Chapter 3

Morphology, Mechanical behavior and Failure mode
3.1 Introduction

In this chapter, the influence of blend ratio crosslinking systems [viz. sulfur (S), dicumyl peroxide (DCP) and mixed (S+DCP) systems], and the dosage of peroxide curing agent on morphology and mechanical properties of SBR/HDPE have been analyzed. The effects of filler addition on mechanical properties were also investigated. The fillers used were Silica, High abrasion furnace (HAF)-Carbon black, China clay and TiO₂ with particle size 0.02, 0.04, 2.0 and 12.0µm respectively. Details of the preparation of the blends were given in Chapter 2. SBR/HDPE blends with 0, 30, 40, 50, 60, 70 and 100% wt of SBR were designated as S₀, S₃₀, S₄₀, S₅₀, S₆₀, S₇₀ and S₁₀₀ respectively. The filled blends were designated as NS, NH, NL and NT were N indicating the loading of the fillers and S, H, L and T represent fillers such as Silica, HAF-carbon black, clay and TiO₂ respectively. For example 10S indicates the 10phr silica loaded system; 20S indicates the 20 phr silica loaded system and so on. The amount of vulcanizing agents and fillers were taken with reference to the rubber phase.

3.2 Results and Discussions

3.2.1 Morphology

The relationship between structure and properties of thermoplastic-rubber blends are complex because it depends on so many parameters\(^1,2\). Figures 3.1 (a-e) depict the scanning electron micrographs (SEM) showing the morphology of the blends over the entire range of composition, i.e. from 30/70 to 70/30 SBR/HDPE. The white portion represents the HDPE phase and dark holes the SBR phase.
Figure 3.1  Scanning electron micrographs of SBR/HDPE blends (a) S30, (b) S40, (c) S50, (d) S60, and (e) S70.

The micrographs of the blends show that in 30 and 40wt% SBR compositions (Figures 3.1a and 3.1b), the rubber phase is preferentially dispersed in the dominant HDPE matrix. This is due to the high viscosity
of the minor rubber phase, which facilitates the formation of a fine dispersion\(^3\). The ability of the low viscosity component to form the continuous phase over a larger composition region than the more viscous component may be related to its ease of deformability, which allows it to form highly extended bodies. In these compositions the dispersed droplets are more or less spherical and somewhat non-spherical drops also coexist. In S\(_{50}\) blend (Figure 3.1c) the spherical morphology changes to somewhat elongated pattern followed by an interpenetrating co-continuous morphology at 60wt\% of SBR (Figure 3.1d). Beyond this level at (70 wt \% of SBR content) there occurs phase inversion, where the HDPE phase is dispersed in the continuous SBR phase (Figure 3.1e).

The size characteristic of the dispersed phase, the number-average diameter (\(D_n\)) and its size distribution, polydispersity index of the different blend compositions were calculated from the following relationships:

\[
D_n = \frac{\sum N_i D_i}{\sum N_i} \tag{3.1}
\]

where \(N_i\) is the number of particles within the diameter range \(i\),

The polydispersity index, which is a measure of the domain size distribution, was also calculated using the equation,

\[
P DI = \frac{D_w}{D_n} \tag{3.2}
\]

In S\(_{30}\) composition the average domain size is 5.8 \(\mu m\) and in S\(_{40}\) composition it increases to 13.7 \(\mu m\). The particle size and size distribution are given in Figure 3.2. The size distribution of the domains
also found to increase with increasing coalescence. The values of $D_n$ are plotted as a function of composition in Figure 3.3a. As can be seen from the figure that $D_n$ of the dispersed SBR phase increases with its content in the blend. The increase is prominent beyond 30wt% of SBR concentration.

![Particle size distribution curves of SBR/HDPE blends](image)

**Figure 3.2** Particle size distribution curves of SBR/HDPE blends

The increase in particle size of the dispersed SBR phase with increase of SBR content is due to the reagglomeration or coalescence of the dispersed SBR particles. The phenomenon of coalescence at a higher concentration of one of the components was reported by several authors$^{4,5}$. When HDPE forms the dispersed phase in 70wt% composition the domain size is slightly less as compared to the composition in which SBR forms the dispersed phase. This is ascribed to the high viscosity of
Figure 3.3  a) Effect of SBR concentration on number average domain diameter ($D_n$) and b) Variation of PDI with SBR concentration
SBR, which prevents the diffusion and reagglomeration of the HDPE phase. The polydispersity index \((D_w/D_n)\) is plotted against composition in Figure 3.3b. From the figure it can be seen that the polydispersity index values increases with increase in rubber content (up to 50wt% of SBR), indicating the increase in non-uniformity in domain size. This is also manifested in the large width of the distribution curves of the blends (Figure 3.2). In S70 composition, the polydispersity index shows a decrease, showing that the size distribution becomes narrower.

The interfacial area per unit volume of each blend was also estimated using the following equation\(^6\).

\[
A = n \times \pi R^2 \tag{3.3}
\]

where \(A\) is the total area occupied by the dispersed phase, \(R\) the radius of the dispersed phase particle and \(n\) the number of particles of the minor phase per unit volume of the blend, which can be estimated from equation (3.4)

\[
n = \frac{\phi_d}{\frac{4}{3} \pi R^3} \tag{3.4}
\]

where \(\phi_d\) is the volume fraction of the dispersed phase. Figure 3.4 shows the variation of interfacial area/unit volume with composition. Interfacial area per unit volume decreases with the SBR concentration, and it shows a minimum value at 50wt% of SBR, due to the high domain size caused by coalescence. At 70wt % of SBR, interfacial area again shows a slight increase, due to the reduced size of the dispersed HDPE domains.
Figure 3.4 Variation of interfacial area/unit volume with composition

