Chapter 7

Ageing Studies on EPDM/SBR Blends

Abstract

The ageing behaviour due to the effects of heat, ozone, γ- radiation and water on EPDM/SBR blends was studied. It has been observed that an increase in EPDM in the blends improves the ozone resistance of the blends. Crack initiation was noted only in blends with lesser amount of EPDM and the cracks in such blends were found deeper, wider and continuous. Tensile strength of blends of different compositions increased after thermal ageing for 96 hrs at 100°C probably due to the continued cross-linking. With 15 kGy irradiation dose, the tensile strength of the blends found to be decreased while it increased with 80 kGy dosage of γ-radiation. The elongation at break showed a decreasing trend with increased dosage of γ-radiation. It has also been observed that the EPDM rich blends showed negligible water uptake.

Results of this chapter have been communicated to Polymer Degradation and Stability
7.1 Introduction

The demand for high temperature, ozone and weather resistant rubbery materials has increased during the last decade. Rubber blends are becoming preferred materials to meet these requirements. Earlier studies on accelerated ageing of rubber vulcanizates show that the properties such as elongation at break, tensile strength and modulus undergo changes due to deterioration [1]. It is well known that for many unsaturated rubbers, the hydrogen atom of α-methylenic carbon is abstracted in the presence of oxygen and an oxidative reaction chain is initiated which propagates auto-catalytically and ends in chain scission. Besides scission of the main chain and of the cross-links, depending upon polymers, ageing causes the formation of more cross-links of the same type as those already present or of a different type, which may be inactive to further scission. Introduction of antioxidants and antiozonents helps to reduce the property loss of rubber vulcanizates due to ageing though these chemicals have many limitations in performance. With the introduction of weather resistant rubbers such as EPDM, hypalon and polysulfide, the efforts to modify the ageing characteristics of highly unsaturated rubbers gained a new momentum, through blending techniques [2].

The effects of degrading agents on each type of polymer will be different and they depend mainly on the chemical structure of the polymer and the type of crosslinking system used. For SBR, the resistance to thermal, gamma and ozone ageing is poor due to the presence of double bonds in the main chain. In EPDM as the reactive carbon-carbon double bond is located on a side chain, the polymer backbone structure is completely saturated and not subject to molecular breakdown via ozone attack or oxidation. Therefore the behaviour of blends of these elastomers against the action of various degrading agents is worth examining.
Excellent reports on the ageing characteristics of rubbery systems exist. For example, Bhowmick and White [3] investigated the thermal, UV- and sunlight ageing of thermoplastic elastomeric NR/PE blends. They found that thermal ageing of the blends caused the tensile properties to deteriorate, especially at longer times, or higher temperatures of ageing after an increase of properties in the initial stage. Deuri et al.[4] investigated the ageing behaviour of IIR/EPDM blends and found that the ageing resistance increased with increase in EPDM content. Koshy et al [5-6] studied the ageing of different rubber-rubber blends. Sulekha et al.[7] reported that the use of oligomer bound antioxidants was an effective means of protecting non-resistant rubbers against surface cracking. Vinod et al.[8] investigated the effects of heat, ozone and high energy radiation on the degradation behaviour of aluminium powder filled NR composites. They found that resistance to degradation was improved, when NR was reinforced with aluminium powder. Many other interesting works have also been reported on the ageing characteristics of polymeric systems [9-19].

SBR is an elastomer extensively used for a wide variety of products, viz., tires and related products, belts, hoses, foot wears, foamed products, mechanical goods etc. SBR, in general, has high resilience, better flex life, lower heat build up and better abrasion resistance. However, with unsaturation sites, it is prone to attack by ozone or oxygen. EPDM is a rubber having excellent temperature and ozone resistance. Furthermore, depending up on the molecular weight, molecular weight distribution, % of ethylene content and % of diene, EPDM gives better tensile/tear strength, hot green strength, higher cure rate, flow at high temperature, higher modulus and lower compound cost.

This chapter examines the ageing characteristics of EPDM/SBR blends with special reference to the effects of heat, ozone, radiation and water. Ageing studies
were conducted on sulphur cured EPDM/SBR blends along with the component elastomers.

7.2 Results and Discussion
7.2.1 Thermal ageing

The mechanical properties of the blends before and after thermal ageing were compared. Figure 7.1 shows a comparison between the tensile strength of the blends before and after aging at 100°C for 96 hours. It is clear from the graph that the tensile strength values were increased with increased weight percentage of EPDM in the blend. Figure 7.2 shows the percentage increase in tensile strength of EPDM/SBR vulcanizate after ageing at 100°C for 96 hrs. The increase in tensile strength of the blends might be due to the continued cross-linking of the blend components by thermal ageing. The effects of temperature and environmental conditions on the performance of polymers, including the degradation mechanisms are available in the literature [20-26]. Generally, the retention of properties depends up on the degradation behaviour of the component elastomers. Amorphous polymers degrade faster than crystalline polymers by heat. This is evident from the crosslink density values given in Table 7.1. The table shows that the crosslink density of the blends increased with increased EPDM composition, which ultimately enhanced the TS. Rubber vulcanizates are cured only at t90. The remaining 10% is kept at an allowance during service. Thermal ageing completes this 10 % curing as clear from the crosslink density values, which subsequently enhance the TS.
**Figure 7.1** Thermal ageing at 100°C: % Increase in tensile strength

