Chapter 3

Morphology and Mechanical Properties: Effect of Blend Ratio, Compatibilisation and Dynamic Vulcanisation

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3.1 Introduction

The properties of rubber-plastic blends are determined by (1) material properties of rubber and plastic phases (2) rubber/plastic proportions (3) phase morphology and (4) interaction at the interface.\textsuperscript{1-3} A thorough understanding of the blend morphology is important since the properties of polymer blends are strongly dependant on the blend morphology.\textsuperscript{4-8} The morphology of heterogeneous polymer blends depends on blend composition, viscosity of individual components, and processing history. Danesi and Porter\textsuperscript{5} reported that for blends with same processing history, the morphology is determined by melt viscosity ratio and composition. Generally, the least viscous component was observed to form the continuous phase over a larger composition range.\textsuperscript{3} During the last few years a large number of studies on the morphology and properties of thermoplastic elastomers from rubber/plastic blends have been reported.\textsuperscript{9-13}

Thermoplastic elastomers from blends of polypropylene (PP) and nitrile rubber (NBR) find applications in cables, oil seals, hoses and other moulded articles by virtue of their easy processability, low density, excellent oil resistance and good mechanical properties. Hence, it is important to study the mechanical properties of these materials in order to understand the final properties of the material.

Several studies have been reported on the rubber modification of polypropylene. The morphology and mechanical properties of PP/EVA blends have been studied by Thomas and co-workers.\textsuperscript{14,15} Kuriakose et al. reported on the NR modification of PP.\textsuperscript{16} Blends of polypropylene with ethylene-propylene
rubbers have been studied by different research groups. The mechanical and thermal properties of PP/polybutadiene blends have been reported by Gupta and Ratnam. Coran and Patel reported the technological compatibilisation of PP/NBR and PE/NBR blends. They have studied the effect of addition of graft copolymer and dynamic vulcanisation on the mechanical properties of these blends. Recently, Baker and co-workers studied the effectiveness of various basic functional groups in polypropylene as compatibilisers in a PP/NBR system using morphological and impact property measurements.

In this chapter, the influence of blend ratio on the morphology and mechanical properties of PP/NBR blends has been presented. The effects of concentration of two compatibilisers, maleic modified polypropylene and phenolic modified polypropylene on the morphology and mechanical properties of the blend are quantitatively investigated. The experimental results have been applied to testify the current compatibilisation theories of Noolandi and Hong. The effects of dynamic vulcanisation and filler addition on the mechanical properties are also investigated.

3.2 Results and discussion

3.2.1 Binary blends

(a) Processing characteristics

The processing characteristics of the blends have been studied from the Brabender Plastographs. The torque-time and torque-temperature relationships obtained from Brabender Plastographs are shown in Figure 3.1. In all the cases, the mixing torque falls rapidly within 3 min of mixing time and then levels off to give uniform values at the end of the mixing cycle indicating good degree of mixing. Favis has reported that the final morphology of the blend is strongly influenced by the time of mixing. All the blends show higher mixing torque than PP, and the torque is found to increase with increase in NBR content. This
is due to the higher melt viscosity of NBR as compared to PP. These results clearly indicate that all the blends have higher melt viscosity than polypropylene. It is also seen from the figure that the mixing temperature of the blends increases with increase in NBR content. This is due to the fact that high shear forces are involved as NBR content increases owing to its higher viscosity compared to PP.

![Graph showing variation of mixing torque and temperature with time of mixing.](image)

**Figure 3.1.** Brabender plastographs showing the variation of mixing torque and temperature with time of mixing.

(b) **Morphology of the binary blends**

The scanning electron micrographs of P'70, P'50 and P'30 from which the NBR phase has been extracted are shown in Figures 3.2a-3.2c. In the P'70 NBR is found to be dispersed as domains in the continuous PP matrix. This is due to the higher melt viscosity and lower NBR content compared to PP in the blend. As the rubber in the blend increases from 30 to 50 wt% the average size of the dispersed NBR phase increases from 5.87 to 17.90 μm. The bigger particle size of the rubber
phase with increase in rubber content is attributed to the reagglomeration or coalescence of the dispersed rubber particles. Occurrence of coalescence at higher concentrations of one of the components has been reported by many authors.²²⁻²⁴ In P₃₀, both NBR and PP phases exist as co-continuous phases. This is associated with the higher proportions of NBR and low viscosity of the PP phase.

