SAN copolymer in the blend. Here too, the reason lies in the decrease of dispersed particle size upon compatibilisation. Smaller size of the dispersed phase enhances the interfacial adhesion with the matrix phase, contributing to the improved rigidity or reduced elastic recoverability.
Fig. 7.26: Principal normal stress difference ($\tau_{11} - \tau_{22}$) vs. SAN concentration in PS$_{50}$ blends, at 190°C.

Fig. 7.27: Elastic shear modulus ($G$) vs. SAN concentration in PS$_{50}$ blends, at 190°C.
Recoverable Elastic Shear Strain

The effects of compatibiliser concentration and shear stress on recoverable shear strain are shown in Fig. 7.28. Uncompatibilised PS$_{50}$ blend has the highest value of $\gamma_R$ in the series. Recoverable shear strain decreases with the addition of SAN copolymer in the blend. This indicates the poor recoverability of the dispersed phase in the compatibilised blends. These droplets may absorb a part of the strain energy of the surrounding matrix and result in smaller values of $\gamma_R$.

The rate of increase of $\gamma_R$ with shear stress (Fig. 7.28), though identical for all compatibilised blend composition, differs considerably from uncompatibilised blend. A noticeable inflexion (or discontinuity) in these plots is noted markedly for uncompatibilised blend at the mid-shear region. The critical value of $\gamma_R$, with respect to shear stress, is the limit where the excessive amount of elastic strain energy starts converting into surface free energy to yield distortion to the extrudate. The inflexion in the $\gamma_R$ plot for the uncompatibilised blend may be considered as the critical zone where the excessively stored elastic strain energy undergoes fluctuation with shear stress.$^{27,29}$ Consequently, more surface free energy may be developed to impart increasing irregularities to the extrudate surface. This is clearly evident from the rapid increase of $\gamma_R$ with shear stress beyond the inflexion point. However, for compatibilised blends, $\gamma_R$ increases with an increase of shear stress without any notable appearance of a critical value. Also the higher magnitude of the steepness in the $\gamma_R$ versus shear stress plots may indicate higher melt fracture and distortion to the extrudate.$^{28}$ The compatibilised blends, due to its much smaller particle size, is less deformable and rigid. In contrast, deformability of the particles of the uncompatibilised blend results in the yielding tendency, and the drastic increase of elastic recoverability beyond the critical shear stress level.
Fig. 7.28: Recoverable elastic shear strain ($\gamma_r$) versus SAN concentration in PS$_{50}$ blends, at 190°C.
The complementary effects of the occurrence of minimum in melt elasticity and maximum in melt viscosity at 2 wt.% SAN concentration indicate the significance of the copolymer in PS$_{50}$ blend. In the flow of two-phase polymer blends, such a behaviour is believed to be due to interfacial tension and hydrodynamic effects such as deformability and size of suspended droplets. In the compatibilised blends, the dispersed phase domains are smaller and less deformable (i.e., lower elastic recoverability), thereby producing greater resistance to flow (i.e., higher melt viscosity). On the contrary, for the uncompatibilised blend, the dispersed phase domains are larger and thus more easily deformable (i.e., greater elastic recoverability). Hence, they produce lesser resistance to flow, accounting thereby for the observed minima in melt viscosity and maxima in melt elasticity.

The reduction in melt elasticity of PS/NBR blends upon compatibilisation with SAN copolymer is a very important and useful information for processing, since extrudate distortion tendency reduces with decreasing melt elasticity. Thus, the processing at higher shear rates without loss of surface smoothness of the product is enabled.

### 7.1.10. Melt Fracture

It has been found that PS does not show distortion of extrudate upto the highest limit of our measurements, i.e. shear rate of 278 s$^{-1}$. Addition of NBR to PS increases the tendency of the blend to undergo extrudate distortion. This is attributed to the decreasing melt strength due to the soft rubbery nature of NBR.