*Figure 3.5* shows the co-continuity (%) as a function of the composition estimated from solvent extraction technique. At 30wt% SBR content co-continuity index is very low ~ 4.2% and in 40wt% SBR it increases to 10.4%. These results are confirmed by the dispersed droplets-matrix morphology of these compositions (*Figure 3.1a & 3.1b*). At a wt fraction of 50wt% SBR, continuity increases sharply to 79% and at 60wt% SBR, the level of continuity becomes 95% and a complete network of SBR is formed. This result is consistent with the morphology shown by the SEM (*Figures 3.1c & 3.1d*) of these blends.
3.2.2 Mechanical properties

The tensile behavior of a polymer is probably the most fundamental mechanical property used in the evaluation of polymers. The tensile stress-strain curves of different SBR/HDPE blends as well as virgin polymers are presented in Figure 3.6 and mechanical properties of the blends are given in Table 3.1. Blends of SBR/HDPE show different failure characteristics. The tensile stress-strain curve of HDPE resembles that of a brittle material. It shows very high initial modulus and breaks at very small elongation. The addition of SBR considerably changes the stress-strain behavior. The stress-strain behavior of any polymer blend will be mainly influenced by the major component that forms the continuous matrix and acts as the main load-bearing unit. In such
systems the particles of the dispersed phase act as stress concentration points introducing weak points in the matrix material. As a result an intrinsically tough matrix breaks at a lower stress compared to the pure matrix. The curves of $S_{30}$, $S_{40}$ and $S_{50}$ blends have elastic and inelastic regions. In the inelastic region, the materials undergo yielding. In SBR rich blends the yielding behavior disappears and the stress-strain curves flatten similar to that of elastomers. The stress-strain curve of SBR is typical of a low modulus rubbery material. Up to 50wt% of SBR the curves exhibit more plastic behavior. This indicates that up to 50wt% of SBR, SBR is dispersed in a continuous HDPE matrix. From 60wt% onwards elastomeric behavior is more pronounced. This is because beyond 60 wt% of SBR onwards, there occurs a phase inversion, where SBR starts to form a continuous matrix.

Figure 3.6 The Tensile stress-strain curves of SBR/HDPE blends
Table 3.1 Mechanical properties of SBR/HDPE blends

<table>
<thead>
<tr>
<th>System</th>
<th>Ultimate Tensile strength (Mpa)</th>
<th>Strain at break (%)</th>
<th>Young’s Modulus (MPa)</th>
<th>Hardness (Shore-A)</th>
<th>Tear strength (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₀</td>
<td>33</td>
<td>13</td>
<td>249.2</td>
<td>99</td>
<td>146.6</td>
</tr>
<tr>
<td>S₃₀</td>
<td>9.3</td>
<td>16</td>
<td>106.8</td>
<td>94</td>
<td>51.4</td>
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<tr>
<td>S₄₀</td>
<td>7.9</td>
<td>26</td>
<td>62.1</td>
<td>90</td>
<td>40.0</td>
</tr>
<tr>
<td>S₅₀</td>
<td>4.3</td>
<td>38</td>
<td>22.3</td>
<td>77</td>
<td>32.7</td>
</tr>
<tr>
<td>S₆₀</td>
<td>3.8</td>
<td>82</td>
<td>17.9</td>
<td>47</td>
<td>23.1</td>
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<tr>
<td>S₇₀</td>
<td>2.4</td>
<td>125</td>
<td>5.3</td>
<td>21</td>
<td>17.7</td>
</tr>
<tr>
<td>S₁₀₀</td>
<td>0.19</td>
<td>486</td>
<td>0.33</td>
<td>10</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Figure 3.7 plots the ultimate tensile strength, yield strength and strain-at break of SBR/HDPE blends as a function of SBR content in the blend. An abrupt decrease in the tensile strength occurs by the addition of SBR. It is clear from the figure that addition of about 30wt% of the SBR content in the blend decreases the tensile strength by 72%. The tensile strength of HDPE, which is 33.2 MPa, was gradually reduced to 4.85 MPa in S₇₀ composition. For blends that consist of 50% or less rubber the value of tensile strength is higher than 7 MPa, which is the minimum value quoted usually for synthetic rubber based thermoplastics. The reduction in tensile strength of the blend by the addition of SBR can be explained in terms of crystallinity. HDPE is a highly crystalline material. The incorporation of the amorphous rubbers leads to a drastic drop in crystallinity. The drop in crystallinity of the plastic with
the incorporation of rubber is due to incomplete crystallization as observed from the decreasing trend of heat of fusion values of HDPE with increasing SBR content in the blend, (data from DSC) shown in Table 3.2. Therefore a reduction in strength with increase in SBR content is attributed to the decrease of crystallinity of the composition. Several studies have been reported on the decrease of crystallinity of the plastic phase upon the addition of the amorphous rubber\(^9\),\(^{10}\). It is also clear from Figure 3.7 that the tensile strength values are lower than the additivity values. This negative deviation of the tensile strength values is due to the lack of interfacial adhesion between the component polymers. Yield strength of the blends also shows the same trend as that of the tensile
strength. The strain-at break of the samples increases as the proportion of rubber increases, due to the greater segmental mobility of the rubber phase compared with the rigid HDPE.

Table 3.2  Heat of fusion values of SBR/HDPE blends

<table>
<thead>
<tr>
<th>System</th>
<th>Heat of fusion (Cal/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0$</td>
<td>216.9</td>
</tr>
<tr>
<td>$S_{30}$</td>
<td>110.3</td>
</tr>
<tr>
<td>$S_{40}$</td>
<td>87.45</td>
</tr>
<tr>
<td>$S_{50}$</td>
<td>53.5</td>
</tr>
<tr>
<td>$S_{60}$</td>
<td>24.71</td>
</tr>
<tr>
<td>$S_{70}$</td>
<td>13.26</td>
</tr>
</tbody>
</table>

