Chapter 3

Mechanical Properties of EPDM/SBR Blends

Abstract

The mechanical properties of EPDM/SBR blends were investigated with special reference to the effects of blend ratio and cross-linking systems. Among the blends, the one with 80/20 EPDM/SBR has been found to exhibit the highest tensile, tear, and abrasion properties at ambient temperature. The observed changes in the mechanical properties of the blends have been correlated with the phase morphology, as attested by scanning electron micrographs. The effects of three different cure systems, viz; sulphur (S), dicumyl peroxide (DCP), and a mixed system consisting of sulphur and peroxide (M), on the blend properties also were studied. The stress-strain behaviour, tensile strength, elongation at break and tear strength have been found to be better for the blends cured by mixed system.

A part of results of this chapter has been published in J. Appl. Polym. Sci., 93, 2606 (2004).
3.1 Introduction
The mechanical properties of polymer blends are highly dependent on blend ratio, characteristics of blend components, processing conditions, extent of interfacial adhesion between the components and phase morphology of the blends. Coran and Patel [1-4] conducted several studies on rubber/thermoplastic blends to correlate their physical and mechanical properties with the characteristics of the blend components. The processing and mechanical properties of butyl-EPDM blends have been reported by Callan et al. [5]. Imoto [6], in the studies on EPDM/EPM compounds, showed that the physical properties of the blends were proportional to blend ratio. Oliveira and Soares [7] examined the effects of curing systems and curing parameters, on the mechanical properties and crosslink density of NBR/EPDM blends. They found that the accelerator type and the sulphur concentration affected the mechanical properties. Ghilarducci et al. [8] investigated the influence of blend composition on the internal friction of NR/SBR compounds. Utracki [9] discussed very interesting correlations between morphology and mechanical properties of different blend systems.

The present chapter describes the cure characteristics and mechanical properties of blends of EPDM and SBR. The cure time, scorch time, cure rate index, tensile strength, tear strength, elongation at break, hardness and abrasion resistance of the blends have been discussed with special reference to the effects of blend ratio and crosslinking systems.
3.2 Results and Discussion
3.2.1 Cure Characteristics

The cure characteristics of EPDM/SBR blends with different vulcanizing systems are given in Table 3.1. Typical rheographs of E$_{100}$S, E$_{80}$S, and E$_{60}$S are given in Figure 1. The optimum cure time ($t_{90}$) shows a gradual increase with increase in EPDM content in the blends for all the cross-linking systems used for this work. The $t_{90}$ has been found to be highest for DCP cured systems compared to sulphur and mixed systems for a given blend ratio.

Among the sulphur cured blends, the scorch time and thus the scorch safety are higher for the blends E$_{60}$S and E$_{80}$S. The scorch safety has been found to be better for DCP cured system for a given blend ratio. The minimum torque (ML) values are found to be higher for sulfur cured systems for a given blend ratio than the DCP and Mixed systems.

The maximum torque (MH), which is a measure of cross-link density, is higher for the blends vulcanized by S and Mixed systems than the DCP system.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Blend Ratio</th>
<th>Optimum Cure time, $t_{90}$ (min)</th>
<th>Scorch Time, $T_S$ (min)</th>
<th>Min Torque, ML (dNm)</th>
<th>Max Torque, MH (dNm)</th>
<th>CRI (min$^{-1}$)</th>
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<tr>
<td>E$_0$S</td>
<td>SBR100/EPDM0</td>
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<td>11.09</td>
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<td>09.64</td>
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<td>0.65</td>
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<td>10.19</td>
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<td>1.68</td>
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<td>30.67</td>
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<td>1.58</td>
<td>12.33</td>
<td>18.42</td>
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<td>3.66</td>
<td>2.06</td>
<td>12.36</td>
<td>24.69</td>
</tr>
<tr>
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<td>SBR100/EPDM100</td>
<td>8.90</td>
<td>4.97</td>
<td>1.69</td>
<td>12.28</td>
<td>51.81</td>
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Figure 3.2 shows the cure characteristics of E\textsubscript{80}S, E\textsubscript{80}P and E\textsubscript{80} Mix systems. It has been found that the rate of cure in mixed and sulphur systems is faster than the DCP system and the torque values are higher in mixed and sulphur systems. The cure rate index (CRI) was calculated using the equation:

\[
\text{CRI} = 100/t_{90}-t_{2}
\]  