Figure 3.2. Scanning electron photomicrographs of NBR/PP blends from which NBR was extracted using chloroform: (a) 30/70 NBR/PP blend. NBR is dispersed as domains in the continuous PP matrix; (b) 50/50 NBR/PP blend: NBR is dispersed as domains in the continuous PP matrix; and (c) 70/30 NBR/PP blend with co-continuous morphology.
(c) **Mechanical properties**

The stress-strain curves of the $P_{100}$, $P_{70}$, $P_{50}$, $P_{30}$ and $P_0$ are shown in Figure 3.3. From the stress-strain curves it is possible to determine the differences in the deformation characteristics of the blends under an applied load. The stress-strain curve of PP is similar to that of a brittle material. It shows very high initial modulus with a definite yield point. The addition of NBR changes the nature of stress-strain curves considerably. The stress-strain curves of PP and blends containing higher proportion of PP have distinct elastic and inelastic regions. In the inelastic region they undergo yielding. The elastic moduli of the blends are found to be reduced considerably with the increase in rubber concentration. The improved rubbery behaviour of $P_{30}$ compared to $P_{70}$ and $P_{50}$ can be explained in terms of the phase inversion of NBR from dispersed to continuous phase on passing from $P_{50}$ to $P_{30}$. The stress-strain behaviour of NBR is typical of uncrosslinked soft elastomer.

**Figure 3.3.** Stress strain curves of the samples.
Figure 3.4 shows the load displacement curves of PP/NBR blends during tearing. Polypropylene tears at a higher load and at a small displacement. NBR undergoes the largest displacement with the minimum tearing force. The tearing behaviour of NBR/PP blends are intermediate between those of PP and NBR. As the NBR content in the blend increases the load required to tear the samples decreases and the displacement increases. This increase in displacement with rubber content may be due to the increased stretching of rubber particles which can bridge the matrix cracks. From the figure it is also seen that the modulus of the blends decreases with increase in rubber content and this reduction is more pronounced in the case of P30. In PP/EVA blends similar behaviour has been reported by Thomas et al. They correlated this behaviour with the morphology of the blends.

![Figure 3.4. Tear load-displacement curves of NBR/PP blends.](image)

Table 3.1 and Figure 3.5 show the variation of mechanical properties as a function of wt % of NBR. Pure iPP has the maximum tensile strength, tear strength and Young’s modulus. From the table it is seen that with the increase in
NBR content, the tensile strength, tear strength and Young’s modulus decrease. The strength of NBR/PP blends depends on the strength of PP phase, which in turn depends on the extent of crystallinity. It has been observed that the crystallinity of the blend was decreased by the incorporation of NBR (Table 3.2). Martuscelli et al. have stated that the spherulite growth of iPP in blends with rubber is hindered by the presence of the rubber phase. Hence the observed decrease in tensile strength, tear strength and Young’s modulus with increase in NBR content is due to the presence of the soft rubber phase and drop in crystallinity of PP phase. It can be noticed from Figure 3.5 that the tensile strength-composition curve shows a negative deviation i.e., blend properties lie below the additivity line. The observed negative deviation is due to the poor interfacial adhesion between the non-polar PP and polar NBR phases, which causes poor stress transfer between the matrix and the dispersed phase. A clear change in the slope of this tensile strength-composition curve is seen between the composition range 50/50 PP/NBR to 30/70 PP/NBR. This is attributed to phase inversion of NBR from dispersed to continuous phase. Such deviation in the slope of mechanical property-composition curves had been reported by Danesi and Porter for PP/EPDM system.

<table>
<thead>
<tr>
<th>Property</th>
<th>$P_{100}$</th>
<th>$P_{70}$</th>
<th>$P_{50}$</th>
<th>$P_{30}$</th>
<th>$P_{0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>35</td>
<td>18.30</td>
<td>9.20</td>
<td>3.50</td>
<td>0.475</td>
</tr>
<tr>
<td>Young’s modulus (MPa)</td>
<td>500</td>
<td>250</td>
<td>135</td>
<td>47</td>
<td>1.5</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>15.6</td>
<td>95.58</td>
<td>43.45</td>
<td>38.64</td>
<td>1267</td>
</tr>
<tr>
<td>Tear strength (N/m)</td>
<td>117.90</td>
<td>85.40</td>
<td>50</td>
<td>21.10</td>
<td>5.36</td>
</tr>
<tr>
<td>Tensile impact strength (J/m²)</td>
<td>1110</td>
<td>1008</td>
<td>320</td>
<td>1448</td>
<td>-</td>
</tr>
<tr>
<td>Hardness shore A</td>
<td>95</td>
<td>95</td>
<td>93</td>
<td>83</td>
<td>28</td>
</tr>
</tbody>
</table>
Figure 3.5. Effect of weight percent of NBR on tensile strength and shore A hardness of NBR/PP blends.