The plots of variation of Young’s modulus and hardness of SBR/HDPE blends with SBR content are shown in Figure 3.8. It is clear from the figure that there is a decrease in modulus as the rubber content increases. A clear change in the slope occurs beyond 50/50 SBR/HDPE composition. This is due to the change in phase morphology of the system to co-continuous nature which is followed by phase inversion. The modulus values of the blend do not obey the additivity rule and exhibit negative deviation due to the poor interfacial adhesion between the two phases. The hardness values are important to determine the resistance of the polymer blends to surface damage or to plastic deformation. The plot of shore-A hardness vs. composition shows that the addition of soft SBR phase in the rigid HDPE matrix decreases its shore-A hardness value, due to matrix softening. The hardness values lie above the additivity line because it is being a surface property, less related to the interfacial bonding between the phases.
The tear strength is an important property, which contributes to the resistance to crack growth. The tear curves of the blends and homopolymers are given in Figure 3.9. The tearing force is highest for HDPE, which shows lowest displacement. It is evident from the figure that the tearing force decreases and displacement increases as the amount of SBR increases. SBR exhibits the lowest tearing force and a highest elongation, which is attributed to high extensibility of the rubber phase. The tear strength values of the blend decrease with the SBR content in the blend (Table 3.1). The dispersed rubber particles act as stress concentrating flaws. In the uncrosslinked samples, when crack is initiated...
due to an external crack, it propagates from one particle to another. The bigger particles of the dispersed phase are unable to bridge the growing crack. When the surfaces are separate due to the crack, no load can be transferred across the crack. So the load, together with an associated bending moment, concentrates itself beyond the crack tip in the uncracked material. As a result of the stress concentration at the tip, the crack grows and the specimen fails. It has been reported that during tearing nucleation failure and micro fracture occur almost in the region of high stresses at the tip of the growing tear. As the content of SBR increases, the particle size also increases. So the tear strength decreases with the SBR content.

Figure 3.9 Tear – load displacement curves of SBR/HDPE blends.
3.2.3 Theoretical modeling

Various models have been applied to account for the deviation of the tensile properties from the ideal behavior. The upper bound parallel model is given by the simple rule of mixtures,

\[ M = M_I \phi_I + M_2 \phi_2 \]  \hfill (3.5)

where \( M \) is any mechanical property of the blend, \( M_I \) and \( M_2 \), the mechanical properties of components 1 and 2 respectively and \( \phi_I \) and \( \phi_2 \) are their corresponding volume fractions. This model is based on the assumption that the components are arranged parallel to one another. The lowest lower-bound series model is given by the equation,

\[ \frac{1}{M} = \frac{\phi_I}{M_I} + \frac{\phi_2}{M_2} \]  \hfill (3.6)

where \( M, M_I, M_2, \phi_I \) and \( \phi_2 \) have their usual meanings.

According to the Halpin-Tsai equation\(^{12}\)

\[ \frac{M_I}{M} = \frac{1 + A_i B \phi_2}{1 - B \phi_2} \]  \hfill (3.7)

where \( B_i = \frac{\left( \frac{M_1}{M_2} - 1 \right)}{\left( \frac{M_1}{M_2} + A_i \right)} \) \hfill (3.8)

In this model, subscripts 1 and 2 represent the continuous and dispersed phases respectively. The constant \( A_i \) depends on the morphology of the system. In the case of elastomer domains dispersed in a continuous hard matrix, \( A_i = 0.66 \) and when the elastomer forms the continuous matrix in which the hard phase forms the dispersed domains \( A_i = 1.5^{12} \). According
to Kunori and Geil\textsuperscript{13} and Nielsen\textsuperscript{14} the tensile fracture of the blend could be attributed to the failure of the adhesion between the discrete phase and continuous matrix, and the equation for this is

\[ \sigma_b = \sigma_m (1 - A_d) + \sigma_d A_d \tag{3.9} \]

where \( \sigma_b, \sigma_m \) and \( \sigma_d \) are the properties of the blend, matrix and the dispersed phase respectively. \( A_d \) is the area occupied by the dispersed phase in the transverse cross section, which was measured by the scanning electron micrographs.

If the fracture is through the interface, the above equation can be written as

\[ \sigma_b = \sigma_m \left(1 - \phi_d^{2/3}\right) + \sigma_d \phi_d^{2/3} \tag{3.10} \]

And when the fracture is through the matrix this becomes,

\[ \sigma_b = \sigma_m (1 - \phi_d) + \sigma_d \phi_d \tag{3.11} \]

where \( \phi_m \) and \( \phi_d \) are the volume fraction of the matrix and dispersed phase respectively.

For perfect adhesion between the matrix and the dispersed phase, Kerner's\textsuperscript{15} equation is given by,

\[ E = E_m \frac{\phi_m E_d}{\phi_d E_m} \left(\frac{7 - 5\nu_m}{7 - 5\nu_m} E_m + \frac{8 - 10\nu_m}{8 - 10\nu_m} E_d\right) + \frac{\phi_m}{15(1 - \nu_m)}\]  

\[ + \frac{\phi_d}{15(1 - \nu_m)} \tag{3.12} \]

where \( E, E_m \) and \( E_d \) are the properties of the blend, continuous phase, and dispersed phase respectively; \( \nu_m \) is the Poisson's ratio of the continuous phase.
Figure 3.10 illustrates the experimental and theoretical curves of Young's modulus of SBR/HDPE blends as a function of soft volume fraction. It is seen that in lower content blends (S30, S40 and S50) the experimental values of modulus are close to that of the Kunori model. Thus, it can be concluded that the fracture advanced through the interface rather than through the matrix. The result is also manifested by the SEM observations of the fracture surfaces, shown in the later part of this chapter (Figure 3.24 a-c), which shows that rubber particles were observed on the fracture surface of S30 composition, supporting the theory that during fracture, when the crack was propagating through the particle-matrix interface, rubber particles were observed on the fracture surface. However, the experimental values of blends having wt % of SBR >50, are close to the series model.
3.2.4 Effect of dynamic crosslinking

Figure 3.11  Nature of crosslinks formed during crosslinking a)Sulfur system (efficient) b) Mixed system and c) DCP system
In the vulcanized system the rubber particles are crosslinked and their size is greatly reduced due to shear induced size reduction during vulcanizate preparation. The dynamically vulcanized plastic/rubber blends possess the ability to melt processed as thermoplastic and possess outstanding elastic recovery after mechanical deformation. As already mentioned in Chapter 2, here we have used three different types of crosslinking systems: sulfur (efficient), peroxide and a mixed system composed of sulfur and peroxide. A schematic representation of the crosslinks formed in these three cases is shown in Figure 3.11. The crosslink density values of these samples are given in Table 3.3. Among the three different vulcanizing systems used, the peroxide cured system showed the highest crosslink density values.

