Chapter 8

Thermal Characteristics

The results of this chapter have been accepted for publication in
Polymer Degradation and Stability
Thermal behaviour of polymers is of much importance as a tool in materials characterisation. Thermal analysis of polymers is important as it plays a major role in the use of polymeric materials in many consumer oriented applications. Fabrication of a variety of articles and their end uses need a detailed understanding of the thermal degradation of polymers.

One of the widely accepted methods for studying the thermal properties of polymeric materials is thermogravimetry (TG). Thermogravimetric data will provide the number of stages of thermal breakdown, weight loss of the material in each stage, threshold temperature, etc. Both thermogravimetry (TG) and derivative thermogravimetry (DTG) provide information about the nature and conditions of degradation of the material. Compatibility of the polymer blends can be studied by differential scanning calorimetry (DSC). This will give the glass transition temperature (Tg) and melting temperature (Tm) of the polymeric material. Miscible blends will show single, sharp transition peak (Tg) intermediate between that of the blend components. Separate peaks will be obtained for immiscible blends. In the case of borderline miscible blends, broad transition peaks are obtained.

Blending of polymers has been reported to have much influence on the thermal stability of individual polymers. The compatibility plays an important role in the overall thermal stability of the blends. Several authors have analysed the thermal properties of blends.

The aim of this chapter is to study the thermal properties of NR/PS blends with and without the addition of the compatibiliser (NR-g-PS). The thermal stability of the blends has been analysed by thermogravimetry. Differential scanning
calorimetry has been used to analyse the glass transition temperatures of the blends. The effects of blend composition and compatibiliser loading on the thermal properties have been analysed.

8.1 Results and discussion

8.1.1 Thermogravimetry (TG)

Thermogravimetric plots of NR and PS are given in Figures 8.1 and 8.2, respectively. Three regions of temperatures (up to 250°C, 250-450°C, and higher than 450°C) are considered in discussing the thermal stability of NR. Below 250°C, solid rubber is quite stable. In the absence of oxygen crude rubber may be kept for long periods with no loss of low-molecular weight products from thermal reactions. Degradation of NR occurs in two steps. First step degradation starts at about 267°C and will be completed at 458°C. During this stage 85.88% weight loss is observed and volatilisation becomes rapid and substantially complete distillation will be occurred. According to Bolland and Orr\(^7\) there is little or no loss of unsaturation of bulk rubber in the temperature range of 200-270°C, although the rubber is undergoing both scission and crosslinking. The second step degradation starts at 460°C and will be completed at 600°C. During this stage, weight loss obtained is 11.11%. About 3.01% pot residue remains above 600°C which is insoluble and intractable and has been likened to cyclised rubber. The first step degradation occurs at a sharp rate compared to second step degradation. The weight loss observed at 300°C is 3.6% and that at 400°C is 78.5%. In the DTG curve, the major peak is observed at 373°C. This corresponds to the complete distillation of NR. Above 300°C, volatilisation becomes rapid. Complete distillation occurs in 30 minutes at temperature near 400°C. Degradation of NR can be explained by the following chemical reactions.\(^8\) A variety of products are obtained; of which the common product is levulinaldehyde.
Figure 8.1. TG and DTG curves of NR.

Figure 8.2. TG and DTG curves of PS.
\[ R\cdot + O_2 \rightarrow ROO\cdot \]
\[ ROO\cdot + RH \rightarrow ROOH + R\cdot \]
\[ 2ROOH \rightarrow ROO\cdot + RO\cdot + H_2O \]

\[
\begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \\
\text{CH}_2-C=CH-\text{CH}_2-\text{CH}_2-C=CH \quad \text{ROO}.
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \\
\text{CH}_2-C=CH-\text{CH}_2-\text{CH}_2-C=CH \quad \text{ROO}.
\end{array}
\]

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\begin{array}{c}
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\text{CH}_2-C=CH-\text{CH}_2-\text{CH}_2-C=CH \quad \text{ROO}.
\end{array}
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\end{array}
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\end{array}
\]

\[
\begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \\
\text{CH}_2-C=CH-\text{CH}_2-\text{CH}_2-C=CH \quad \text{ROO}.
\end{array}
\]
In the case of polystyrene, degradation is observed in a single step (Figure 8.2). Up to 240°C it is stable and thereafter a sharp degradation occurs. Degradation will be completed at 510°C and during this stage the weight loss observed is 99.05%, i.e., above 510°C no residue remains because the products of degradation are volatile. The weight loss at 300°C is 3.53% and that at 400°C is 84.9%. In the DTG curve, the major peak is observed at 372°C which corresponds to the complete chain scission to volatile monomers along with minute amounts of dimer, trimer, tetramer and pentamer. Polystyrene degrades at elevated temperature (above 300°C) to a mixture of low molecular weight compounds. These include styrene (40%), toluene (2.4%), methyl styrene (0.5%) and other products having an average molecular weight of 264.