Table 3.2. Crystallinity of PP/NBR blends (from DSC data).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P100</td>
<td>55.3</td>
</tr>
<tr>
<td>P70</td>
<td>33.9</td>
</tr>
<tr>
<td>P50</td>
<td>20.9</td>
</tr>
<tr>
<td>P30</td>
<td>13.7</td>
</tr>
</tbody>
</table>

The elongation at break of PP/NBR blend is found to increase with the addition of 30 wt % NBR and after that it decreases with increase in rubber content (Table 3.1). The elongation at break also shows negative deviation. This decrease in elongation at break at higher rubber content is due to the poor interfacial adhesion between the homopolymers.
From the table, it is also seen that the tensile impact strength decreases with the addition of NBR up to 50 wt %.

In immiscible blends, the tensile impact strength usually depends on the particle size of the dispersed phase. Smaller and uniformly distributed particles are more effective to initiate crazes and to terminate them before they develop into catastrophic sizes. The decrease in tensile impact strength in PP/NBR blends up to 50 wt % of NBR is due to the poor interfacial adhesion and higher particle size of the dispersed NBR phase as seen in the SEM photographs of P70 and P50 (Figure 3.2). The poor interfacial adhesion causes premature failure as a result of the usual crack opening mechanism. Karger-Kocsis et al.26 have shown that with the increase in the particle size of the dispersed rubber phase, the tensile impact strength of PP/EPDM blend decreases. After 50 wt % of NBR, the tensile impact strength is found to increase sharply. This sharp increase in impact strength may be due to the continuous nature of the NBR phase, which forms a co-continuous structure with the plastic phase (Figure 3.2). Similar results were reported in the case of PP-EVA system.27

From Table 3.1 it is seen that the addition of 30 wt % of NBR does not change the hardness. However, further addition of NBR decreases the hardness. The hardness-composition curve shows a slope change beyond 50 wt % of NBR (Figure 3.5). The reduction in hardness and the slope change in the curve at higher proportion of NBR (>50%) can be explained by the phase inversion of NBR from dispersed to continuous phase on passing from 50/50 PP/NBR to 30/70 PP/NBR blend. It is interesting to see that the hardness values show a positive deviation.

Applicability of various composite models such as parallel, series, Halpin-Tsai and Coran's models has been used to predict the mechanical properties of these blends. The highest upper bound parallel model is given by the rule of mixtures

\[ M = M_1 \phi_1 + M_2 \phi_2 \]  (3.1)
where $M$ is any mechanical property of the composite, $M_1$ and $M_2$ are the mechanical properties of component 1 and 2 respectively and $\phi_1$ and $\phi_2$ are the volume fractions of components 1 and 2 respectively. This equation holds for models in which the components are arranged parallel to one another so that an applied stress elongates each component by the same amount. The lowest lower bound series model is found in models in which the components are arranged in series with the applied stress. The equation for this case is

$$\frac{1}{M} = \frac{\phi_1}{M_1} + \frac{\phi_2}{M_2}$$  \hspace{1cm} (3.2)$$

According to Halpin-Tsai equation$^{28,29}$

$$\frac{M_1}{M} = \frac{(1 + AiBi\phi_2)/(1 - Bi\phi_2)}{1/Ai}$$ \hspace{1cm} (3.3)$$

$$Bi = \frac{(M_1/M_2 - 1)/(M_1/M_2 + Ai)}{1/Ai}$$ \hspace{1cm} (3.4)$$

In the Halpin-Tsai equation, subscripts 1 and 2 refer to the continuous phase and dispersed phase respectively. The constant $Ai$ is defined by the morphology of the system. For elastomer domains dispersed in a continuous hard matrix, $Ai = 0.66$.