Table 3.3. Crosslink density of different S30 blends

<table>
<thead>
<tr>
<th>System</th>
<th>Crosslink density, $\nu(\text{gm-mol/cc})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S30 S</td>
<td>$0.126 \times 10^{-3}$</td>
</tr>
<tr>
<td>S30 M</td>
<td>$0.362 \times 10^{-3}$</td>
</tr>
<tr>
<td>S30 D</td>
<td>$1.396 \times 10^{-3}$</td>
</tr>
<tr>
<td>S30 D1</td>
<td>$0.577 \times 10^{-3}$</td>
</tr>
<tr>
<td>S30 D2</td>
<td>$0.981 \times 10^{-3}$</td>
</tr>
<tr>
<td>S30 D3</td>
<td>$1.14 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

The reduction in particle size during dynamic vulcanization results in a decrease in interfacial tension and an increase in interfacial adhesion. Moreover, the process of diffusion and recombination of the dispersed particles observed in the case of uncrosslinked blends are resisted by dynamic crosslinking.
Figure 3.12 Scanning electron micrographs showing the morphology of S30 blends crosslinked by three different systems (a) Sulfur (b) Mixed and (c) DCP
Figures 3.12(a-c) depict the morphology of S30 blends crosslinked with three different systems. These figures show that the rubber particles are finely dispersed in the predominant and continuous plastic matrix. The number density of SBR domain in the crosslinked samples is more while the average size is less, due to the higher mixing torque exerted by them than the uncrosslinked blends. In the case of sulfur cured blend, it can be seen that there is only a marginal reduction in particle size occur; and in mixed cured system vulcanized SBR component is more finely dispersed in the HDPE matrix giving rise to a finer morphology. However no dispersed phase can be distinguished on the cryofractured section of DCP cured blend. This indicates that in DCP system the crosslinking is more effective, which is evident from the fine and uniform distribution of SBR phase.

The morphology of S30 and S70 blends prior to and after the three types of dynamic vulcanization is diagrammatically presented in Figure 3.13. The morphology of S70 blend undergoes dramatic changes during dynamic crosslinking. In this system the SBR and the HDPE phases have to undergo a phase inversion to maintain the thermoplasticity of the blend. This is because as crosslinking proceeds, the viscosity of the rubber phases increases, causing less viscous HDPE to form a continuous phase even at low volume fraction of plastic phase. In S30 composition, where rubber is already in the dispersed state, no phase inversion takes place but rubber phase is more finely dispersed.
Figure 3.13 Diagramatic morphology of $S_{30}$ and $S_{70}$ blends prior to and after dynamic vulcanization with different vulcanizing systems
The tensile stress-strain curves of crosslinked S\textsubscript{30} blends using sulfur, mixed and peroxide systems are compared with that of the uncrosslinked blend in Figure 3.14. The differences in deformation characteristics of blends under an applied load can be understood from the stress-strain curves. The mechanical properties of dynamically crosslinked SBR/HDPE blends are given in Table 3.4. The superior performance of vulcanized blends can be attributed to improved interfacial bonding between the two polymers as a result of vulcanization. The vulcanized system display higher values of tensile
Table 3.4. Mechanical properties of dynamically crosslinked SBR/HDPE blends.

<table>
<thead>
<tr>
<th>System</th>
<th>Ultimate Tensile Strength (MPa)</th>
<th>Strain at- break (%)</th>
<th>Tear strength (Mpa)</th>
<th>Young’s Modulus (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_{30}</td>
<td>9.3</td>
<td>16.1</td>
<td>51.4</td>
<td>106.8</td>
</tr>
<tr>
<td>S_{30} S</td>
<td>12.4</td>
<td>18.0</td>
<td>54.3</td>
<td>154.8</td>
</tr>
<tr>
<td>S_{30} M</td>
<td>15.4</td>
<td>19.1</td>
<td>57.1</td>
<td>159.0</td>
</tr>
<tr>
<td>S_{30} D</td>
<td>16.2</td>
<td>21.2</td>
<td>77.5</td>
<td>169.7</td>
</tr>
<tr>
<td>S_{50} S</td>
<td>7.5</td>
<td>70.4</td>
<td>38.1</td>
<td>44.2</td>
</tr>
<tr>
<td>S_{50} M</td>
<td>10.4</td>
<td>51.2</td>
<td>44.3</td>
<td>45.7</td>
</tr>
<tr>
<td>S_{50} D</td>
<td>11.2</td>
<td>75.2</td>
<td>50.0</td>
<td>52.3</td>
</tr>
<tr>
<td>S_{70} S</td>
<td>3.1</td>
<td>65.1</td>
<td>27.5</td>
<td>25.7</td>
</tr>
<tr>
<td>S_{70} M</td>
<td>5.5</td>
<td>21.0</td>
<td>32.9</td>
<td>25.3</td>
</tr>
<tr>
<td>S_{70} D</td>
<td>3.4</td>
<td>25.6</td>
<td>40.3</td>
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<td>S_{30} D_{1}</td>
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<td>18.4</td>
<td>53.6</td>
<td>108.8</td>
</tr>
<tr>
<td>S_{30} D_{2}</td>
<td>14.8</td>
<td>19.1</td>
<td>67.5</td>
<td>144.0</td>
</tr>
<tr>
<td>S_{30} D_{3}</td>
<td>15.9</td>
<td>20.0</td>
<td>72.2</td>
<td>159.9</td>
</tr>
</tbody>
</table>

strength, elongation at break, modulus and hardness. The increase in strain-at break is due to the increased chain entanglement caused by increasing degree of crosslinking. The molecular entanglements are
able to prevent slipping between the individual chains in response to an applied stress and hence result in higher tensile strength. All dynamically crosslinked samples show higher modulus compared to the uncrosslinked ones. The increase in the extent of crosslinking is responsible for the increase in modulus\textsuperscript{18,19}. The changes in modulus values are in line with that of tensile strength. Variation of these properties with the increase in the SBR content also follows the same trend as observed in the case of uncrosslinked blends. From Table 3.4, it can be seen that the variation in mechanical properties due to crosslinking is more pronounced in S\textsubscript{30} (high plastic content) composition. This is because dynamic vulcanization in blends is more effective when the low modulus portion, the rubber phase, which is to be crosslinked is dispersed in a high modulus thermoplastic matrix\textsuperscript{20}.