**Figure 7.2** Thermal ageing at 100°C - Comparison of tensile strength before and after ageing
Table 7.1 Crosslink density of unaged and aged EPDM/SBR blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crosslink density ×10^4 (gmol/cc)</th>
<th>Before thermal ageing</th>
<th>After thermal ageing</th>
</tr>
</thead>
<tbody>
<tr>
<td>E₀S</td>
<td>0.22</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>E₂₀S</td>
<td>2.83</td>
<td>4.04</td>
<td></td>
</tr>
<tr>
<td>E₄₀S</td>
<td>2.87</td>
<td>3.36</td>
<td></td>
</tr>
<tr>
<td>E₆₀S</td>
<td>2.91</td>
<td>3.33</td>
<td></td>
</tr>
<tr>
<td>E₈₀S</td>
<td>2.92</td>
<td>3.18</td>
<td></td>
</tr>
<tr>
<td>E₁₀₀S</td>
<td>-</td>
<td>0.15</td>
<td></td>
</tr>
</tbody>
</table>

Figure 7.3 Comparison Modulus at 100% - Before and after thermal ageing of EPDM/SBR blends at 100°C
**Figure 7.4** Comparison of EB (%) – Before and after thermal ageing at 100°C

**Table 7.2** Percentage retention of elongation at break – Effect of thermal ageing on EPDMSBR blends at 100°C

<table>
<thead>
<tr>
<th>Elongation at break (%)</th>
<th>% Retention</th>
</tr>
</thead>
<tbody>
<tr>
<td>E₀S</td>
<td>67.94</td>
</tr>
<tr>
<td>E₂₀S</td>
<td>74.73</td>
</tr>
<tr>
<td>E₄₀S</td>
<td>71.01</td>
</tr>
<tr>
<td>E₆₀S</td>
<td>86.19</td>
</tr>
<tr>
<td>E₈₀S</td>
<td>93.82</td>
</tr>
<tr>
<td>E₁₀₀S</td>
<td>70.20</td>
</tr>
</tbody>
</table>

Figure 7.3 illustrates the percentage increase in modulus (100%) of the EPDM/SBR blends after thermal ageing at 100°C for 96 hrs. The graphs show that the modulus of all the blend compositions increases after thermal ageing. The variations in the elongation at break values of the blends after thermal ageing are
presented in Figure 7.4. It has been found that the elongation at break of the vulcanizate decreases due to thermal ageing. Thermal ageing leads to the formation of additional cross-links in the blends. It is clear from Table 1 that the crosslink densities increase after ageing. In general, the elongation at break of a vulcanizate with higher crosslink density is shorter than that of a vulcanizate with a lower density [27]. The trends of EB among the blends are in the order E_{80}S>E_{60}S>E_{40}S>E_{20}S>E_{0}S which is in agreement with the above observation.

Figure 7.5 reveals that the hardness of all the EPDM/SBR blends increases after thermal ageing. This increase is also associated with the increase in crosslink density.

Figure 7.5 Comparison of hardness (shore A) – Before and after thermal ageing at 100°C
7.2.2 Ozone ageing

The optical photographs of the surfaces of the ozone aged samples presented in Figure 7.6 shows that no cracks were developed on the EPDM rich blends. However, cracks were seen initiated on the surfaces of SBR rich blends, E₀S, E₁₀S, E₂₀S and E₃₀S at lesser exposure of time. In blend E₃₀S, shallow type cracks were appeared after 17 hrs of ageing. Moderate cracks were developed in blend E₂₀S after 7 hrs of ozone ageing. Deep cracks were noted in E₀S after 4 hrs of ageing while cracks were noted in E₁₀S only after 6hrs of ageing. However blend compositions, E₄₀S, E₅₀S, E₆₀ S, E₇₀S, E₈₀S E₉₀S and E₁₀₀S were not affected by ozone ageing even for 120 hrs. Obviously, the crack growth in SBR due to ozone attack is effectively controlled and prevented by the highly ozone resistant EPDM in these blends.
Figure 7.6 (a) to (f) Optical photomicrographs of ozone exposed (120 h) Sulphur cured EPDM/SBR blends
Figure 7.6 (g) to (k)

Figure 7.6 (g) to (k) Optical photomicrographs of ozone exposed (120 h) Sulphur cured EPDM/SBR blends

Figure 7.7 shows the trends in ozone crack initiation and crack resistivity of EPDM/SBR blends with respect to time.
7.2.3 Gamma \(\gamma\) irradiation

The \(\gamma\)-radiation interacts with polymers in two ways; chain scission, which results in reduced tensile strength and elongation, and cross linking, which increases tensile strength but reduces elongation. Generally, polymers containing aromatic ring structures are resistant to radiation effects. The radiation resistance in aliphatic polymers depends upon their levels of unsaturation and substitution.