For an incompatible blend, values of mechanical properties are expected to be in between upper bound parallel model ($M_U$) and lower bound series model ($M_L$). According to Coran's equation,$^3$

$$M = f(M_U - M_L) + M_L$$ \hspace{1cm} (3.5)$$

where $f$ can vary between zero and unity. The value of $f$ is a function of phase morphology. The value of $f$ is given by

$$f = V_H^n (nV_S + 1)$$ \hspace{1cm} (3.6)$$

where $n$ contains the aspects of phase morphology, $V_H$ and $V_S$ are the volume fractions of hard phase and soft phase respectively. The change in $f$ with respect to $V_H$ is greatest when $V_H = -(n-1)/n$. Thus the value of $f$ could be considered as the volume fraction of hard phase material that corresponds to a phase inversion.
Figure 3.6 shows the experimental and theoretical curves of Young's modulus as a function of soft phase volume fraction. It can be seen from the figure that experimental data are very close to the Coran's model, in which the value of \( n = 2.2 \). The value of \( n = 2.2 \), corresponds to \( V_H = 0.545 \) as the hard phase volume fraction that corresponds to a phase inversion of NBR from dispersed to continuous phase. This result is consistent with the experimental results from morphology and mechanical property studies.

**Figure 3.6.** Experimental and theoretical values of Young’s modulus as a function of volume fraction of NBR phase.

### 3.2.2 Compatibilisation

**(a) Morphology of compatibilised blends**

The effect of maleic anhydride modified polypropylene and phenolic modified polypropylene as compatibilisers on the morphology of the 70/30 PP/NBR blend is shown by the SEM micrographs of Figures 3.7 and 3.8, respectively. The micrographs 3.7a–3.7d indicate blends containing 1, 5, 10 and 15% MA-PP respectively and micrographs 3.8a–d indicate blends containing
3, 7.5, 10 and 15% Ph-PP, respectively. The morphology of uncompatibilised blend was already given in Figure 3.2a. From the SEM micrographs, it is seen that the size of the dispersed NBR phase decreases with the addition of modified polymers. This reduction in particle size with the addition of modified polymers is due to the reduction in interfacial tension between the dispersed NBR phase and polypropylene matrix.

Figure 3.7. Scanning electron micrographs of P70 blends compatibilised with MA-PP: (a) 1% Ma-PP, (b) 5% MA-PP, (c) 10% MA-PP and (d) 15% MA-PP.
The average domain size of the compatibilised blends were analysed as a function of compatibiliser concentration (Figure 3.9). The number average domain size of the unmodified blend is $5.87 \mu m$. From the Figure, it is seen that in the case of MA-PP compatibilised blends, addition of 1% MA-PP causes a domain size reduction of 35%. Further addition of MA-PP does not change the domain size.
size considerably, but a levelling off is observed. In the case of Ph-PP compatibilised blends, the average diameter of the dispersed NBR phase decreases up to the addition of 10 wt% Ph-PP. By the addition of 10 wt% Ph-PP, the domain size is reduced by 77% of the domain size of the unmodified blend. However, further addition of compatibiliser increases the domain size. The equilibrium concentration at which the domain size levelled off can be considered as the so-called critical micelle concentration (CMC), i.e., the concentration at which micelles are formed. Generally, CMC is estimated from the plot of interfacial tension versus copolymer concentration. Since the interfacial tension is directly proportional to the domain size, the estimation of CMC from the plot of domain size versus concentration is warranted. The CMC values indicate the critical amount of compatibiliser required to saturate unit volume of interface. The increase in domain size above CMC may be due to the formation of micelles of compatibiliser at the continuous polypropylene phase. This is schematically represented in Figure 3.10. Several authors have reported the interfacial saturation of binary polymer blends by the addition of compatibilisers. Thomas and Prud’homme reported that in PS/PMMA blends at lower concentrations of copolymer, the dispersed phase size decreases linearly with increasing copolymer concentration, whereas at higher concentration, it levelled off. Noolandi and Hong also suggested that there is a critical concentration of block copolymer at which micelles are formed in the homopolymer phases. All the above experimental observations including the present study and theoretical predictions of Noolandi and Hong suggest that there is a critical concentration of compatibiliser required to saturate the interface of a binary blend. The compatibiliser concentration above this critical concentration, may not modify the interface any more, but forms compatibiliser micelles at the bulk phase.
Figure 3.9. Effect of compatibiliser concentration on the domain size of the dispersed phase of P$_{70}$.