![Tensile stress-strain curves of S\textsubscript{30} composition with different DCP loading.](image-url)
Figure 3.15 represents the tensile stress-strain curves of the S30 composition having different DCP loading. The addition of DCP continuously changes the deformation pattern. Figure 3.16 illustrates the variation of ultimate tensile strength and strain at-break as a function of DCP concentration. The mechanical properties of these blends seem to be sensitive to the variation in the dosage of the DCP. Both ultimate strength and strain at-break increase with DCP content. It is also observed that the tensile strength increases with increase in peroxide concentration up to 3% and after that it levels off. This may due to the fact that the rubber particle size is reduced and stabilized with crosslinking at high DCP content. Dao\textsuperscript{21,22} reported that rubber particle growth is inhibited and stabilized at high crosslink density. The morphological observations of the blends (Figure 3.17 a-d) also support this fact.

![Graph showing influence of DCP concentration on ultimate tensile strength and strain at-break of S30 blend.](image-url)
Figure 3.17 Scanning electron micrographs of S₃₀ blend crosslinked with varying DCP dosages a) 1% b) 2% c) 3% and d) 4%
Figures 3.17 (a-d) show the SEM of S_{30} blends crosslinked with varying DCP dosages. Blend containing 1% DCP, the morphology changes to some what elongated pattern with further break-up into smaller spherical droplets. Further increase in DCP content tremendously decreases the particle size and a leveling-off of the domain size can be seen after 3% DCP. The distribution of particles also becomes uniform. The morphological observations are in accordance with the tensile strength of the samples. The modulus values are also in line with that of tensile strength values. (Table 3.4)

![Figure 3.18](image.png)

**Figure 3.18** Tear-load displacement curves of dynamically vulcanized S_{30} composition using sulfur, mixed and DCP systems

The tear curves of crosslinked S_{30} blends are presented in *Figure 3.18*. All crosslinked samples tears at a higher load and elongation
than the uncrosslinked composition. The improvement in interfacial adhesion during dynamic vulcanization helps to inhibit the propagation of a growing crack during tearing and enhances the resistance to tear. It is observed that DCP crosslinked blends tears at the highest load and displacement; sulfur crosslinked blend tears at the lowest load and elongation; mixed system takes the medium position. The tear strength of different crosslinked compositions are also presented in Table 3.4. All the crosslinked blends show an enhancement in tear strengths values. It has been reported that smaller and uniformly distributed rubber phase can effectively control the initiation and termination of cracks\textsuperscript{23}. In the crosslinked samples the particle size is reduced to a very large extent. So there will be a large number of particles per unit area in the tear path, which can undergo a very large strain in response to an applied stress and to obstruct the advancing tear front. The stretched rubber particles span the crack during crack propagation by acting like small springs between its faces\textsuperscript{24}. The tearing strain of the elastomer particles increases, as its size is reduced\textsuperscript{25}. The increase in tear strength in the case of vulcanized blends is attributed to the smaller size and higher elongation of the crosslinked SBR particles. Tear strengths of the crosslinked samples are in accordance with their crosslink density values and the domain size of the dispersed phase. As far as the tear strength is concerned the performance of blends vulcanized with DCP system is superior to others.

Of the three crosslinking systems used in these blends, peroxide system appears to be more effective in imparting best mechanical properties; sulfur system the least and mixed system takes the medium position. The enhancement in properties is in line with the reduction in the dispersed domain size and the crosslink density. The notable changes in mechanical properties with peroxide cured system are attributed to the
fine particle size of the dispersed phase and higher value of crosslink density compared with the other two systems.

3.2.5 Effect of fillers

3.2.5a Reinforcing characteristics

In order to ascertain the manipulations occurred in these blends by the addition of fillers, the effects of fillers such as silica, HAF-Carbon black, clay and TiO₂ on the mechanical properties of dynamically crosslinked SBR/HDPE blends were studied.

The distribution of fillers between the separate polymer depends on so many factors including unsaturation, polarity, relative viscosity of the polymers, their different affinity for the filler and the formation of bound rubber. It also depends on the mode of filler addition and the processing history. Curing rate may affect the dispersion of the filler in the thermoplastic and elastomer phases and the chemical nature of the curing system can also affect the interaction between the filler and the polymers. In rubber-plastic blends, the bulk of the filler was always found in the rubber phase due to the high unsaturated value. Extent of reinforcement was determined from the Krau’s equation.

\[
\frac{V_{ro}}{V_{rf}} = 1 - m (\phi / 1 - \phi) \quad (3.13)
\]

where \( m = 3C (1 - V_{ro}^{1/3}) + V_{ro} - 1 \) \quad (3.14)

Here \( \phi \) is the volume fraction of filler in the filled vulcanizate and \( C \) is a constant characteristic of the filler, but independent of the polymer, the solvent or the degree of vulcanization. \( V_{rf} \) is the fraction of rubber in the solvent swollen filled sample given by the following equation.
\[ V_{rf} = \frac{(d - \phi w)\rho_p^{-1}}{(d - \phi w)\rho_p^{-1} + A_s\rho_s^{-1}} \]  