Extrudate of PS$_{50}$ blend and its compatibilised composition with SAN have been examined for their surface characteristic at the $\gamma_s$ of 139 s$^{-1}$ by taking SEM photomicrographs (Fig. 7.29a & b). Extrudate of PS$_{50}$ (Fig. 4.31) showed surface roughness. The poor interfacial adhesion between PS and
Figure 7.29: Scanning electron micrographs of the extrudate surface of PS/NBR 50/50 blends compatibilised with SAN;
(a) 2 wt.% SAN, Mag. 100x (b) 10 wt.% SAN, Mag. 100x
(c) 2 wt.% SAN, Mag. 800x (d) 10 wt.% SAN, Mag. 800x.
NBR phases enhances the mobility of the low viscous PS particles. This contributes to the voids and cavitations generated in a direction normal to the extrusion axis. These are plastic deformations resulting from the extensive stretch of the surface during the extrusion process. The low magnification scanning electron micrograph of compatibilised blend extrudates clearly support the contention that the die swell ratio of PS/NBR blend decreases with addition of SAN. Also, we observed an increasing level of smoothness imparted to the extrudate surface upon compatibilisation. This is due to the fact that, owing to the enhanced interfacial adhesion, the compatibilised compositions are devoid of particulate units of the dispersed phase to undergo effective inter-diffusion. Thus, the incorporation of SAN into PS reduces the extrudate distortion tendency.

In order to get an insight into the micro-structure of the extrudate surface of compatibilised blends, photomicrographs of higher magnification have been evaluated (Fig. 7.29c & d). The microstructure of the relatively smooth extrudate surface of 2 and 10 wt.% SAN compatibilised blends exhibit oriented features of a smoothly flown melt along the flow direction. Fig.7.29(d) shows the existence of SAN aggregates as micelles on the extrudate surface when 10 wt.% SAN was incorporated in PS blend.

7.1.11. State of dispersion in processed blends

Scanning electron micrographs of cryogenically fractured surfaces of blend extrudates have been studied to understand the phase morphology of the SAN-compatibilised PS blends.

Domains of PS in the virgin and compatibilised blends are clearly distinguishable from a comparison of Figs. 7.30, 4.33 & 4.34 (chapter 4). The uncompatibilised PS domains are large and of irregular shapes, while they are smaller and round in shape for the SAN incorporated compositions. The smaller size of the PS domains in the compatibilised blends result in lower melt elasticity.
Figure 7.30: Scanning electron micrographs of PS/NBR 50/50 (compatibilised with 2 wt.% SAN) blend extrudates, extruded at $\gamma = 139$ /s. (a) core region, (b) outer region. (Mag : 800x).
The resistance to flow would increase with decreasing size and flexibility of the rigid PS particulates. The observed higher viscosity of compatibilised blends than that of the virgin blend is in agreement with this view. The blend compatibilised with 10 wt.% SAN shows aggregation of phases. The effect of cohesive forces of each phase is expected to produce greater resistance to flow in such stratified structures.

As observed in the case of uncompatibilised PS50 extrudate in chapter 4, the PS phase tends to stratify towards the peripheral region. The migration of PS phase towards the periphery is attributed to the reduced interaction of the NBR matrix and PS phase. However, compatibilisation enhances the interfacial adhesion. Consequently, the agglomeration tendency of PS droplets towards the peripheral region is reduced. Thus, incorporation of SAN results in more uniform phase morphology throughout the extrudate.

7.1.12. Thermal properties

The thermal properties of the compatibilised blends were studied using differential scanning calorimetry and thermogravimetry.

The effect of SAN copolymer on the glass transition temperature of PS/NBR blends was studied at three blend ratios, viz. 30/70, 50/50, and 70/30. The DSC profiles of the compatibilised blend does not show any considerable difference from the uncompatibilised one (Fig. 7.31a & b). As with the uncompatibilised PS/NBR compositions, the blends containing SAN copolymer also exhibit the two glass transitions pertaining to the homopolymer phases.

Figs. 7.32 and 7.33 show the variation of glass transition temperatures of PS/NBR (50/50) and (70/30) blends with the addition of SAN copolymer. Addition of SAN copolymer in PS/NBR system results in a small inward shift of \( T_{g,NBR} \) and \( T_{g,PS} \). Incorporation of SAN does not have any noticeable effect
on the glass transition temperatures of the homopolymer phase. The glass transitions corresponding to PS and NBR phases indicate that addition of the compatibiliser does not make the system single phase. In other words, incorporation of the compatibiliser does not promote molecular level miscibility. This is in agreement with the conclusions made by Paul,\textsuperscript{12} who suggested that if two polymers are far from being miscible, then no copolymer is likely to make them one phase system. In a completely immiscible system, the main role of the copolymer is to act as an interfacial agent.

It may be noted that the effect of SAN to bring about the inward shift in the $T_g$ seems to be the highest in PS\textsubscript{70} blends. The $T_g\text{NBR}$ shifts by as much as 6°C with the addition of 2 wt.% of SAN in PS\textsubscript{70} blend. This is presumably because SAN copolymer is able to locate at the interface better when the less viscous PS is the matrix, enhancing the interaction between the two phases.

