CHAPTER 6

BLENDS OF NR AND HNBR
CHEMICAL CHANGES TAKING PLACE DURING AGING
6.1. Introduction

Stress relaxation properties assume importance in static and dynamic application under stress. The stress under a constant deformation decays by an amount substantially proportional to the logarithm of the period of deformed state. The stress relaxation measurement is considered as a high speed method for predicting the long term behavior of rubber vulcanizates.\textsuperscript{1-5} Stress relaxation of an elastomeric material is found to depend on various factors such as, composition of the mix, nature and type of cross links, cross link density, hysteresis behavior of the compound, type of plasticizers and antioxidants used and testing conditions such as, temperature, strain level and strain rate. Kalfayen, et al.\textsuperscript{6} described stress relaxation as a tool to study aging characteristics since it gives an idea about the rate of network scission and formation during aging. Bhagavan, et al.\textsuperscript{7} have been studied the stress relaxation behavior of jute fibre-nitrile rubber composites and reported a two stage relaxation pattern. Stress relaxation in rubber containing reinforcing fillers was reported by Cotton and Boonstra.\textsuperscript{8}

In this chapter the stress relaxation behavior of NR and HNBR blends was studied at different temperatures and the effect of DCNR was evaluated. The scission and cross-linking reactions taking place during aging was studied by selective solvent swelling.

The stress relaxation of the blends was studied using Zwick Universal Testing Machine, (Model 1474) at 100\degree C, 130\degree C and 150\degree C. The calculation of permanent set during stress relaxation was from the scission and cross linking reactions that take place during intermittent and continuous stress relaxation as reported by Andrews, et al.\textsuperscript{9}

For a homogeneous network in which all network chains are at equilibrium at length \( l \), the equation relating stress and elongation to attain length \( l_{u} \) in terms of concentration of network chains in rubber is given by

\[
f = s k T [ (l / l_{u})^2 - (l / l_{u}) ]
\]

Where \( f \) is the stress per unit cross-sectional area, \( s \) is the number of network chains per unit volume of rubber, \( k \) is the Boltzmann's constant and \( T \) is the absolute temperature.
Thus at a fixed extension and constant temperature, the stress produced is entirely due to load sharing of rubber chains. Hence if network chains break, then the stress would decay. There for, at any time, \( t \)

\[ f(t) \propto s(t) \]

\[ f(t)/f(0) = s(t)/s(0) \] ...........................(2)

\( f(0) \) and \( s(0) \) denote the corresponding values at time = 0.

It is possible that if any new chains are produced, then some will bear load and some may not. Hence, in a rubber sample maintained at a fixed extension, there will be two types of network. One type of network is in equilibrium with the stretched condition. If the unstretched and stretched lengths are denoted by \( l_u \) and \( l_x \) respectively and the final length or set length by \( l_s \), then we may write for the two sets of network the following two equations.

\[ f_u = s_u kT \left[ (l_s/l_u)^2 - (l_u/l_s)^2 \right] \] ...............................(3)

\[ f_x = s_x kT \left[ (l_x/l_u)^2 - (l_u/l_x)^2 \right] \] ...............................(4)

where \( f_u \) is the stress per unit attained cross sectional area which have their equilibrium at unstretched length and \( s_u \) the number of those chains. \( f_x \) and \( s_x \) are the corresponding stress and number of chains which are in equilibrium at the extended length.

For equilibrium at permanent set, \( f_u = -f_x \) .............................(5)

Substituting (3) and (4) in (5) and on simplification we get

\[ s_u l_x^2/s_x l_u^2 = l_x^3 - l_s^3/l_u^3 \] ...............................(6)

\% permanent set = \[ (l_s - l_u)/(l_x - l_u) \] \times 100 ...........................(7)

\[ = (l_s/l_u - 1)/(l_x/l_u - 1) \] \times 100 ...........................(8)

From simplification of equation (6) we get

\[ l_s/l_u = \left\{ (l_x/l_u)^3 - 1/ (s_u/s_x) (l_x/l_u)^2 + 1 \right\}^{-1/3} \] ...........................(9)

Substituting equation (9) in equation (8) we get

\% permanent set = \[ \{ C_1/(s_u/s_x) (C_2 + 1) + 1 \}^{1/3} - 1 \] \times C_3 ...........................(10)

where \( C_1, C_2 \) and \( C_3 \) are constants.