Figure 3.10. Schematic representation of the formation of micelle above critical micelle concentration.
The interfacial saturation point can be further explained by Taylors theory. In Taylors theory\(^{37}\) of particle deformation the critical Weber number, \(W_e\), is given by the equation

\[
W_e = \frac{\eta_m d_n \dot{\gamma}}{2\tau_{12}} \tag{3.7}
\]

where \(\eta_m\) is the viscosity of the matrix, \(d_n\) the number average diameter of the dispersed phase, \(\dot{\gamma}\) is the shear rate and \(\tau_{12}\) is the interfacial tension. From the equation, it is clear that there is a critical value of \(W_e\) below which there is no particle deformation and as a result there is a point of critical particle size. At this point the compatibiliser attains maximum interfacial area and therefore there must be a maximum quantity of compatibiliser required to saturate the interface.

The theories of Noolandi and Hong can be applied to these highly incompatible PP/NBR blends for concentrations less than CMC. According to them the interfacial tension is expected to decrease linearly with the addition of compatibiliser below CMC, and above the CMC a levelling off is expected. The expression for interfacial tension reduction (\(\Delta \gamma\)) in a binary blend \(A/B\) upon the addition of a divalent copolymer \(A-b-B\) is given by equation (1.1)\(^{35,36}\)

\[
\Delta \gamma = K(d\phi_c)\left[(1/2\chi + 1/Z_c) - 1/Z_c\exp(Z_c\chi/2)\right] \tag{3.8}
\]

where \(K\) is a proportionality constant.
The plot of particle size reduction as a function of the volume percent of the compatibiliser is shown in Figure 3.11. It can be seen that at low copolymer concentrations (below the CMC), $\Delta d$ decreases linearly with increasing copolymer volume fraction, whereas at higher concentrations (above the CMC), it levels off, and this is in agreement with the theories of Noolandi and Hong.

![Figure 3.11](image.png)

**Figure 3.11.** Effect of volume fraction of compatibiliser on the particle size reduction of $P_{70}$.

The domain size distribution curves for the MA-PP and Ph-PP compatibilised blends are shown in Figures 3.12 and 3.13 respectively. In the case of unmodified blend, a high degree of polydispersity is evident by the large width of the distribution curve. With the increasing concentration of the compatibiliser (Ph-PP and MA-PP) the polydispersity decreases as evidenced by the decrease in the width of the distribution curve. In the case of Ph-PP compatibilised blend, a sharp distribution is obtained with the addition of 10% Ph-PP. Willis and Favis$^{32}$ have also shown that the addition of compatibiliser to polyolefin/polyamide system not only reduces the dimensions of the minor phase, but also results in uniform distribution of minor phase.
Figure 3.12. Effect of MA-PP concentration on domain size distribution of P_{70}.

Figure 3.13. Effect of Ph-PP concentration on domain size distribution of P_{70}.
The mechanism of compatibilising action and the difference in the behaviour of MA-PP and Ph-PP as compatibilisers in NBR/PP can be explained as follows. In the maleic anhydride modified polypropylene, maleic anhydride groups are grafted on to PP chain back bone as shown in Figure 3.14.

![Reaction scheme for the maleic anhydride modification of polypropylene.](image)

The FTIR spectrum of maleic anhydride grafted PP is shown in Figure 3.15. The peak present at 1710 cm\(^{-1}\) indicate the presence of carboxyl groups, originating from maleic anhydride grafted on PP chains. The compatibilising action of this
MA-PP is due to the dipolar interaction between the maleic anhydride groups of MA-PP and NBR.

When PP is melt mixed with dimethylol phenolic resin and SnCl₂, dimethylol groups are grafted on to PP backbone chain as shown in Figure 3.16. When the Ph-PP was added to PP/NBR blend, there is a possibility for the formation of graft copolymer between PP and NBR as shown in Figure 3.16. This graft copolymer acts as an emulsifier at the interface and thus reduces interfacial tension leading to small and uniform distribution of NBR phase as seen in the SEM micrographs (Figure 3.8). It is also important to mention that the Ph-PP can also act as compatibiliser due to the dipolar interaction between the dimethylol groups of Ph-PP and polar NBR phase.