(3.1)

where \(t_{90}\) is the cure time and \(t_{2}\) is the scorch time. The CRI values are also given in Table 2.1. Cure rate index for the present blend systems has been found to increase with increase in SBR content for all the vulcanizing systems. The values have been found to be lowest for peroxide system.
A high CRI value shows higher vulcanization rate. Therefore, SBR is the cure- activating component for the systems. For a given blend ratio, the CRI is highest for blends cross linked by S and lowest for those with DCP curing systems.

3.2.2 Mechanical properties

Figure 3.3 shows the stress- strain curves of sulphur cured EPDM/SBR blends. It is clear from the graphs that as the EPDM content of the blends increases, the % strain increases. This deformation behaviour is due to the orientation of crystalline regions of EPDM under the applied stress. The ultimate stress values are found to
be highest E$_{80}$S blend system. Figure 3.4 represents tensile strength vs EPDM weight % of sulphur cured blend systems. Among different compositions, the blend, E$_{80}$S (EPDM 80/SBR20) shows the highest tensile strength.

![Figure 3.3](image)

**Figure 3.3.** Effect of blend ratio on the stress-strain curves of sulphur cured EPDM/SBR blends.

The tensile strength values of the blends are found higher compared to that of the component elastomers. This positive deviation can be attributed to the mutual reinforcement of SBR and EPDM in the blends [10]. The synergism in tensile strength can also be attributed to strain hardening [11-14]. Materials, which undergo strain hardening, during stretching, have higher strength at break than materials those do not undergo it. During strain hardening both amorphous and
lamella r components attempt to orient along the drawing direction. These orientations cause close packing of chains, thereby increasing the intermolecular forces of attraction, which accounts for the higher stress at rupture. Due to stretching, EPDM in the present blend system undergoes deformation leading to high orientation of chains along with a reorganization of crystalline entities in the pull direction.

**Figure 3.4** Effect of blend ratio on tensile strength

Figure 3.5 shows the effect of different cross-linking systems viz; sulphur, DCP and mixed on the tensile strength of EPDM/SBR blends. The graphs clearly show that the tensile strength increases in all the blends with increase in EPDM content. Among the different vulcanizing systems, for a given blend ratio, the tensile strength has been found to be highest for the mixed cure system (S+DCP) and the
lowest for the DCP system. The difference in the tensile strength with respect to curing systems can be attributed to the difference in the type of crosslinks introduced between the macromolecular chains during vulcanization. The ‘S’ vulcanization introduces polysulphidic linkages, the DCP cure, C-C linkages by a free radical mechanism and the mixed cure, both polysulphidic and rigid C-C linkages. A schematic representation of the network crosslinking is given in Figure 3.6.

![Figure 3.5](image)

**Figure 3.5** Effect of different cross-linking systems on the tensile strength
The effect of blend ratio on elongation at break for the blends cured by sulphur, DCP and Mixed systems is presented in Figure 3.7. It has been found that the elongation at break increases with increase in EPDM content. The increase in EB can be correlated to the rearrangement of EPDM crystallites under an applied stress. In DCP and mixed cured blends, the elongation at break values has been found to be lower compared to sulphur cured systems. This is definitely associated with the higher flexibility of the molecular chains with polysulphidic linkages.