Figure 7.8 shows that the \(\gamma\)-irradiation at 15-kGy doses lowered the tensile strength of EPDM rich blends compared to the un-irradiated blends (control samples). This indicates.
Figure 7.8 Effect of gamma irradiation on the tensile strength of EPDM/SBR blends at 15-kGy irradiation dose.

Figure 7.9 Effect of gamma irradiation on the EB (%) of EPDM/SBR blends at 15-kGy irradiation dose.
that lower dose rate of irradiation performed under oxygen leads to a rapid decrease of the gel content due to chain scission and decrease in cross-linking. Meanwhile the increase in TS of SBR rich blends at lower level irradiation might be due to the presence of aromatic rings in the polymer, which are relatively degradation resistant. However, higher dosage of radiations enhances additional cross-linking, which increases tensile strength but reduces elongation [28]. The elongation at break was found to be lowered by chain scission due to the radiation effect, as shown in Figure 7.9. Figures 7.10 and 7.11 illustrate the comparison of tensile strength and elongation at break respectively of the blend, with a control sample, containing 80 wt % of EPDM at 80 kGy irradiation. It is clear from Figure 7.10 that tensile strength was increased at 80-kGy dosages compared to the EPDM/SBR blend at 15 kGy dose and also to the unirradiated control sample.

When SBR is the continuous phase, the matrix is more γ-resistant and at lower dosages, the cross-linking reaction predominates over chain scission and in such blends the TS increases. However, EPDM having an aliphatic chain is weak to resist γ-radiation of lower doses where chain or cross-link degradation is dominating over additional cross-link formation. However, when dosage is enhancing, the cross-link formation can get activated and a dominance of cross-linking reaction where scission can give better results. Similar observations exist in literatures [29].
Figure 7.10 Effect of $\gamma$-irradiation dose on the TS of the effective blend E$_{80}$S - Comparison with control sample

Figure 7.11 Effect of $\gamma$-irradiation dose on the EB of the effective blend E$_{80}$S - Comparison with control sample
7.2.4 Water ageing

Figure 7.12 illustrates the water uptake (mass %) of various EPDM/SBR blends after water immersion. The results show that the water uptake was negligible in majority of the blends due to the presence of water resistant EPDM. For instance, in blend E$_{80}$S, the percentage of water uptake after 7, 14, 21 and 42 days of water ageing have been noted only as 1.63, 2.09, 2.87 and 3.19 % respectively.

<table>
<thead>
<tr>
<th>Samples</th>
<th>After 7 days</th>
<th>After 14 days</th>
<th>After 21 days</th>
<th>After 42 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>E$_{100}$S</td>
<td>+0.07</td>
<td>+0.25</td>
<td>+0.331</td>
<td>+0.44</td>
</tr>
<tr>
<td>E$_{80}$S</td>
<td>+0.48</td>
<td>+0.70</td>
<td>+0.726</td>
<td>+1.12</td>
</tr>
<tr>
<td>E$_{60}$S</td>
<td>+0.48</td>
<td>+0.87</td>
<td>+0.938</td>
<td>+1.32</td>
</tr>
<tr>
<td>E$_{40}$S</td>
<td>+0.99</td>
<td>+1.31</td>
<td>+1.549</td>
<td>+2.23</td>
</tr>
<tr>
<td>E$_{20}$S</td>
<td>+1.63</td>
<td>+2.09</td>
<td>+2.499</td>
<td>+3.05</td>
</tr>
<tr>
<td>E$_{0}$S</td>
<td>+2.09</td>
<td>+2.58</td>
<td>+2.898</td>
<td>+3.26</td>
</tr>
</tbody>
</table>

7.3 Conclusion

Thermal, ozone, gamma and water ageing studies were conducted on EPDM/SBR blends with special reference to the effects of blend ratio. A comparison of the mechanical properties of the blends before and after thermal ageing showed an increase in the tensile strength due to the continued cross-linking while a decrease in the elongation at break. The percentage increase in tensile strength of the blends was found to increase with increase in EPDM content because of its relatively crystalline nature. The ozone ageing studies showed that cracks were initiated only in few blends in which the amount of EPDM was lesser to prevent crack growth. No ozone cracks were noticed in blends with EPDM level above 30-wt %. The Y-
irradiation studies showed that the radiation interacts with polymers by chain scission and cross-linking. The chain scission resulted in reduced tensile strength and elongation and the cross-linking added an increased tensile strength and reduced elongation. The negligible water uptake in the blends showed that the EPDM/SBR blends could be successfully applied in any severe outdoor weathering applications.
References


