CHAPTER 6

THERMAL STUDIES OF BLENDS OF WHOLE TYRE RUBBER WITH NATURAL RUBBER AND SYNTHETIC RUBBERS

In the previous chapters utilisation of reclaimed rubber (WfR) in different blends is discussed. It is found that blending of whole tyre reclaim with virgin rubber results in improvement in mechanical properties and cure characteristics. In this chapter thermal property of the blends of WfR with natural rubber, butadiene rubber, acrylonitrile rubber and styrene butadiene rubber is discussed.

PART 1

Thermal analysis of blends of whole tyre reclaim with Natural rubber and Butadiene rubber

61.1. Preparation of blends

In this experiment blends of whole tyre reclaim with natural rubber and butadiene rubber are prepared and its thermal stability is evaluated using Thermogravimetric analysis. The formulation of the mixes is given in the table 6.1.1. Sample preparation and test method employed are given in the chapter 2.
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Table 6.1.1. Formulation of the mixes

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mix No</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
</tr>
<tr>
<td>NR</td>
<td>100</td>
<td>80</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BR</td>
<td>-</td>
<td>-</td>
<td>100</td>
<td>80</td>
</tr>
<tr>
<td>WfR</td>
<td>-</td>
<td>40</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.5</td>
<td>2.5</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>MBTS</td>
<td>0.5</td>
<td>0.5</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>TMTD</td>
<td>0.2</td>
<td>0.2</td>
<td>0.4</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Note: NR - Natural rubber, BR- butadiene rubber, WTR- whole tyre reclaim. ZnO - 5 g, Stearic acid - 2 g, 4020 - 1 g are common to all mixes. Weight of the reclaimed rubber is adjusted so as to get rubber hydrocarbon of 100.

Thermal Analysis

The thermal degradation of the blends was studied by Universal V3. 2B T A Instrument. All the analyses were carried out using 10 mg samples on platinum pan in an atmosphere of nitrogen. The heating rate of was 10° C/ minute.

![Figure 6.1.1 TGA curve of NR gum and NR/ WTR blend](image)

Figure 6.1.1 TGA curve of NR gum and NR/ WTR blend
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Figure 6.1.2 DTA of NR/WTR blend

Figure 6.1.3. TGA curve of BR gum and BR/ WTR blend
Table 6.1.4. DTA of BR/WTR blend

Figure 6.1.1 to figure 6.1.4 represent TGA curves of the mixes A to D. Percentage of mass loss of the substance is plotted against temperature. The following characteristics were noted from the thermogravimetric curves: the temperature of onset of degradation (T_i), temperature at which the rate of decomposition is maximum (T_{max}) and the weight of residue at 600 °C and are tabulated in the table 6.1.2.

Table 6.1.2 Degradation characteristics of WTR blends

<table>
<thead>
<tr>
<th>Mix No</th>
<th>T_i (°C)</th>
<th>T_{max} (°C)</th>
<th>Residue (%)</th>
<th>Peak rate of decomposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix A</td>
<td>343.62</td>
<td>430</td>
<td>6.20</td>
<td>1.4</td>
</tr>
<tr>
<td>Mix B</td>
<td>341.98</td>
<td>431</td>
<td>10.31</td>
<td>1.1</td>
</tr>
<tr>
<td>Mix C</td>
<td>357.07</td>
<td>509</td>
<td>5.13</td>
<td>1.6</td>
</tr>
<tr>
<td>Mix D</td>
<td>356.83</td>
<td>515</td>
<td>12.46</td>
<td>1.1</td>
</tr>
</tbody>
</table>

From 6.1.1 and 6.1.2 it is clear that the degradation pattern of NR is not significantly altered by the presence of WTR. Both the mixes A and B have the almost similar temperature of initiation of degradation and the temperature of peak rate of degradation (T_{max}). This may be arising from the fact that the WTR predominantly consists of natural rubber. The rate of
degradation at \(T_{\text{max}}\) is however higher for the NR gum compound. The lower rate of degradation for the WTR blend may be attributed to the WTR contains only about 50\% of rubber hydrocarbon that is involved in the degradation reaction. The actual rubber hydrocarbon in the blend is about 83\% and the observed rate of degradation of the blend is approximately 80\% of the virgin natural rubber. The weight of residue at 600 °C is higher for mix B. The 6.2 \% of the residue for the mix A is mainly due to the presence of 5 \% of zinc oxide included in the recipe. The higher residue of the blend may be attributed to the presence of inorganic fillers in the WTR.