The stress value given by continuous curve is proportional to \( s_u \) and that given by intermittent curve is proportional to \( s_u + s_x \).

If \( f(t)/f(0) \) values given by continuous curve is designated as \( U \) and the difference in \( f(t)/f(0) \) values of the intermittent and continuous curves as \( X \), then
\[
\frac{s_u}{s_x} = \frac{U}{X} \\
% \text{Permanent set} = \left\{ C_1/(U/X) (C_2 + 1) + 1 \right\}^{1/3} - 1 \]

\[
C_1 = (\frac{l_x}{l_u})^3 - 1 \\
C_2 = (\frac{l_x}{l_u})^2 \\
C_3 = 100 / (\frac{l_x}{l_u}) - 1
\]

The test samples used were dumbbell pieces cut from tensile sheets vulcanized at 150°C, from mixes of NR, HNBR, 50/50 blend of NR/HNBR and blend containing 7 parts of DCNR of 15% chlorine content prepared as per Table 4.1.

6.2. Stress relaxation characteristics

The net cross-linking and chain scission reactions occurring during aging was obtained from intermittent and continuous stress relaxation studies. The stress relaxation characteristics and permanent set obtained at temperature of 130°C for 50/50 blend and blend containing DCNR are as shown in Figures 6.1 and 6.2, respectively. The experimental values of permanent set obtained for blends agreed with the calculated values and hence they obey the two-network theory of aging.\(^\text{10,11}\) The continuous and intermittent stress relaxations of the blends at 100°C and 130°C are shown in Figure 6.3 and 6.4 respectively. The change in modulus for the intermittent stress relaxation was very less at 100°C and 130°C, due to the better aging characteristics of HNBR. It had been observed earlier that the relaxed modulus of HNBR was less sensitive to temperature changes and showed a slight increase at high temperature of 140°C.\(^\text{12}\) At both 100°C and 130°C, there were more scission reactions in the absence of DCNR as a higher stress relaxation was observed for both continuous and intermittent stress relaxation measurements. Probably interfacial bonds help in having a lower stress relaxation for the blend containing DCNR. The intermittent stress relaxation also showed a lower level of chain scission for the blend containing DCNR as compared to the pure blends during aging. However, at 150°C, there was more cross-linking and more scission reactions for pure blend than DCNR containing blends as observed from Figure 6.5.
Figure 6.1. Intermittent and continuous stress relaxation along with calculated and experimental permanent set for 50/50 NR/HNBR blends at 130°C.

Figure 6.2. Intermittent and continuous stress relaxation along with calculated and experimental permanent set for the modified NR/HNBR blends at 130°C.
Figure 6.3. Intermittent and continuous stress relaxation of pure and modified NR/HNBR blends at 100°C.

Figure 6.4. Intermittent and continuous stress relaxation of pure and modified NR/HNBR blends at 130°C.
6.3. Selective solvent swelling

The scission and cross linking reactions occurring during vulcanization and aging for the individual matrices were studied by selective solvent swelling of the unaged and aged samples. The samples were subjected to aging for 70°C for 5 days, 120°C for 5 days and 150°C for one day. The aged and unaged samples were tested for selective swelling of the individual matrices by immersion in the solvents to equilibrium swelling time, which was taken as 48 hours. The solvents used were methyl ethyl ketone and n-heptane. The weight of solvent absorbed per gram of the sample was calculated from measurement of swollen weight.
6.4. Network structure of blends by selective solvent swelling