The TG and DTG curves of PS\textsubscript{50} with 2 and 5 wt.% SAN are shown in Fig. 7.34 and 7.35, respectively. In the case of the uncompatibilised blend, the temperature onset of rapid degradation is 340°C, and, the complete degradation takes place in the range of 407-500°C. The DTG curve shows a single and noticeable peak at 441°C. In the case of blends with 2 and 5 wt.% SAN, the onset of rapid degradation occurs at 424 and 435°C, respectively. The temperature onset of rapid degradation ($T_{\text{onset}}$) and the temperature at which 50% mass loss occurs ($T_{50\text{\%}}$) are plotted as a function of SAN concentration in PS\textsubscript{50} blends in Fig. 7.36. In the case of blends with 2 and 5 wt.% SAN, the DTG peaks are at 458 and 467°C. The peak in the DTG curve gives the temperature at which the rate of mass loss is the highest.

Table 7.6 gives the weight loss of the blends at different temperatures. It is clear that as compared to the degradation behaviour of uncompatibilised blend, the compatibilised blend shows improved thermo-oxidative stability.
Fig. 7.31a: DSC profile of PS/NBR 30/70 blend with 2 wt.% of SAN copolymer.

Fig. 7.31b: DSC profile of PS/NBR 50/50 blend with 2 wt.% of SAN copolymer.
Fig. 7.32: Variation of the glass transition temperature with SAN copolymer concentration in PS/NBR 50/50 blend.

Fig. 7.33: Variation of the glass transition temperature with SAN copolymer concentration in PS/NBR 70/30 blend.
Fig. 7.34: TG and DTG plots showing the mass loss % and mass loss rate vs. temperature, for PS/NBR 50/50 blends added with 2 wt.% of SAN copolymer.

Fig. 7.35: TG and DTG plots showing the mass loss % and mass loss rate vs. temperature, for PS/NBR 50/50 blends added with 5 wt.% of SAN copolymer.
Table 7.6. Weight loss and DTG peak values of PS/NBR blends compatibilised with SAN.

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<tr>
<th>Wt.% of SAN in PS/NBR 50/50 blend</th>
<th>Weight loss at 300°C</th>
<th>Weight loss at 400°C</th>
<th>Weight loss at 500°C</th>
<th>DTG peak °C</th>
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<td>87.6</td>
<td>468.3</td>
</tr>
</tbody>
</table>

Fig. 7.36: Plot of the temperature at which the onset of degradation and 50% of mass loss occur, as a function of SAN content in PS/NBR 50/50 blend.
7.2. **Compatibilisation using ABS copolymer**

A favourable intermolecular interaction between ABS/NBR and ABS/PS is expected on the basis of structural similarity. The speculative model depicting the interfacial activity of the copolymer is shown in Fig. 7.37. Due to the close affinity of the respective phases, styrene-segments of the copolymer diffuse into the PS-phase, while the acrylonitrile- and butadiene-segments diffuse into the NBR-phase. This leads to strong interface adhesion between the two phases. This type of interfacial activity of the compatibiliser molecule would result in a substantial improvement in the mechanical properties of the blend. Kleiner et al., Fayt et al., and Koshida et al. attributed the improvement in the properties on compatibilisation to the improved interfacial adhesion and packing densification.

### 7.2.1. Morphology

Fig. 7.38 shows the optical micrograph of PS$_{30}$, PS$_{50}$ and PS$_{70}$ blends with the addition of 2 wt.% of ABS. The photographs may be compared with the optical micrograph of the respective blends without the addition of ABS in Fig. 4.7. Addition of ABS copolymer decreases the phase separation and reduces the particle size. In PS$_{50}$ blend, about 80% reduction in the particle size is observed by the addition of 2 wt.% of ABS. The SEM photographs of the PS$_{50}$ABS2wt.% and PS$_{50}$ABS5wt.% melt-mixed blends are shown in Fig. 7.39. With the addition of a small amount of block copolymer, the sizes of the etched out dispersed phases represented by dark holes are reduced drastically. It can be clearly seen that the addition of the copolymer reduces the domain size of the minor component within the matrix of the major component, and that the decrease of particle size is sensitive to the amount of copolymer added.