(3.15)

where \( w \) is its the weight of the sample, \( d \) is its deswollen weight, \( \rho_p \) is the density of the polymer, \( \rho_s \) is the density of the solvent, and \( A_s \) is the amount of solvent absorbed. In the case of an unfilled system, \( \phi = 0 \). The volume fraction of rubber in the solvent swollen unfilled sample \( (V_r) \) is given by

\[ V_r = \frac{d\rho_p^{-1}}{d\rho_p^{-1} + A_s\rho_s^{-1}} \]  

(3.16)

The slope of the curve obtained by plotting \( V_{ro}/V_{rf} \) versus \( \phi(1 - \phi) \) provides information on the extent of reinforcement\(^{28} \). The higher the \(-ve\) slope, the higher will be the reinforcement. Reinforcing ability was also analyzed using Cunneen and Russell\(^{29} \)

\[ V_{ro}/V_{rf} = ae^{-z} + b \]  

(3.17)

where \( z \) is the weight fraction of filler in the vulcanizate and \( a \) and \( b \) are constants characteristic of the system. By plotting \( V_{ro}/V_{rf} \) against \( e^{-z} \), values of \( a \) (slope) and \( b \) (intercept) were determined. The higher the value of \( a \), the higher is the reinforcement.

The plots of Kraus as well as Cunneen and Russell equations for various fillers are shown in Figures 3.19a and 3.19b respectively and the slope values are presented in Table 3.5. From both equations the reinforcing ability of the filled blends is in the order silica > HAF-black > clay > TiO2. This suggests that as far as the extent of reinforcement is concerned silica filler is superior to others.
Figure 3.19  a) Krau's plots and  b) Cunneen and Russell plots of filled SBR/HDPE blends
Table 3.5 Values of slope of filled SBR/HDPE system

<table>
<thead>
<tr>
<th>Type of Filler</th>
<th>Krau’s equation</th>
<th>Cunneen –Russell equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>-1.832</td>
<td>1.066</td>
</tr>
<tr>
<td>HAF-black</td>
<td>-1.032</td>
<td>0.557</td>
</tr>
<tr>
<td>China clay</td>
<td>-0.560</td>
<td>0.264</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.322</td>
<td>0.141</td>
</tr>
</tbody>
</table>

3.2.5. b Mechanical properties

The stress-strain curves of SBR/HDPE blends filled with four different fillers at equivalent volume loading (30phr) are given in Figure 3.20. The general pattern of the stress-strain curves does not get much affected by the addition of fillers. However, for a given strain, all filled systems exhibit higher stresses than the unfilled polymer blend. Comparatively higher value of failure stress was obtained for silica followed by HAF black-filled blends. This indicates that both silica and HAF-black fillers had exerted reinforcing character to the SBR/HDPE blend. However the nature of the reinforcement is different for both the fillers. In the case of silica, its reinforcement is attributed specifically to the adhesion type of interaction between the amorphous filler and the polymer macromolecules. It has been reported that small particle size of the fillers is of prime importance in elastomer reinforcement where as the chemical nature of the filler appears to be of secondary importance. A high degree of reinforcement and a very high dependence of reinforcement on particle size are observed in the primary particle size range of 10 to 100 nm. Average particle sizes of different fillers are given in Table 3.6.
Figure 3.20  Tensile stress –strain curves of filled SBR/HDPE blends

Table 3.6  Average particle sizes of fillers

<table>
<thead>
<tr>
<th>Type of Filler</th>
<th>Average particle size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>.02</td>
</tr>
<tr>
<td>HAF-Carbon black</td>
<td>.04</td>
</tr>
<tr>
<td>China clay</td>
<td>2.0</td>
</tr>
<tr>
<td>TiO₂</td>
<td>12.0</td>
</tr>
</tbody>
</table>

The relatively very small particle size of the particle (~0.02 µm) which is far below the size of about 1 µm, which is always considered as a high upper limit for particulate fillers to start acting as reinforcing filler\(^{32}\). Since the size of silica particle is less than the distance between cross-link sites of ~500Å\(^{0}\), allows for high adhesion to take place and hence high reinforcement is attained\(^{33}\).
## Table 3.7 Mechanical properties of filled SBR/HDPE systems.

<table>
<thead>
<tr>
<th>System</th>
<th>Ultimate tensile strength (Mpa)</th>
<th>Strain – at break (%)</th>
<th>Tear strength (Mpa)</th>
<th>Young’s modulus (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gum (S₃₀D)</td>
<td>16.2</td>
<td>21.2</td>
<td>77.5</td>
<td>169.7</td>
</tr>
<tr>
<td>10S</td>
<td>23.0</td>
<td>26.4</td>
<td>109.2</td>
<td>180.9</td>
</tr>
<tr>
<td>20S</td>
<td>26.4</td>
<td>27.6</td>
<td>110.1</td>
<td>262.7</td>
</tr>
<tr>
<td>30S</td>
<td>31.3</td>
<td>29.7</td>
<td>118.0</td>
<td>294.2</td>
</tr>
<tr>
<td>10H</td>
<td>22.2</td>
<td>22.6</td>
<td>101.6</td>
<td>178.2</td>
</tr>
<tr>
<td>20H</td>
<td>22.8</td>
<td>25.0</td>
<td>104.2</td>
<td>214.0</td>
</tr>
<tr>
<td>30H</td>
<td>24.5</td>
<td>16.2</td>
<td>110.4</td>
<td>249.5</td>
</tr>
<tr>
<td>10L</td>
<td>21.4</td>
<td>25.2</td>
<td>96.4</td>
<td>177.3</td>
</tr>
<tr>
<td>20L</td>
<td>21.9</td>
<td>25.8</td>
<td>102.8</td>
<td>189.4</td>
</tr>
<tr>
<td>30L</td>
<td>20.5</td>
<td>17.6</td>
<td>100.8</td>
<td>238.2</td>
</tr>
<tr>
<td>10T</td>
<td>18.8</td>
<td>13.3</td>
<td>87.7</td>
<td>170.0</td>
</tr>
<tr>
<td>20T</td>
<td>19.9</td>
<td>15.3</td>
<td>88.1</td>
<td>189.7</td>
</tr>
<tr>
<td>30T</td>
<td>20.3</td>
<td>19.0</td>
<td>93.0</td>
<td>211.1</td>
</tr>
</tbody>
</table>
However, in the case of HAF-black the presence of different active centers on its surface participate in the formation of chemical as well as physical bonding between the filler and the matrix molecules improving the tensile strength of the blends. The surfaces of carbon black filler act as stress homogenizers allowing slippage and redistribution of stress among polymer chains. They also serve to deflect or arrest growing cracks. The interaction of SBR with HAF-black is not covalent bonding, but it may be hydrogen bonding\textsuperscript{31}. Such bonds are presumably labile under stress. The sliding of polymer molecular segments across the filler interface is a mechanism for energy dissipation. Dissipation of strain energy by additional relaxational mechanisms introduced by C-black also contributes towards the improvement in the tensile strength of C-black filled vulcanizates. Mechanical energy dissipation by the addition of particles in a visco elastic medium has been studied by Radok and Tai\textsuperscript{34}. The mechanism of mechanical rupture of polymer chains during processing gives free chain ends which can react with free radicals on the C-black, with a result equivalent to a giant crosslink at the morphological scale. As a result stiffer, stronger and tougher products with enhanced mechanical properties will be obtained.