During swelling by n-heptane the NR matrix of the blend swelled highly while the HNBR phase swelled lightly and the tendency was reversed during swelling by methyl ethyl ketone. The swelling characteristics of unaged and aged pure NR, HNBR, blend and modified blend in both MEK and n heptane are shown in Table 6.1. The per cent volume of n-heptane absorbed by pure NR, HNBR, blend and modified blend is shown in Figure 6.6. The weight of n-heptane absorbed by NR matrix of the unaged blend (shown as 30°C in the figure) was the additive average of the weight of solvent absorbed by NR and HNBR. Thus the level of cross-linking of the NR phase in the blend was to the same level as observed for the pure NR vulcanizate. The weight of solvent absorbed by the blend in the presence of DCNR was less than the additive average (shown by dotted line in the figure). It was clear that there was restriction to swelling of NR phase by the lightly swollen HNBR phase and this showed the formation of interfacial cross-links. The restriction to solvent swelling by formation of interfacial bonds had been reported earlier.\textsuperscript{13-14} This was also supported by the $V_r$ values obtained from the selective solvent swelling of the blend using n-heptane and methyl ethyl ketone. (Table 6.2) DCNR added as an interface modifier in binary blends, was considered as filler during calculations of $V_r$. A higher $V_r$ values in presence of DCNR as compared to pure blends show formation of interfacial bonds.

In the case of HNBR matrix of the blend, the weight of MEK absorbed was higher than the additive average of weight of MEK absorbed by pure HNBR and NR. Thus, the HNBR matrix in the blend was not vulcanized to the same level as pure HNBR. However, there was interfacial bonds formed, as there was restriction to penetration of HNBR phase by MEK in presence of DCNR. This was due to the lower cross linking of the HNBR phase that a lower rheometric torque was registered for the blends in comparison with either NR and HNBR. The higher rheometric torque recorded for the modified blend (Figure 4.2) should be due to the formation of these interfacial bonds. The better mechanical properties of the modified blend (Table 4.5) also attributed to this.
6.5. Change in network structure during aging

NR matrix of the blend undergone cross linking reaction during aging at low temperatures and scission reactions during aging at high temperature as seen from a reduced swelling of the samples aged at 70°C for five days and 120°C for five days and a higher swelling of the samples aged at 150°C for one day. HNBR phase was less sensitive to cross link formation during aging due to the observation that the weight of MEK absorbed by aged samples remained almost same. Weight of solvent absorbed by blend containing DCNR was lower for both the aged and unaged samples. This was in agreement with the physical properties obtained for the vulcanizates after aging (Table 5.1).
Table 6.1. Weight of solvent absorbed during selective solvent swelling by aged and unaged samples.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>MEK (wt. of solvent absorbed/g of rubber)</th>
<th>n-heptane (wt. of solvent absorbed/g of rubber)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>150/1</td>
<td>120/5</td>
</tr>
<tr>
<td>NR</td>
<td>3.92</td>
<td>1.5</td>
</tr>
<tr>
<td>HNBR</td>
<td>0.23</td>
<td>0.20</td>
</tr>
<tr>
<td>NH</td>
<td>1.27</td>
<td>0.51</td>
</tr>
<tr>
<td>NHC7</td>
<td>1.05</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Table 6.2. Vr of NR and HNBR matrices, in 50/50 binary blends, assuming DCNR as filler.

<table>
<thead>
<tr>
<th>Vr</th>
<th>Parts of DCNR present</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>NR phase</td>
<td>0.102</td>
</tr>
<tr>
<td>HNBR phase</td>
<td>0.114</td>
</tr>
</tbody>
</table>
6.6. Conclusion

Stress relaxation studies showed that during aging, NR matrix underwent cross linking at lower temperature and scission at higher temperature, whereas HNBR phase was less sensitive towards temperature up to 150°C. In the case of NR/HNBR blend, there were more scission reactions in the absence of DCNR. Solvent swelling studies also showed that, there was restriction to swelling of NR phase by the lightly swollen HNBR phase in the presence of DCNR indicating interfacial bonds which was further supported by Vr values.

References