The variation of the size of the dispersed phase with ABS loading in PS/NBR blends is shown in Fig. 7.40. The reduction in domain size is due to the decrease in the interaction energy between the homopolymers caused by the localisation of the ABS copolymer in the interfacial area. The interfacial activity of the copolymer decreases the interaction energy and hence the domain size decreases.
COMPATIBILIZATION USING ABS IN NBR/PS BLENDS

Fig. 7.37: Schematic mechanism illustrating the interfacial activity of ABS terpolymer in PS/NBR blends.
Figure 7.38: Optical micrographs of solution-casted PS/NBR blends compatibilised with ABS; (a) PS30 ABS 2wt.%, (b) PS50 ABS 2wt.% and (c) PS70 ABS 2wt.%. 
Figure 7.39: Scanning electron micrographs of melt-mixed PS/NBR blends compatibilised with ABS; (a) PS50 ABS 2wt.%; (b) PS50 ABS 5wt.%. 
As explained earlier (section 7.1), the optimum amount of ABS copolymer required to saturate unit volume of the interface (CMC) values are estimated from the intersection of the straight line obtained at low concentration and the leveling-off line at higher concentration (Fig. 7.41). In PS30 blend, the concentration of ABS required for attaining CMC is found to be about 1.10\%. The corresponding values for PS50 and PS70 blends are 1.60 and 1.10\%, respectively. The higher CMC values for PS50 blends compatibilised with ABS is due to the large size of the dispersed phase.

The polydispersity curves of the compatibilised compositions are shown in Fig. 7.42. The particle size distribution of the dispersed phase is controlled by the ABS copolymer concentration in the blend. The incompatible blend contains large number of bigger particles in the absence of copolymer and therefore the polydispersity is high. An uniformity in particle size and narrower distribution is attained when the copolymer concentration reaches the critical micelle concentration. Similar results have been reported by Willis et al.\textsuperscript{22} and Djakovic et al.\textsuperscript{32}
Fig. 7.41: Plot of reduction in the particle size as a function of ABS content in PS/NBR blends

Fig. 7.42: Plot showing the size distribution of the dispersed domains in PS/NBR blends, compatibilised with ABS copolymer
7.2.2. Mechanical properties

The stress-strain curves of PS$_{30}$ blends as a function of compatibiliser concentration is given in Fig. 7.43. The deformation nature of the blend varies with the copolymer concentration. Addition of ABS copolymer changes the deformation nature of the blend considerably. For the blends containing 1, 2, 5 and 10 wt.% ABS, the stress increases almost linearly with strain till failure occurs. It is clear from the curves that addition of ABS in PS$_{30}$ blends increases the elongation-at-break considerably.

The mechanical properties of PS$_{30}$, PS$_{50}$, and PS$_{70}$ blends compatibilised with ABS is summarized in Table 7.7. The blends exhibit considerable improvement in tensile properties upon the addition of ABS. It can be seen that tensile strength increases and reaches a leveling-off at 5 wt.% ABS copolymer concentration. Further addition makes little change in tensile strength. According to Majumdar et al.,

![Stress strain curves of 50/50 PS/NBR blends as a function of ABS copolymer concentration](image_url)
Table 7.7: Mechanical properties of PS/NBR/ABS blends

<table>
<thead>
<tr>
<th>Wt% of ABS in PS/NBR</th>
<th>Young's modulus (MPa)</th>
<th>Stress-at-break (MPa)</th>
<th>Break strain (%)</th>
<th>Tear strength (N/mm)</th>
<th>Notched Izod impact strength (J/m)</th>
</tr>
</thead>
<tbody>
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<th>Stress-at-break (MPa)</th>
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a reduction in the dispersed phase domain size, and the presence of the compatibiliser at the interface broadens the interfacial region through penetration of the copolymer chains into the adjacent phase. These factors described herein translated on the macro-scale into higher tensile strength and failure elongation for the blends.

Compatibilisation of PS/NBR blends by ABS enhances the resistance to tear. The leveling-off observed in tear strength at 5 wt.% ABS is due to the interfacial saturation of the compatibiliser.

There is a clear dependence of toughness on the ABS concentration. Compared with the binary blends, the Izod impact strength of the ternary blend was significantly improved. Perhaps, the adhesion between PS and NBR matrix was improved as a result of compatibilisation. For example, Izod impact strength of PS$_{50}$ABS$_{2}$wt.% blend is 569 J/m higher than that of the PS$_{50}$ blend. These features can be tentatively explained based on the fact that ABS provides efficient compatibilisation by reducing surface tension and improving both NBR dispersion and interfacial adhesion between PS and NBR phases. ABS stays preferentially on the surface of dispersed domains. The presence of such an interfacial agent would require less energy for breaking large dispersed particles during melt blending, thus giving domains to adhere to the continuous phase. The enhanced adhesion between the elastomeric phase and glassy polymer results in improvement of the impact strength.