The mechanical properties of all filled blends are given in Table 3.7. The variations in tensile strength of the filled blends are compared with that of gum sample in Figure 3.21a. From the figure it is apparent that the tensile strength increases significantly as the concentration of silica is increased, due to better reinforcement at higher
loading. In the case of HAF-black also there is a notable enhancement in ultimate strength of the blends. This is because the available active sites for a fixed polymer content increase with the increase in filler loading. In the case of clay-filled systems even though there is an initial enhancement of tensile strength up to 20phr, there is a deterioration of strength on further loading. This may be due to dilution effect. At higher loading of the filler a decrease in the volume fraction of the polymer in the system occur which leads to degradation in ultimate properties. Among the different filled systems TiO$_2$ filled blends exhibits the least tensile strength values. This is due to the weak semi-reinforcing nature of TiO$_2$. Here TiO$_2$ acts merely as an extender.

The variation of strain-at break with filler content of SBR/HDPE blends with the four different fillers is given in Figure 3.21b. In the case of silica filled blends, there is a gradual increase in strain at –break with increase in filler content. Since the particle size of silica is $\sim 0.02\mu m$ which is extremely small, it may possible to assume that a certain extent of disturbance to occur to the ordered content i.e. crystallinity of HDPE$^{33}$. Also it would be possible that some kind of softening of polymer phases would take place resulting in high degree of interphase adhesion between the filler particles and both HDPE and SBR phases. This will lead to an increase in the strain. Where in the black filled system, the strain- at break is found to increase as the content of filler particles increase up to 20phr.
Figure 3.21 Variations of a) tensile strength b) strain-at break with filler content
At 30phr of filler content, there is a notable reduction in strain at-break. This is due to the stiffening of the matrix by higher degree of polymer-filler interaction, which is responsible for the enhancement of tensile strength. In the clay filled system also, on increasing the filler loading more than 20phr the strain-at-break decreases, which is attributed to the dilution effect. That is, at higher filler loading the probability of forming loose agglomerates in the matrix would increase and a decrease in the volume fraction of the polymer in the system occurs. So the extension capacity of the blend would be very much reduced and hence degradation in strain at-break takes place. All the TiO₂ filled blends show less strain at-break than that for the base polymer. Reduction in strain-at-break is due to the decreased deformability of a rigid interphase between the filler and the matrix material.

The tear curves of SBR/HDPE blends filled with four different fillers at 30phr loading are compared in Figure 3.22. All filled samples tear at a higher load than the unfilled system. The dependence of tear strength on different filler content is depicted in Figure 3.23. It is clear from the figure that for all fillers (except clay), the tear strength of the blends increases with filler content. During tearing the filler particles present in the tear path obstruct the advancing tear front; hence the increase in tear strength occurs with the addition of fillers. The clay filled compositions with higher clay loading (30phr) show a reduction in tear resistance, due to the low level interaction between the clay and the rubbers loose agglomerates are formed in the matrix, which act as stress raisers and enhance the progress of the fracture path causing premature failure. Among different fillers used TiO₂ posses the lowest tear resistance.
Figure 3.22  Tear-load displacement curves of filled SBR/HDPE blends

Figure 3.23  Dependence of tear strength on filler content

![Graph](image-url)
The primary intention of filler incorporation is to increase the stiffness of the resultant material. As expected, the modulus is increasing steadily with filler content (Table 3.7). This is a common phenomenon, i.e. filler addition results in greater modulus\textsuperscript{35-37}. When silica is used as the filler, there is a drastic increase in Young’s modulus with filler loading. This characteristic stiffness arises from the high degree of affinity between the silica particles and the polymer, they tend to aggregate within the matrix to form a three-dimensional reticulate structure. The increased moduli of the filled blends are due to the reduced elasticity and increased rigidity of the matrix. The variations in mechanical properties are in accordance with the reinforcing ability, i.e. in the order silica > HAF > clay > TiO\textsubscript{2}.