Figure 6.1.3 and 6.2.4 show the thermal degradation of Butadiene and its blends with WTR. Though the overall pattern of degradation is the same, there is marked improvement in the thermal stability of the BR in the presence of WTR. While the \(T_i\) is shifted from 357.07 °C to 356.83 °C, the peak degradation is temperature is shifted from 509.69 °C to 515.26 °C in the case of mix containing WTR. The improved thermal stability of the blend may be attributed to the combined effect of reinforcing filler in WTR and the higher cross-link density. The rate of degradation is lower in the case of butadiene blend also. The residue at 600 °C is higher for the blend.

The order of the degradation reaction was calculated by the Freeman- Carroll\(^{(1)}\) method using the equation

\[
(\Delta \log \frac{dW}{dt}) = n \cdot \Delta \log W_r - (\Delta E/2.3 \cdot R) \cdot \left(\frac{1}{T}\right)
\]

where \(dW/dt\) is the rate of reaction, \(n\) is the order of reaction, \(R\) is the gas constant and \(T\) is the absolute temperature and \(W_r\) is proportional to the amount of reactant remaining.

The above equation can be rearranged to

\[
\frac{\Delta \log dW/dt}{\Delta \log W_r} = n - \frac{\Delta E/2.3 \cdot R}{\Delta \log W_r} \cdot \frac{1}{T}
\]

The order and activation energy can be obtained from the intercept and gradient of the plots of the left side of the equation (2) versus \(\Delta (1/T)/\Delta \log W_r\). Figure 6.1.5 and 6.1.6 represents plot of \((\Delta \log dW/dt)/\Delta \log W_r\).
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$\Delta \log W_r$ against $\Delta (1/T) / \Delta \log W_r$ of NR gum and NR/WTR blend respectively. Intercepts shows the degradation reaction follows first order reaction mechanism. Similarly Figure 6.1.7 and 6.1.8 represents plots of $(\Delta \log dW/dt)/\Delta \log W_r$ against $\Delta (1/T) / \Delta \log W_r$ of BR gum and BR/WTR blend respectively. Intercepts of the plot indicates that the degradation reaction follows first order mechanism.

Figure 6.1.5 Freeman-Carroll plot for NR gum

Figure 6.1.6 Freeman-Carroll plot for NR blend

180
Figure 6.2.7 Freeman-Carroll plot for BR gum

Figure 6.2.8 Freeman-Carroll plot for BR blend
PART 2
Effect of silane coupling agent and Maleic anhydride on thermal stability

In this section the thermal degradation of WTR/NBR and WTR/SBR blends are discussed. The effect of grafting of maleic anhydride and use of coupling agent on the thermal stability of the blend is also discussed.

6.2.1. Preparation of blends

Blends of NBR and SBR with WTR were prepared in a blend ratio 80:40. Formulation of the mixes is given in the table 6.2.2. Sample preparation and test method employed are given in the chapter 2.

Table 6.2.1. Formulation of the mixes

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mix. No</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>NBR</td>
<td>100</td>
</tr>
<tr>
<td>SBR</td>
<td>---</td>
</tr>
<tr>
<td>WTR</td>
<td>---</td>
</tr>
<tr>
<td>WTR MA-g-WTR</td>
<td>---</td>
</tr>
<tr>
<td>Si 69</td>
<td>---</td>
</tr>
</tbody>
</table>

Note: NBR - Acrylonitrile butadiene rubber. WTR whole tyre reclaim SBR-styrene butadiene rubber. ZnO - 5 g, Stearic acid - 2 g, 4020 - 1 g, MBTS - 0.8 g, TMTD - 0.4 g, Sulphur - 2 g are common to all mixes. Amount of WTR was adjusted so as to get 100 grams of rubber hydrocarbon.
Figure 6.2.1. TGA curve of different blends of NBR blends with WTR

Figure 6.2.2. DTA of NBR/WTR blend
Figure 6.2.3. TGA curve of different blends of SBR blends with WTR

Figure 6.2.4 DTA of SBR/WTR blends

Figure 6.2.1 to 6.2.4 represent TGA curve of blends of whole tyre reclaim with acrylonitrile butadiene rubber and styrene butadiene rubber (mixes A to H). Percentage of mass loss of the substance is plotted against temperature. The temperature of onset of the weight loss, temperature peak rate of degradation, the higher rate of degradation and the weight of residue are given in the table 6.2.2.
Table 6.2.2 Degradation characteristics of NBR/WTR and SBR/WTR blends