Figure 3.15. FTIR spectrum of the maleic anhydride modified polypropylene
Figure 3.16. Reaction scheme for the dimethylol phenolic modification of polypropylene.
(b) **Mechanical properties of compatibilised blends**

The mechanical properties of immiscible polymer blends are affected by the addition of compatibilisers. Figure 3.17 shows the variation of tensile strength of 70/30 PP/NBR blend with weight percent of two compatibilisers Ph-PP and MA-PP. With the increase in compatibiliser concentration, the tensile strength is found to increase up to 10 weight percent of compatibiliser and then levels off for both the compatibilisers. This increase in tensile strength is due to the increase in interfacial adhesion between PP and NBR phases which is evident from the SEM micrographs (Figures 3.7 and 3.8). The highest tensile strength of 10% Ph-PP compatibilised blend is due to the lowest particle size of NBR domains in this system. In the case of MA-PP compatibilised blends, the increase in tensile strength is due to the increased dipolar interaction between the MA-PP and NBR phase which causes an increase in interfacial adhesion between PP and NBR phases, although there is no reduction in particle size with the increase in MA-PP concentration beyond 1%. Similar results have been reported for Nylon/PP system.39

![Figure 3.17. Effect of compatibiliser concentration on the tensile strength of P70.](image-url)
The variation of tensile modulus at 5 and 10% elongation and tensile impact strength with the Ph-PP concentration is shown in Figure 3.18. The tensile modulus is found to increase with increase in concentration of Ph-PP up to 10% and after that it levels off. From the figure it is seen that the tensile impact strength of the blend increases significantly with the addition of Ph-PP up to 10% and after that it decreases drastically. This result is consistent with the literature reports on the increase of the tensile impact strength with reduction in particle size of dispersed phase. The reduction in tensile impact strength for the blend containing 15 wt% Ph-PP is due to the formation of compatibiliser micelles in the homopolymer phases. Similar results have been reported for LDPE/PDMS system by Santra et al.40

![Figure 3.18](image)

**Figure 3.18.** Effect of Ph-PP concentration on the modulus at 5% and 10% elongation and tensile impact strength of P<sub>70</sub>.

The effect of phenolic modified polypropylene on the tear strength of 70/30 PP/NBR blend is shown in Figure 3.19. It is observed that the tear strength of the blend increases with increase in Ph-PP concentration up to 10 wt% and after that it levels off. It can be noticed that the tear strength of the blend is increased by 50%
upon the addition of 10% compatibiliser. The increase in tear strength with Ph-PP concentration is due to the increased interfacial adhesion between the PP and NBR phases and also due to the reduction in particle size of the dispersed NBR phase. During tearing, usually the rubber particles which bridge the growing crack stretch to large extent before failing.\textsuperscript{41,42} The tearing strain of the rubber particles increases with the reduction in particle size. It has been reported that the stretched rubber particles span the crack during crack propagation by acting like little springs between its faces.\textsuperscript{41} Thus in PP/NBR blend, the addition of Ph-PP decreases the size of NBR domains which bridge the growing crack and this reduction in domain size leads to increased stretching of NBR particles during tearing. Again the increased interfacial adhesion between PP and NBR phase helps to inhibit the propagation of growing crack during tearing. This will obviously increase the tear strength of PP/NBR blends with the addition of Ph-PP. The levelling off observed in the tear strength after 10 wt% of Ph-PP is due to the interfacial saturation.

**Figure 3.19.** Effect of Ph-PP concentration on the tear strength of P \textsubscript{70}. 

\begin{center}
\includegraphics[width=\textwidth]{tear_strength.png}
\end{center}
3.2.3 Dynamic vulcanisation

The vulcanisation of rubber phase during mixing has been investigated as a way to improve the physical properties of several thermoplastic elastomers based on rubber/plastic blends. In the present study, three types of crosslinking systems have been used. These include accelerated sulphur vulcanisation which produces predominantly S-S linkages, peroxide system which give rise to only C-C linkages and mixed system which produces both sulphide linkages and C-C linkages. The schematic representation of the network structure in the three cases are shown in Figure 3.20.

![Schematic representation of network structure](image)

Figure 3.20. Schematic representation of the network formed during dynamic vulcanisation using (a) sulphur, (b) peroxide and (c) mixed systems.
The morphology of 70/30 PP/NBR blends vulcanised with sulphur, DCP and mixed systems is shown in Figure 3.21. From the figures it is seen that in sulphur cured system, the size of the dispersed NBR domains is larger than those of peroxide and mixed systems. In peroxide cured system, the distribution is more fine and uniform and hence the crosslinking is more effective in DCP system. However this effect of crosslinking is not so predominant on the properties of the peroxide vulcanised system due to the degradation of PP phase in presence of DCP.\(^{43}\)

Figure 3.21. Morphology of dynamically vulcanised P\(_{70}\) blends: (a) PS\(_{70}\), (b) PC\(_{70}\) and (c) PM\(_{70}\).
The stress-strain curves of dynamic vulcanised PP/NBR blends are shown in Figure 3.22. The effect of vulcanising systems on deformation behaviour can be obtained from the stress-strain curves. The modulus of the blends were lowered by dynamic vulcanisation. It can also be seen from the figure that the elongation at break decreased upon dynamic vulcanisation for blends with higher loadings of PP. The blends with higher concentrations of PP showed distinct elastic and inelastic regions and in the inelastic region the systems undergo necking/yielding.