3.2.6 Fractography

3.2.6.a Unfilled blends

Scanning electron micrographs of the tensile and tear fractured surfaces of uncrosslinked SBR/HDPE blends are given in Figures 3.24 (a-c) and Figures 3.25 (a-c) respectively, which show the characteristic elements of the morphology. The continuous and dispersed phases are distinctly discernible. In Figure 3.24a, the HDPE domains are large and irregular. In the failed surface of S\textsubscript{50} blend (Figure 3.24b), only holes referring to voiding in or around the rubber particles is observed. Delamination of the SBR particles from the matrix seems to be the cause of voiding during the plastic deformation process. In the fractured surface of S\textsubscript{70} composition (Figure 3.24 c) the HDPE domains seems to be elongated. The elongated domains of HDPE indicate that the phase has undergone deformation.
Figure 3.24  Scanning electron micrographs of the tensile fractured surfaces of a) S₃₀ b) S₅₀ and c) S₇₀ blends
Figure 3.25  Scanning electron micrographs of the tear fractured surfaces of a) S$_{30}$ b) S$_{50}$ and c) S$_{70}$ blends.
Marked constrictions can be seen in the tear fractured surface of the S$_{30}$ blend (*Figure 3.25.a*), which is due to the extreme flow of the material under the action of the stress. Long drawn out HDPE domains can be seen in the micrograph. Oval shaped, large and smooth holes are also present in the fractured surface formed by the detachment of the domains of the dispersed rubber phase, which indicates a lack of adhesion between the two phases. In the tear fractured surface of S$_{50}$ sample (*Figure 3.25 b*), the detachment of domains of the dispersed SBR phase created the voids, which is attributed to the lack of interfacial adhesion between the domains and the matrix. However, S$_{70}$ blend (*Figure 3.25 c*) exhibits a smooth fractured surface due to the high rubber content in it.

In order to assess the effect of dynamic vulcanization on the failure mode of SBR/HDPE blends, scanning electron micrographs of the tensile and tear fractured surfaces of dynamically vulcanized S$_{30}$D compositions were taken and are presented in *Figure 3.26 a* and *Figure 3.26b* respectively. *Figure 3.26 a* shows ductile type failure with high extent of deformation as evidenced by the presence of fibrils on the fractured surface. The addition of DCP increases the ductility of the macromolecules. It has been reported that the formation of fibrils is a characteristic feature of ductile type failure and the length of the fibrils indicates the degree of deformation of the material during failure$^{38}$. The fibrils also indicate the maximum stretching of the composition ($E_b=21.2\%$) before failure. In the tear fractured surface of S$_{30}$D composition (*Figure 3.6.b*) fibrils and peaks can be seen. The alignment of the macromolecules in fibrils is seen from top to bottom. Here the phases are stretched like fibers due to the increased ductility of the samples by the addition of DCP. During tearing the two parts separate and the ends rebound forming slight peaks. The presence of peaks and fibrils are characteristics features of ductile failure$^{38}$.
Figure 3.26  Scanning electron micrographs of the a) tensile and b) tear fractured surfaces of crosslinked $S_{30}$ blends.
3.2.6 b  Filled blends

The fracture and failure process of filled polymers are extremely complicated. This is due to many reasons such as the existence of local inhomogeneity in the materials, several possible failure modes, that are closely related to interfacial strength, dewetting, stress concentration at the interface and relative brittle or ductile nature of the filler and the matrix materials.

The tensile fractographs of various filled blends are depicted in Figures 3.27(a-d). In general, addition of fillers increases the ductility of the blend as evidenced from the presence of elongated fibrils on the fractured surfaces of the blends. Silica filled system, shows a large number of filler particles on its surface, which is due to high reinforceability of silica compared to other systems (Figure 3.27.a.) The fractograph of HAF-black filled system (Figure 3.27b) indicates that the surface has a continuous HDPE phase in the form of a network with a continuous rubber phase filling the gaps resulting in an intermesh. Filler aggregates can be seen on the surface as loose particles. The fractured surfaces of clay filled blends also exhibit deformed phases. However fractured surface of TiO2 filled system does not shows any fibrils on its fractured surface, which is due its decreased deformability of a rigid interphase between the filler and the matrix material. The reduction in strain-at break values compared to that of the gum sample also supports this fact.
Figure 3.27  Scanning electron micrographs showing the tensile fractured surfaces of a) 30Silica b) 30HAF-Black c) 30Clay and d) 30TiO2
Figure 3.28  Scanning electron micrographs showing the tear fractured surfaces of a) 30Silica b) 30HAF-Black c) 30Clay and d) 30TiO₂
Figures 3.28 (a-d) show the SEM photomicrographs of the tear fractured surfaces of various filled blends. In the silica filled system, the tear path is found to deviate and the branching of the tear path also can be seen. This is due to the restrictions of crack propagation by filler particles, which is a characteristic of strong materials\(^{38}\). HAF- black filled system also exhibits branching of the tear path, as evident from Figure 3.28b. The clay filled system (Figure 3.28c) shows some parabolic tear paths, which indicates the low resistance offered by these particles towards crack propagation. In TiO\(_2\) filled system, the tear paths are found relatively less branched than those of silica. The tear strengths of these systems are also poor compared with other filled systems.

The mechanical characterization of SBR/HDPE blends shows a clear influence of the composition on the properties considered. The morphology indicated a two-phase structure in which the high-viscosity SBR phase was dispersed as domains in the continuous low viscosity HDPE matrix up to 50wt% of the SBR concentration. An interpenetrating co-continuous morphology was obtained for S\(_{60}\) composition, which was followed by phase inversion in S\(_{70}\) blend. The size of the dispersed phase was found to increase with increasing concentration of that phase, which is associated with coalescence. It was seen that, a sensible increase of the ultimate properties with vulcanization is obtained; the improvement being more noticeable in S\(_{30}\) composition (with higher plastic percentages in the blend). DCP dosages had a significant effect on the extent of crosslinking. The uniform distribution of SBR phase in HDPE matrix upon DCP vulcanization indicates that the selected technological conditions in preparing the blends are suitable to obtain a fine dispersion of the two polymers. Fractographic studies also show the lack of interfacial adhesion between the domains and the matrix in the
unvulcanized samples and dynamically vulcanized blend shows high extent of interaction as evidenced by the presence of fibrils on the fractured surface. The nature of the filler and filler loading has a dramatic effect on the mechanical properties of SBR/HDPE blends. Filled blends showed improved mechanical properties such as enhanced tensile strength, Young's modulus and tear strength values when fillers are incorporated. As far as the extent of reinforcement and ultimate properties concerned, the silica filler was found to be superior to others.

3.3. References