<table>
<thead>
<tr>
<th>Material</th>
<th>Ti °C</th>
<th>T_max °C</th>
<th>Higher rate of degradation</th>
<th>Residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix A</td>
<td>377</td>
<td>497</td>
<td>1.25</td>
<td>6.28</td>
</tr>
<tr>
<td>Mix B</td>
<td>376</td>
<td>496</td>
<td>0.988</td>
<td>12.02</td>
</tr>
<tr>
<td>Mix C</td>
<td>310</td>
<td>465</td>
<td>0.85</td>
<td>12.38</td>
</tr>
<tr>
<td>Mix D</td>
<td>379</td>
<td>495</td>
<td>1.17</td>
<td>12.49</td>
</tr>
<tr>
<td>Mix E</td>
<td>385</td>
<td>490</td>
<td>1.325</td>
<td>6.05</td>
</tr>
<tr>
<td>Mix F</td>
<td>363</td>
<td>503</td>
<td>0.875</td>
<td>15.11</td>
</tr>
<tr>
<td>Mix G</td>
<td>342</td>
<td>463</td>
<td>0.825</td>
<td>15.58</td>
</tr>
<tr>
<td>Mix H</td>
<td>373</td>
<td>503</td>
<td>0.903</td>
<td>16.46</td>
</tr>
</tbody>
</table>

Figure 6.2.1 and 6.2.2 represent TGA of different compounds of nitrile rubber (mix A to D). The figure 6.2.2 shows nitrile rubber whole tyre reclaim blend-containing MA-g-WTR shows lower onset temperature. All other mix has almost same onset temperature. The major degradation reaction occurs around 496 for first three mixes. The blend with coupling agent shows lower T_max showing low thermal stability. Rate of degradation is maximum for gum compounds. Since WTR contain only 50% of rubber hydrocarbon addition of whole tyre reclaim to the NBR matrix normally reduce amount of rubber hydrocarbon and thus reduces the rate of degradation. As in the case of blends of whole tyre reclaim with natural rubber and butadiene rubber ash content of the blend of nitrile rubber also higher than the gum compound.

In the case of SBR/WTR blends TGA pattern is almost identical (Figure 6.2.3 to 6.2.4) in all cases. Onset temperature of the blends decreases with the addition of reclaim to styrene butadiene matrix. Blend contains MA-g-WTR show relatively low onset temperature. T_max increases with the addition of reclaim to the styrene butadiene matrix indicating higher thermal stability. But blend with MA-g-WTR shows lower T_max. Like NBR
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compounds, rate of degradation of SBR gum compound is higher compared to the blend. This may be attributed to the presence of lower quantity of the rubber hydrocarbon in the blend. In the styrene butadiene blend also higher amount of ash content is obtained, due to the presence of other inorganic filler in the reclaim.

Figure 6.2.5 and 6.2.6 represent Freeman Carroll plots for different blends of acrylonitrile rubber and styrene butadiene with whole tyre reclaim. As in the case of natural rubber and butadiene rubber order of the degradation reaction can be evaluated from the plots of $\frac{\Delta \log dW/dt}{\Delta \log Wr}$ against $\Delta (1/T) / \Delta \log Wr$. The order and activation energy can be obtained from the intercept and gradient. Intercepts of the plot indicate that the degradation reaction follows first order mechanism.

![Freeman Carroll plot for NBR compounds](image)

Figure 6.2.4 Freeman -Carroll plot for NBR compounds
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6.4. Conclusion

Thermal stability of the blends of whole tyre reclaim with various rubbers such as Natural rubber, Butadiene rubber, Acrylonitrile butadiene rubber and Styrene butadiene rubber were evaluated thermogravimetrically. The incorporation of WTR into these rubbers does not alter the temperature of onset degradation. However, peak degradation temperature is increased in the case of NR, BR and SBR showing higher thermal stability. No significant change in $T_{\text{max}}$ occurred in the NBR compounds on WTR blending. The modification of by maleic anhydride grafting decreases the thermal stability indicated by the lower peak degradation temperature. Use of silane coupling agent results in higher $T_{\text{max}}$. This shows that use of silane coupling agent is a better choice in this regard. Kinetic study shows that the degradation reaction follows first order kinetics.

6.5. Reference


Figure 6.2.5 Freeman-Carroll plot for SBR compounds.