**Figure 3.6** Schematic representation of crosslinking of EPDM/SBR blends cured by S, P and M systems.
The cross-linked state of the blends has been measured in terms of cross-link density. The cross-link density of the blends was calculated from the tensile values using the kinetic theory of elasticity [15] 

\[
v = \frac{\sigma}{(\lambda^{-1}/\lambda^2)RT}
\]  

where \(v\) is the crosslink density (number of cross links per cc), \(\sigma\) is the modulus, \(\lambda\) is the extension ratio, \(R\) is the gas constant and \(T\) is the temperature on absolute scale. Figure 3.8 represents the effect of different crosslinking systems viz; S, P and M on the crosslink density of the blends. It is seen that the crosslink density of S and M cured blends increases with EPDM content for all the blend ratios.

**Figure 3.7** Effect of blend ratio on elongation at break
However with increase the weight % of EPDM, the values have been found to decrease in peroxide cured systems. This can be due to uneven distribution of DCP in EPDM and SBR phases. It is interesting to note that the crosslink densities of the component elastomers are far lower compared to the blends, which complements the effect of blending on achieving better mechanical properties.

**Figure 3.8** Effect of different crosslinking systems on crosslink density
Table 3.2 Young’s Modulus and cross-link density of EPDM/SBR blends

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Young’s Modulus (100%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E₀S</td>
<td>0.09</td>
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<tr>
<td>E₂₀S</td>
<td>1.25</td>
</tr>
<tr>
<td>E₄₀S</td>
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<tr>
<td>E₆₀S</td>
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<td>E₈₀S</td>
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<td>E₁₀₀S</td>
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<tr>
<td>E₀P</td>
<td>-</td>
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<td>E₂₀P</td>
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<td>E₄₀P</td>
<td>1.22</td>
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<td>E₆₀P</td>
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<td>E₈₀P</td>
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<tr>
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</tr>
<tr>
<td>E₁₀₀M</td>
<td>0.85</td>
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</table>

The Young’s modulii for the blends are given in Table 3.2. It has been found that the Young’s modulii are comparatively higher for sulphur and mixed cure systems than DCP. This can be attributed to the flexible polysulphidic crosslinks in sulphur system and a mixture of polysulphidic and C-C crosslinks in mixed system.

The dependency of tear strength on the weight percentage of EPDM is shown in Figure 3.9. Tear strength of the blends also shows synergism due to strain-induced crystallization. The tear strength has been found to increase with increased weight percentage of EPDM and the highest tear strength is for blend with 80 wt % of EPDM. Among the vulcanizations systems, the tear strength is highest for the mixed system.
Figure 3.9 Effect of blend ratio and crosslinking systems on tear strength

Figure 3.10 Effect of blend ratio on abrasion resistance
The abrasion resistance in terms of volume loss has been studied for sulphur cured blends. The change in abrasion resistance with weight percentage of EPDM is shown in Figure 3.10. The abrasion loss has been found to be minimum for the blend E$_{80}$S. A marginal increase in the hardness of the blends has also been noted with increase in weight percentage of EPDM in the blends except in DCP cured systems where the values are decreased as shown in Figure 3.11. This is definitely due to the rigid C-C crosslinks in DCP cured blends.

Figure 3.11 Effect of blend ratio on hardness
3.3 Morphology

SEM has been successfully used by researchers to study the morphology of polymer blends [16-19]. The SEM photographs of unfractured specimens of E₈₀ blends cured with DCP, sulphur and mixed systems are presented in Figures 3.12a, 3.12b and 3.12c respectively. Figure 3.12a exhibits the SEM of DCP cured E₈₀P blend having a flake like structure filled with pores which ultimately leads to lower mechanical properties. In Figure 3.12b it can be seen that the phase domains are globular shaped and are of relatively uniform size. The domains of SBR particles have been found to be dispersed in the EPDM matrix, which prevents crack growth in the blend during tensile stress. In the mixed system, E₈₀M (Figure 3.12c), it has been found that the particles are more uniform in size and they are interwoven with the globular structure.