In the case of PS, the degradation depends upon whether it is above or below 300°C. Between 200-300°C the molecular weight falls, but no volatile products are evolved. Below 300°C, random scission probably involves initial homolysis as shown below.

\[
\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH} \rightarrow \text{CH}_2-\text{CH}_2 + \text{CH}_2
\]

Since below 300°C no volatile products results, (A) and (B) are believed to undergo a cage disproportionation. In this temperature range depolymerisation does not occur. The products (C) and (D) are stable up to 300°C.

As compared to the degradation pattern of individual components, degradation behaviour of the blend is slightly different. It has been reported that a
marginal stability can be achieved by the incorporation of a second polymer. The TG and DTG plots of different NR/PS blends are given in Figures 8.3-8.5. All DTG curves show two peaks, a minor peak and a major one. These correspond to the respective monomer evolution. Table 8.1 gives the DTG peak values of different blends. The first peak value near 400°C corresponds to NR degradation and the second peak value near around 440°C corresponds to PS degradation. In the case of blends, two peaks are obtained in all the cases, corresponding to the degradation of the two component polymers NR and PS. It was found that as the NR content increases, both these peak values increase. The temperatures at which degradation start are 140, 193 and 250°C for S40, S50 and S60 NR/PS blends respectively. As the NR content increases, improvement in the initial decomposition behaviour of the blends is observed.

Figures 8.3. TG and DTG curves S40.
Figures 8.4. TG and DTG curves $S_{80}$

Figures 8.5. TG and DTG curves $S_{81}$
Table 8.1. DTG peak values of different NR/PS blends.

<table>
<thead>
<tr>
<th>Samples</th>
<th>1st peak (°C)</th>
<th>2nd peak (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_{40}</td>
<td>391.2</td>
<td>434.6</td>
</tr>
<tr>
<td>S_{50}</td>
<td>392.8</td>
<td>437.8</td>
</tr>
<tr>
<td>S_{60}</td>
<td>393.9</td>
<td>440.6</td>
</tr>
<tr>
<td>S_{G_a}</td>
<td>395.8</td>
<td>438.2</td>
</tr>
<tr>
<td>S_{G_b}</td>
<td>395.9</td>
<td>440.9</td>
</tr>
<tr>
<td>S_{G_c}</td>
<td>395.9</td>
<td>442.2</td>
</tr>
</tbody>
</table>

McNeill and Gupts\(^{10}\) reported using thermogravimetry that both the rate of volatile formation and the rate of chain scission of polyisoprene are reduced when blended with polystyrene. In the pyrolysis of polyisoprene/ polystyrene blends, each component degrades in a manner different from that observed when polyisoprene is degraded separately. But the products of pyrolysis are identical both qualitatively and quantitatively. PS appears to be stabilised against thermal degradation at 340°C when blended with polyisoprene alone although its chain scission appears to be accelerated at 292°C. It can be explained by assuming that polyisoprene generates small radicals during chain scission in the first stage of degradation. As these radicals diffuse into the polystyrene phase, hydrogen abstraction takes place, and the radicals which would normally contribute to degradation of the polyisoprene (PI) are thus stabilised. Subsequently PS chains undergo scission at sites adjacent to the radical centres. The resulting PS radicals decompose slowly below 300°C. Above this temperature, there is an apparent inhibition of its depolymerisation by dipentene formed from the degradation of PI. This inhibition could result through the hydrocarbon abstraction by PS radicals from the dipentene or by coupling.

The weight loss of component polymers and the different blends are given in Table 8.2. It can be seen that at 300 and 400°C, the weight loss of the blend is lower than the blend components. It reveals that blending can improve the thermal
properties of the materials. As the NR content increases, the weight loss increases at both the temperatures. This is because NR is more susceptible to thermal degradation as compared to polystyrene.