The variation of the ultimate properties with the addition of ABS in PS/NBR blends is in agreement with the reduction in size of the dispersed phase. For instance, in Fig. 7.44, the Young's modulus and the domain size are plotted as a function of ABS concentration. The Young's modulus of uncompatibilised PS$_{50}$ blend is 50 MPa and the domains show an average size of 22 μm. Addition of 2 wt.% of ABS reduces the domain size to 4 μm and the Young's modulus becomes 87.6 MPa, an increase of 37 MPa with respect to the uncompatibilised composition. The reduction in domain size and increase in Young's modulus continue till the interface is saturated. The saturation of PS/NBR blend interface by ABS is indicated by the leveling-off of domain size and tensile properties profiles in Fig. 7.44.
7.2.3. Melt-flow properties

The shear stress versus shear rate plots for the PS$_{50}$ blends with different concentration of ABS are shown in Fig. 7.45. The flow behaviour index values ($n'$) were calculated from the slope of the linear plots, using the power law equation (Eq. 4.17). The dependence of $n'$ values of the blend on the concentration of ABS can be seen in Table 7.8. This implies that the dependence of the melt flow properties of the compatibilised blends is less affected by the level of shear stress, than was seen in chapter 4 for uncompatibilised PS/NBR blends. In the compatibilised blends, the lesser effect of shear stress is due to the presence of smaller domains.

Table 7.8: Flow behaviour index ($n'$) of PS$_{50}$ blends compatibilised with various amounts of ABS copolymer, at 190°C.

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<th>ABS 0wt.%</th>
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</table>
Fig. 7.45: Plots of shear stress vs. shear rate at 190°C, for PS/NBR blends containing various amounts of ABS copolymer.

Fig. 7.46: Shear viscosity at different shear rates as a function of the concentration of ABS copolymer in PS/NBR blends, measured at 190°C.
Variations of melt viscosity with ABS concentration in the ternary blends is illustrated in Fig. 7.46. The melt viscosity of the ternary blends, at a constant shear stress show a maximum situated around 2 wt.% ABS content. This indicates that 2 wt.% ABS concentration is a critical value in the NBR/PS/ABS ternary system. As the shear rate increases, differences in viscosity between different blends narrow down.

The flow activation energy for PS/NBR/ABS system is given in Table 7.9. The PS_{50} blends compatibilised with ABS possess lower activation energy than the uncompatibilised one due to their lower temperature sensitivity.

The melt elasticity parameters, viz. die-swell ratio, $\gamma_R$ and G values are shown in Table 7.10. The G values increase, while die swell and $\gamma_R$ decrease with the addition of ABS in PS/NBR 50/50 system. This indicates that the copolymer which goes into the interface, reduces the interfacial tension and decreases the size of the dispersed domains. Hence, the compatibilised blend is less susceptible to deformation and has lower melt elasticity than the uncompatibilised blend.

The presence of ABS in the blend reduces its tendency to undergo melt fracture or extrudate distortion. It was seen earlier that uncompatibilised PS_{50} blend exhibits surface irregularities and considerable extrudate distortion. The compatibiliser makes the blend rigid and reduces the surface distortion.
Table 7.10: Melt elastic properties* of PS/NBR (50/50) blends compatibilised with ABS copolymer.

<table>
<thead>
<tr>
<th>Concentration of ABS in PS&lt;sub&gt;n&lt;/sub&gt; (Wt %)</th>
<th>Die-swell, (d&lt;sub&gt;v&lt;/sub&gt;/d)</th>
<th>Elastic shear modulus (G), dynes/cm² (x 10&lt;sup&gt;7&lt;/sup&gt;)</th>
<th>Recoverable shear strain (γ&lt;sub&gt;r&lt;/sub&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.50</td>
<td>2.97</td>
<td>4.73</td>
</tr>
<tr>
<td>1</td>
<td>1.51</td>
<td>3.11</td>
<td>4.65</td>
</tr>
<tr>
<td>2</td>
<td>1.46</td>
<td>3.55</td>
<td>4.16</td>
</tr>
<tr>
<td>5</td>
<td>1.45</td>
<td>3.53</td>
<td>4.07</td>
</tr>
<tr>
<td>10</td>
<td>1.45</td>
<td>3.61</td>
<td>4.07</td>
</tr>
</tbody>
</table>

* measured at a shear rate = 139/s, temperature = 190°C.