Figure 3.22. Stress-strain curves of unvulcanised and dynamically vulcanised: (a) $P_{70}$, (b) $P_{50}$ and (c) $P_{30}$ blends.
The tensile strength and tear strength of dynamic vulcanised blends are shown in Table 3.3. The mechanical properties of the blends with 70 wt % of PP decreased upon dynamic vulcanisation and that with 50 and 30 wt % of PP show an increase for tensile strength values. When considering the various vulcanised systems, it can be seen that for blends with higher loadings of PP, the sulphur vulcanisation gave comparatively better effect. As the concentration of rubber increases, the trend gets reversed, and DCP vulcanisation leads to better properties. The mixed vulcanised system takes an intermediate position. In the case of thermoplastic elastomers the strength depends mainly on the strength of hard phase matrix. We have seen that in P70 and P30, NBR is the dispersed phase and PP the matrix. Therefore, the blends the strength depends mainly on the strength of PP phase. The vulcanisation of PP based blends using DCP leads to the degradation of PP phase. Hence for blends with higher loadings of PP, showed lower properties on dynamic vulcanisation using DCP though the crosslinking is more effective by DCP. However at higher loadings of rubber, the DCP crosslink the rubber phase preferentially than degrading PP and hence leads to better properties.

**Table 3.3.** Mechanical properties of dynamic vulcanised PP/NBR blends.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
<th>Tear strength (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS70</td>
<td>18.364</td>
<td>79.77</td>
</tr>
<tr>
<td>PC70</td>
<td>17.23</td>
<td>63.01</td>
</tr>
<tr>
<td>PM70</td>
<td>17.17</td>
<td>81.28</td>
</tr>
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<td>PS50</td>
<td>9.88</td>
<td>47.64</td>
</tr>
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<tr>
<td>PM30</td>
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<td>18.26</td>
</tr>
</tbody>
</table>
3.2.4 *Filled PP/NBR blends*

The mechanical properties of filled PP/NBR blends were studied for various fillers such as carbon black, cork, silica and silane treated silica. The stress-strain curves of unvulcanised P\(_{70}\) and P\(_{30}\) blends with 30 phr filler loadings are given in Figures 3.23a and 3.23b, respectively. The stress-strain curves indicate that the modulus of the blends decreased upon the incorporation of fillers. The deformation behaviour of the blends are not much varied on the filler addition. The blend with 70 wt % of PP shows higher initial modulus, and yielding. The P\(_{30}\) blends showed lower initial modulus. The stress-strain curves of both the blends show distinct elastic and inelastic regions.

![Stress-strain curves of (a) P\(_{70}\) and (b) P\(_{30}\) blends with 30 phr filler loading.](image)

The tensile and tear properties of unvulcanised PP/NBR blends with 30 phr filler loading is given in Table 3.4. From the table it is seen that the properties of blend with various fillers vary with concentration of rubber phase. At 30 wt % NBR, among the different fillers, cork showed highest improvement in tensile and tear strength values while silica showed the lowest value. At 50 wt % NBR also, cork filler showed better properties. However, as the NBR content increased to 70 wt % the trend is reversed, cork filled system showed the lowest tensile and tear strength and silica filled system showed the highest values. It can also be seen
from the table that the addition of carbon black adversely affects the properties in all cases. The treatment of silica with silane coupling agent improved the properties only in the case of 70 wt % of PP and in other two blend compositions the properties decrease.