Table 8.2. Weight loss of various NR/PS blends.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight loss at 300°C (%)</th>
<th>Weight loss at 400°C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>3.60</td>
<td>78.5</td>
</tr>
<tr>
<td>PS</td>
<td>3.53</td>
<td>84.9</td>
</tr>
<tr>
<td>40/60 NR/PS (S40)</td>
<td>0.84</td>
<td>33.7</td>
</tr>
<tr>
<td>50/50 NR/PS (S50)</td>
<td>1.01</td>
<td>36.4</td>
</tr>
<tr>
<td>60/40 NR/PS (S60)</td>
<td>1.67</td>
<td>38.6</td>
</tr>
</tbody>
</table>

Compatibiliser has much influence on the thermal properties of the blends (Figures 8.6-8.9). For 50/50 NR/PS blends without compatibiliser, the degradation starts at 190°C. Upon the addition of 1.5% graft copolymer, the degradation temperature was raised to 214°C. Further addition of 1.5% graft copolymer (total 3%) raised the degradation temperature to 227°C. Finally, the temperature at which degradation starts was raised to 250°C upon the addition of 4.5% graft copolymer. This is because, the graft copolymer addition improves the compatibility which in turn will be reflected in the thermal properties. Table 8.3 gives the weight loss at 300 and 400°C. Weight loss is decreased upon the addition of the compatibiliser throughout the temperature range which in turn is an indication of improvement of thermal properties. The morphology of the different NR/PS blends are shown in Figure 4.3 indicates the compatibilising action of the copolymer (NR-g-PS). In the case of blend without compatibiliser (Figure 4.3a) the domain size is higher. Upon compatibiliser loading, the domain size decreases (Figures 4.3b–4.3d) which is an indication of interfacial saturation.
Figures 8.6. TG and DTG curves $SG_a$

Figures 8.7. TG and DTG curves $SG_b$
Figures 8.8. TG and DTG curves SG$_a$

Figures 8.9. TG and DTG curves SG$_d$
8.1.2 Differential scanning calorimetry studies (DSC)

The thermal behaviour of NR/PS blends with and without the addition of graft copolymer was analysed by DSC. Figure 8.10 shows the DSC traces of NR and PS. Glass transition temperature (Tg) was recorded at the half height of the corresponding heat capacity jump. The glass transitions of pure NR and PS are found to be -49 and +101°C, respectively. Glass transition values of the various blends without and with the graft copolymer are given in Tables 8.4 and 8.5, respectively. The blends show two glass transitions even the presence of the graft copolymer are shown in Figures 8.11 and 8.12. This reveals that the blends are incompatible and phase separated. This is in agreement with the conclusions made by Paul\textsuperscript{11} who suggested that if two polymers are far from being miscible, then no copolymer is likely to make one phase system, the main role of the copolymer is to act as an interfacial agent.

### Table 8.3. Weight loss of NR/PS blends (compatibilised).

<table>
<thead>
<tr>
<th>Percentage of graft copolymer</th>
<th>Weight loss at 300°C (%)</th>
<th>Weight loss at 400°C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.01</td>
<td>36.04</td>
</tr>
<tr>
<td>1.5</td>
<td>0.92</td>
<td>34.19</td>
</tr>
<tr>
<td>3</td>
<td>0.91</td>
<td>32.9</td>
</tr>
</tbody>
</table>

### Table 8.4. Glass transition temperature of different NR/PS blends.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg value (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>-49</td>
</tr>
<tr>
<td>PS</td>
<td>+102</td>
</tr>
<tr>
<td>$S_{40}$</td>
<td>-49 and +113</td>
</tr>
<tr>
<td>$S_{50}$</td>
<td>-52 and +101</td>
</tr>
<tr>
<td>$S_{60}$</td>
<td>-52 and +112</td>
</tr>
</tbody>
</table>
Table 8.5. Glass transition of different NR/PS blends (compatibilised).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg value (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{S0}$</td>
<td>-52 and +101</td>
</tr>
<tr>
<td>$SG_a$</td>
<td>-54 and +118</td>
</tr>
<tr>
<td>$SG_b$</td>
<td>-55 and +119</td>
</tr>
<tr>
<td>$SG_c$</td>
<td>-54 and +112</td>
</tr>
</tbody>
</table>

Figure 8.10. DSC curves of (A) NR and (B) PS.
Figure 8.11. DSC curves of NR/PS blends (Non-compatibilised) (A) S_{40}, (B) S_{50}, (C) S_{60}.

Figure 8.12. DSC curves of NR/PS blends (compatibilised) (A) S_{50}, (B) S_{G_a}, and (C) S_{G_b}. 
8.2 References