![SEM photographs of cryogenically fractured specimens of EPDM/SBR blends](image)

**Figure 3.12** SEM photographs of cryogenically fractured specimens of EPDM/SBR blends

The SEMs shown in Figures 3.13a, 3.13b, 3.13c, 3.13d, 3.13e and 3.13f explain the morphology of tensile fractured surfaces of sulphur cured EPDM/SBR blends in different blend ratios. Figure 3.13a exhibits the SEM of pure EPDM, vulcanized by sulphur with a characteristic ductile failure and rough surface. The absence of a dispersed phase in it causes easy crack propagation and for poor tensile properties. Figure 3.13b shows the changes in morphology with the introduction of SBR in to EPDM. The SEM of blend E₈₀S shows that small domains of the dispersed phase SBR is distributed relatively uniformly throughout the matrix. Earlier studies [20-22]
showed that crack bifurcation in blends can be prevented by small and uniformly distributed minor phase in the matrix. It can be noted that the particle size of the minor phase in blend $E_{80}S$ is small and uniform which helped to toughen the matrix and prevent crack propagation. The miscibility of the blend was found increased.

The results of DMA and DSC are complementary to this observation. It is noteworthy that the blend $E_{80}S$ has given better tensile values. As SBR particles are agglomeration of the dispersed phase particles happen. Consequently,
miscibility of the blends decreases and the crack propagation increases in the blends E60S, E40S and E20S as represented by Figures 3.13c, 3.13d and 3.13e. Figure 3.13f represents the SEM of pure SBR. The morphology studies show that a better distribution of dispersed phase exists in E80 composition.

3.4 Model Fitting

The mechanical behaviour of EPDM/SBR blends has been modeled by using various composite models such as parallel, series and the Halpin-Tsai equation. The parallel model (highest upper-bound model) is given by the equation [23].

\[ M = M_1 \phi_1 + M_2 \phi_2 \]  
(3.3)

where \( M \) is the mechanical property of the blend and \( M_1 \) and \( M_2 \) are the mechanical properties of components 1 and 2, respectively and \( \phi_1 \) and \( \phi_2 \) are the volume fractions of the components 1 and 2 respectively. In parallel model, the components are considered to be arranged parallel to one another so that the applied stress elongates each of the components by the same amount. The arrangement of the components in the blend is in series with the applied stress in the lowest bound series model. The equation [24] used is,

\[ \frac{1}{M} = \phi_1 M_1 + \phi_2 M_2 \]  
(3.4)

The equation, according to Halpin-Tsai is

\[ \frac{M_1}{M} = \frac{(1 + A_i B_i \phi_2)}{1 - B_i \phi_2} \]  
(3.5)

where \( B_i \) is given as

\[ B_i = \frac{(M_i/M_2 - 1)/M_1}{M_1/M_i + A_i} \]  
(3.6)
In this equation, the subscript 1 and 2 represent the continuous and dispersed phase, respectively. The value of $A_i$ for elastomer domains dispersed in hard continuous matrix is, 0.66. The experimental results are compared with the theoretical models in Figures 3.14 and 3.15. The graphs show that for tensile strength (Fig 3.13), the experimental value of $E_{80S}$ lie relatively closer to the parallel model as the weight percentage of EPDM increases.

**Figure 3.14** Comparison of experimental values with various models on the tensile strength of sulphur cured EPDM/SBR blends
Figure 3.15  Comparison of experimental values with various models on the Young’s modulus of sulphur cured EPDM/SBR blends.

3.5 Conclusion

The effects of blend ratio and three cure systems on the mechanical properties of EPDM/SBR blends were investigated. The properties such as elongation at break, tensile strength, tear strength and abrasion resistance increased with increase in EPDM content in the blends. A similar trend was also found for hardness in sulphur and mixed systems but in peroxide, the property was found to be decreased. Among the different vulcanizing systems, the tensile and tear strength were higher for the mixed systems compared to S and DCP systems. The elongation at break was higher for sulphur-cured blends due to the flexible polysulphidic linkages. The abrasion resistance of the blends was found to be increased with EPDM
content. The results have been interpreted in terms of the morphology of the blends as attested by SEM photographs. The experimental observation has been compared with different theoretical models.
References