7.2.4. Thermal properties

Glass transition temperatures of the PS/NBR blends with and without ABS copolymer are given in Table 7.11. The T<sub>g</sub>’s of the blends does not show any substantial variation with either blend composition or compatibiliser concentration. As with the uncompatibilised blend, the blend with ABS copolymer also showed two glass transitions. The DSC profile of PS/NBR 50/50 with 2 wt % of ABS is shown in Fig. 7.47. The incorporation of ABS in PS/NBR does not make the blend a one-phase system.

Compatibiliser has significant influence on the thermal properties of the blends. Fig. 7.48 shows the variation of the temperatures onset of rapid degradation for the ABS- compatibilised blends. For PS/NBR 50/50 blend without ABS, the rapid degradation starts at 340°C. Upon the addition of 2 wt % of ABS, the rapid degradation was raised to 428°C. Further addition of 3wt % of the copolymer raised the degradation temperature to 442°C. Similarly, temperature at which 50% of mass loss occur increases on addition of ABS in PS/NBR system (Fig. 7.48). Table 7.12 gives the weight loss at various temperatures. Weight loss is decreased upon the addition of the compatibiliser, which is an indication of the improved thermal stability of ABS- compatibilised PS/NBR blends. As the ABS concentration in the blend increases, the DTG peak value increases (Table 7.12). Thus, the temperature at which maximal rate of degradation occurs increase upon compatibilisation with ABS.
Fig. 7.47: DSC profile of PS/NBR 50/50 blend with 2 wt.% of ABS copolymer.

Table 7.11: Glass transition temperature* of PS/NBR blends compatibilised with ABS copolymer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ of NBR-rich phase ($^\circ$C)</th>
<th>$T_g$ of PS-rich phase ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS/NBR (30/70)</td>
<td>-26.1</td>
<td>+101.0</td>
</tr>
<tr>
<td>PS/NBR (30/70) ABS 2 wt.%</td>
<td>-25.6</td>
<td>+100.9</td>
</tr>
<tr>
<td>PS/NBR (30/70) ABS 10 wt.%</td>
<td>-23.1</td>
<td>+100.4</td>
</tr>
<tr>
<td>PS/NBR (50/50)</td>
<td>-23.1</td>
<td>+97.0</td>
</tr>
<tr>
<td>PS/NBR (50/50) ABS 2 wt.%</td>
<td>-20.1</td>
<td>+96.6</td>
</tr>
<tr>
<td>PS/NBR (50/50) ABS 10 wt.%</td>
<td>-21.3</td>
<td>+96.5</td>
</tr>
<tr>
<td>PS/NBR (70/30)</td>
<td>-26.5</td>
<td>+99.6</td>
</tr>
<tr>
<td>PS/NBR (70/30) ABS 2 wt.%</td>
<td>-23.0</td>
<td>+99.3</td>
</tr>
<tr>
<td>PS/NBR (70/30) ABS 10 wt.%</td>
<td>-22.6</td>
<td>+98.4</td>
</tr>
</tbody>
</table>

* Based on DSC measurements.
Table 7.12: Weight loss and DTG peak values of PS/NBR blends compatibilised with ABS copolymer.

<table>
<thead>
<tr>
<th>Wt.% of ABS in PS/NBR 50/50 blend</th>
<th>Weight loss at 300°C</th>
<th>Weight loss at 400°C</th>
<th>Weight loss at 500°C</th>
<th>DTG peak °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.8</td>
<td>21.2</td>
<td>79.5</td>
<td>432.2</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>6.1</td>
<td>90.5</td>
<td>457.0</td>
</tr>
<tr>
<td>5</td>
<td>1.0</td>
<td>5.8</td>
<td>89.0</td>
<td>468.8</td>
</tr>
<tr>
<td>10</td>
<td>0.67</td>
<td>2.1</td>
<td>85.2</td>
<td>474.3</td>
</tr>
</tbody>
</table>

Fig. 7.48: Plot of the temperature at which the onset of degradation and 50% of mass loss occur, as a function of ABS content in PS/NBR 50/50 blend.
7.3. SAN and ABS as compatibilisers for PS/NBR system: A comparison