### Table 3.4. Mechanical properties of filled PP/NBR blends with 30 phr filler loading.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
<th>Tear strength (N/m)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P70</td>
<td>18.30</td>
<td>89.00</td>
<td>95.68</td>
</tr>
<tr>
<td>P70C30</td>
<td>16.76</td>
<td>82.82</td>
<td>22.97</td>
</tr>
<tr>
<td>P70K30</td>
<td>19.02</td>
<td>95.54</td>
<td>8.38</td>
</tr>
<tr>
<td>P70Si30</td>
<td>15.95</td>
<td>86.44</td>
<td>26.44</td>
</tr>
<tr>
<td>P70TSi30</td>
<td>16.89</td>
<td>91.89</td>
<td>28.35</td>
</tr>
<tr>
<td>P50</td>
<td>9.20</td>
<td>50.00</td>
<td>43.45</td>
</tr>
<tr>
<td>P50C30</td>
<td>8.05</td>
<td>39.77</td>
<td>44.70</td>
</tr>
<tr>
<td>P50K30</td>
<td>9.73</td>
<td>45.05</td>
<td>18.47</td>
</tr>
<tr>
<td>P50Si30</td>
<td>8.05</td>
<td>39.60</td>
<td>44.23</td>
</tr>
<tr>
<td>P50TSi30</td>
<td>7.59</td>
<td>34.81</td>
<td>34.38</td>
</tr>
<tr>
<td>P30</td>
<td>3.50</td>
<td>21.00</td>
<td>38.64</td>
</tr>
<tr>
<td>P30C30</td>
<td>2.97</td>
<td>18.16</td>
<td>11.64</td>
</tr>
<tr>
<td>P30K30</td>
<td>2.64</td>
<td>16.88</td>
<td>8.23</td>
</tr>
<tr>
<td>P30Si30</td>
<td>4.06</td>
<td>28.60</td>
<td>21.29</td>
</tr>
<tr>
<td>P30TSi30</td>
<td>3.41</td>
<td>19.10</td>
<td>13.52</td>
</tr>
</tbody>
</table>

The effect of filler loading on mechanical properties was also studied. The stress-strain curves of unvulcanised P50 blends with 10, 20 and 30 phr loading of carbon black and silica are shown in Figures 3.24a and 3.24b respectively. From
the curves it is seen that the incorporation of fillers did not improve the modulus, for all loadings. However, the nature of stress-strain curves are not changed with filler addition, i.e., filled samples also show elastic and inelastic sections, with yielding in the inelastic section. The tensile strength, tear strength and elongation at break values of the blends are given in Table 3.5 for both unvulcanised and vulcanised blends. The addition of 10 phr silica, T-silica, cork and carbon black increased the tensile strength values, however further addition reduces the values, for both crosslinked and uncrosslinked blends. It is also seen from the table that in the case of crosslinked filled blends, the treatment of silica with silane coupling agent improved the tensile and tear properties.

Figure 3.24. Stress-strain curves of P50 blends with (a) carbon black and (b) silica.
Table 3.5. Mechanical properties of filled P₅₀ blends.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
<th>Tear strength (N/m)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unvulcanised</td>
<td>Vulcanised</td>
<td>Unvulcanised</td>
</tr>
<tr>
<td>P₅₀</td>
<td>9.20</td>
<td>9.88</td>
<td>50.00</td>
</tr>
<tr>
<td>P₅₀Si₁₀</td>
<td>10.28</td>
<td>8.67</td>
<td>53.13</td>
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<tr>
<td>P₅₀Si₂₀</td>
<td>9.21</td>
<td>8.03</td>
<td>42.31</td>
</tr>
<tr>
<td>P₅₀Si₃₀</td>
<td>8.05</td>
<td>8.34</td>
<td>39.60</td>
</tr>
<tr>
<td>P₅₀TSi₁₀</td>
<td>9.94</td>
<td>9.06</td>
<td>46.40</td>
</tr>
<tr>
<td>P₅₀TSi₂₀</td>
<td>8.43</td>
<td>10.37</td>
<td>42.00</td>
</tr>
<tr>
<td>P₅₀TSi₃₀</td>
<td>7.59</td>
<td>8.45</td>
<td>34.81</td>
</tr>
<tr>
<td>P₅₀K₁₀</td>
<td>9.55</td>
<td>10.53</td>
<td>48.54</td>
</tr>
<tr>
<td>P₅₀K₂₀</td>
<td>8.81</td>
<td>10.35</td>
<td>49.24</td>
</tr>
<tr>
<td>P₅₀K₃₀</td>
<td>9.73</td>
<td>9.00</td>
<td>45.05</td>
</tr>
<tr>
<td>P₅₀C₁₀</td>
<td>10.05</td>
<td>9.22</td>
<td>49.66</td>
</tr>
<tr>
<td>P₅₀C₂₀</td>
<td>7.97</td>
<td>9.08</td>
<td>41.24</td>
</tr>
<tr>
<td>P₅₀C₃₀</td>
<td>8.05</td>
<td>8.31</td>
<td>39.77</td>
</tr>
</tbody>
</table>

3.3 References