A comparison of the tensile and tear properties of PS/NBR (50/50) blends compatibilised with SAN and ABS was carried out (Fig. 7.49). It was found that addition of SAN to PS/NBR blends improved the tensile and tear properties much more than ABS did in the corresponding blends, while causing a similar reduction in dispersed phase size. This indicates that the deformation and fracture mechanisms are strongly influenced by the nature of the compatibiliser.
7.4: Compatibilising effect of SAN and ABS: Mechanism

In order to explain the increase in ultimate properties of PS/NBR using SAN and ABS copolymers, two models differing in the number and arrangement of the phases were examined. The core-shell model consists of three phases: the matrix, the dispersed particles, and a shell on the dispersed particles with the properties of the copolymer. It is assumed that the shell has good adhesion to both the particle core and the matrix. The interpenetration model has only two phases. It is assumed that the copolymer imparts good adhesion between matrix and particles without forming a separate phase and without altering the properties of the matrix and particles.

(a) Core-shell model

The addition of SAN and ABS to PS/NBR (70/30) system is considered in the following discussion. The effect of the presence of SAN surrounding the NBR particles in the core shell would be to increase the effective modulus of the composite particle, owing to the higher modulus of SAN compared to NBR. The calculation involves two steps. In the first, the average modulus of the core-shell particle was estimated from Kerner's equation (Eq. 4.8, chapter 4) by considering a composite comprising of spherical PS particles dispersed in a matrix of the SAN copolymer. The modulus of such a composite particle is expected to increase gradually with increasing SAN concentration relative to PS. In the second step, the calculated modulus of the composite sphere was combined with the modulus of PS to calculate the modulus of the blend using Kerner equation. For this, the composite spheres were assumed to be dispersed in PS matrix.

While the copolymers were chosen to enhance the probability that they would be located preferentially at the interface, all the copolymer was not necessarily located at the interface. Some fraction could have been dispersed in the continuous phase. In order to incorporate the concept of a distributed copolymer into the calculation of the moduli of the blends using
Fig. 7.50: Modulus of PS/NBR (70/30) compatibilised with SAN and ABS predicted from the core-shell model with 70%, 50% and 30% of the compatibiliser at the interface.
the core-shell model, it was necessary to consider four limiting cases: (a) all the copolymer in the shell of the core-shell particle, (b) 70% of SAN forming shell on the NBR particle and 30% dispersed in the matrix PS phase, (c) 50% of SAN forming shell on the NBR particle and 50% dispersed in the PS matrix (d) 30% of SAN forming shell on the NBR particle and 70% dispersed in the PS matrix.

The result predicted a nominal increase in the blend modulus with increasing copolymer concentration, in the case of both SAN and ABS (Fig. 7.50a & b). The experimentally observed moduli values have been compared in the figures. Thus, we see that, a model with all the copolymer in the shell of the core-shell particle predicted a blend modulus that was quite low. The intermediate case, where some fraction of the copolymer coated the NBR particles and the remainder was dispersed in the PS matrix also predicted much lower moduli than that actually observed on adding the compatibilisers. Thus, the modulus of the compatibilised blend is found to be higher than that predicted on the basis of core-shell model.

(b) Interpenetration model

According to interpenetration model, the styrene- and acrylonitrile-segments of SAN were capable of selectively penetrating the PS and NBR phases to facilitate good interconnection between the phases, without forming a coating as in core-shell model. For ABS as compatibiliser, acrylonitrile- and butadiene-segments were presumed to penetrate into NBR phase, and styrene-segments into PS phase. This type of interpenetration is expected to improve the stress and strain transfer between the phases. Thus, the effective modulus of the blend would substantially increase upon the addition of the copolymer.

The conformation of the compatibiliser at the interface can be predicted based on the interfacial area in the blends. Three different physical models illustrating the conformation of the compatibiliser at
Fig. 7.51: Schematic illustration of the different conformations of the compatibiliser (copolymer A-B) at the blend interface.
the interface are given in literature. In the fully extended model, the blocks are assumed to extend into the corresponding homopolymer phases (Fig. 7.51a). In such a case, the occupied area at the interface is the cross-sectional area of the extended copolymer molecule. In the case of poly(styrene-co-acrylonitrile) as well as (poly(acrylonitrile-co-butadiene-co-acrylonitrile), the theoretical average cross-sectional area of the extended copolymer molecule and, hence, the area it occupies at the interface is ~0.5 nm². In the flat model, the occupied copolymer lies almost completely flat at the interface, in which case the occupied area is the lateral surface area of the entire copolymer molecule (Fig. 7.51b). Using the experimental values of root mean square radius of gyration of PS, the lateral surface area of the copolymers was estimated. The lateral surface area of SAN and ABS copolymers is approximately equal to 106 nm².

The area occupied by the copolymer molecule at the blend interface, \( \Sigma \), was calculated by using the expression suggested by Paul et al.,

\[
\Sigma = \frac{3 \phi_A M}{mRN} \quad \text{.........(7.5)}
\]

where \( M \) is the molecular weight of the copolymer, \( N \) the Avogadro’s number, \( \phi_A \) the volume fraction of the homopolymer A in a A/B blend, \( R \) the radius of the dispersed domains and \( m \) the mass of the copolymer required to saturate unit volume of the blend interface (i.e. CMC).

The values of interfacial area (\( \Sigma \)) for the two blend systems are given in Table 7.13 and 7.14. The experimental (\( \Sigma \)) values lie between 13.09 - 73.53 nm² for SAN-compatibilised blends and 4.18 - 19.15 nm² for ABS-compatibilised blends. These values are in between the values obtained from the two models (0.5 and 106 nm²). This suggests that neither of these models represent the actual situation. The behaviour of the copolymers is intermediate to those of the two models; a portion of the copolymer remains at the interface and rest penetrates into the corresponding homopolymer phases (Fig. 7.51c).
Table 7.13: Dispersed phase diameter (2R) at CMC and Σ values of PS/NBR systems with SAN copolymer as compatibiliser.

<table>
<thead>
<tr>
<th>Blend system</th>
<th>CMC (%)</th>
<th>Radius at CMC, R (µm)</th>
<th>Σ (nm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS/NBR (30/70)</td>
<td>1.35</td>
<td>3.07</td>
<td>13.09</td>
</tr>
<tr>
<td>PS/NBR (50/50)</td>
<td>1.20</td>
<td>0.44</td>
<td>73.53</td>
</tr>
<tr>
<td>PS/NBR (70/30)</td>
<td>1.10</td>
<td>0.55</td>
<td>38.50</td>
</tr>
</tbody>
</table>

Table 7.14: Dispersed phase diameter (2R) at CMC and Σ values of PS/NBR systems with ABS copolymer as compatibiliser.

<table>
<thead>
<tr>
<th>Blend system</th>
<th>CMC (%)</th>
<th>Radius at CMC, R (µm)</th>
<th>Σ (nm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS/NBR (30/70)</td>
<td>1.10</td>
<td>0.40</td>
<td>19.15</td>
</tr>
<tr>
<td>PS/NBR (50/50)</td>
<td>1.60</td>
<td>2.10</td>
<td>4.18</td>
</tr>
<tr>
<td>PS/NBR (70/30)</td>
<td>1.10</td>
<td>0.75</td>
<td>10.21</td>
</tr>
</tbody>
</table>

It may be noticed from Table 7.13 that the area occupied by the SAN molecule at the interface (Σ) in PS₅₀ and PS₇₀ blends is higher than in PS₃₀ blend. The PS-rich blends show higher interfacial area than the NBR-rich blends. This implies that, when the low viscous PS is the continuous phase, the interaction between the copolymer and the homopolymers is higher compared to blends in which NBR is the continuous phase. This is due to the fact that the compatibiliser molecule has high diffusional mobility in the low viscous PS matrix phase. Therefore, it can easily locate at the interface. Greater interaction increases interfacial area (hence high Σ values) and reduces interfacial tension. As the PS content is reduced, the increased
viscosity of matrix (NBR) retards the mobility of the copolymer. Hence, the orientation and the amount of copolymer locating at the interface is reduced, resulting in the reduction of interaction between the compatibiliser and the homopolymers. Hence the area occupied by SAN at the interface for PS$_{30}$ ($\Sigma = 13.09\text{nm}^2$) is lower than that of PS$_{50}$ ($\Sigma = 73.53\text{nm}^2$) and PS$_{20}$ ($\Sigma = 38.50\text{nm}^2$). A comparison of the $\Sigma$ values of blends compatibilised with SAN and ABS shows that the latter occupies much lesser area at the blend interface.

According to Wu\textsuperscript{16}, the interfacial tension ($\gamma_{12}$) and interfacial thickness ($L$) are related by the following equation:

$$\gamma_{12} = 7.6 / (L)^0.86.$$  \hspace{1cm} \text{...... (7.6)}$

This indicates that the superior compatibilising action of the SAN copolymer compared to ABS copolymer is due to the larger increase in interfacial thickness and a consequent reduction in interfacial tension.
References


