6.1 Introduction

Thermal degradation of polymers can be considered to be the effect of different concurrent chemical reactions, which are often accompanied by other physical phenomena such as evaporation and ablation [1], that introduce further complications in the modelling of the degradation kinetics. The development of affordable models able to describe the degradation kinetics of polymers has been the concern of many authors [2-6]. The macroscopic phenomenon observed during thermal degradation of polymers is the loss of weight caused by elimination of low molecular weight substances produced by chain unzipping and free radical reactions and by other physical phenomena, such as plasticiser and solvent evaporation [7-11]. Thermal analysis of polymers is an important method in
the characterisation of polymers and in establishing service conditions. The threshold temperature for breakdown determines the upper limit of temperature in fabrication [12,13].

Thermogravimetric analysis (TGA) can help in understanding the degradation mechanism and thus assist any effort to enhance the thermal stability of a polymeric material. This analysis needs only a small quantity of the sample. Thermogravimetric data provide the different stages of thermal breakdown, weight of the material in each stage, threshold decomposition temperature etc. Both TG and differential thermogravimetry (DTG) curves provide information about the nature and conditions of degradation of materials. Thus, thermogravimetric analyser, which measures weight loss as a function of time (isothermal test) and temperature (dynamic test at constant heating rate) [14] is the most suitable instrument for these studies. For a system that loses material while it is reacting, weight loss can be related to the degree of reaction. In this case, it is possible to correlate the TGA measurements directly with the extent of degradation reaction, the values of which are the sum of all the possible reactions that give rise to weight loss during the degradation process. This fact precludes the use of TGA for kinetic studies where many different modes of degradation occur simultaneously. The kinetic parameters such as activation energy and the reaction order can be calculated using both dynamic and isothermal tests [15].

The thermal stability of individual polymers can be enhanced to a greater extent by blending them with other polymers or by reinforcing with fibres [16-21]. Navarro et al. has reported the thermal degradation of recycled polypropylene toughened with elastomers [22]. Agung et al. [23]
has evaluated the thermal characteristic of abaca fibre reinforced high impact polystyrene (HIPS) composites. The thermal stability of polypropylene composites reinforced with short carbon fibres were studied by Rezaei et al. [24]. Smita et al. [25,26] have evaluated the thermal behaviour of MAPE treated jute/HDPE and MAPP treated sisal/PP composites. The influence of short glass fibre on the thermal stability of PP/EPDM was evaluated by Weizhi et al. [27].

This chapter attempts to analyse the thermal degradation of PS/NR blend with respect to the blend ratio, dynamic vulcanisation, effect of short Nylon-6 fibre, RFL-coated Nylon-6 fibre; and untreated and surface treated Nylon fibre in conjunction with a compatibiliser.

6.2 Experimental

The formulation of the blends and composites are given in Table 6.1. PS/NR blends and its composites based on short Nylon-6 fibres were prepared by melt-mixing in a Thermo Haake Polylab QC, followed by compression moulding as described in Chapter 2.

Table 6.1 Formulation of the mixes.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Mix No.</th>
<th></th>
<th></th>
<th></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>
<td>E</td>
<td>F</td>
<td>G</td>
</tr>
<tr>
<td>PS*</td>
<td>100</td>
<td>0</td>
<td>85</td>
<td>85</td>
<td>85</td>
<td>85</td>
<td>85</td>
</tr>
<tr>
<td>NR*</td>
<td>0</td>
<td>100</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Dicumyl peroxide (phr)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2(2.8)**</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Untreated N6 fibre [F(U)] (wt.%)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>RFL-coated N6 fibre [F(R)] (wt.%)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Surface Treated N6 fibre[F(T)] (wt.%)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>MA-g-PS wt. (%)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.75</td>
<td>0.75</td>
</tr>
</tbody>
</table>

*parts per hundred polymer
** Concentration expressed in milliequivalents.

6.3 Results and Discussions

6.3.1 Effect of blend ratio & dynamic vulcanisation

The derivative TGA (DTG) of polystyrene (PS), natural rubber (NR) and 85/15 PS/NR blend are shown in Figure 6.1. The temperature of onset of decomposition ($T_i$), maximum decomposition temperature ($T_{\text{max}}$), peak rate of decomposition ($R_{\text{max}}$), temperature at 50 % loss and residual weight at 600 °C are given in Table 6.2.

![Figure 6.1: DTG curve of PS, NR and 85/15 PS/NR blend.](image)

It is clear from the Figure 6.1 and Table 6.2 that PS starts to degrade at a temperature of 262 °C in a single step with a maximum decomposition rate of 16 %/min. While NR starts degradation at a lower temperature of 227 °C in a single step with maximum rate of decomposition of 16.6 %/min. The temperatures at which maximum degradation occurs are about 380 °C and 350 °C for PS and NR, respectively. The temperature at which 50 %
Thermal degradation of blends and composites based on Polystyrene/Natural rubber and Nylon-6 fibre

loss of material occurs is higher for PS (368 °C) in comparison to NR (350 °C). In the case of 85/15 PS/NR blend, the onset of decomposition is similar to that of PS as the amount of NR in the blend is low. However, the temperature of maximum decomposition increases to 389 °C. But the peak rate of decomposition increases from 16 to 18.4 %/min. The temperature at 50 % degradation of the blend increased from 368 to 377 °C.

With the dynamically vulcanised blends, the onset temperature of decomposition has increased to 270 °C when compared to the unvulcanised blend. However, there is no change in the temperature of maximum decomposition, the peak rate of decomposition and the temperature at 50 % degradation for the dynamically vulcanised blends. The DTG curve of the unvulcanised and vulcanised blend are shown in Figure 6.2. The residue remaining at 600 °C is higher for the dynamically vulcanised blends when compared to the unvulcanised blend. This may be attributed to the presence of extender such as calcium carbonate or clay present in 40 % active dicumyl peroxide (DCP). The dynamically vulcanised blends have improved thermal stability than the unvulcanised blends.
Table 6.2 Thermal degradation characteristics of PS/NR blend.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Mix No.</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset of decomposition (T&lt;sub&gt;i&lt;/sub&gt;), °C</td>
<td>A 262</td>
<td>B 227</td>
<td>C 260</td>
<td>D 270</td>
</tr>
<tr>
<td>Maximum decomposition Temp. (T&lt;sub&gt;max&lt;/sub&gt;), °C</td>
<td>382</td>
<td>350</td>
<td>389</td>
<td>389</td>
</tr>
<tr>
<td>Peak rate of decomposition (R&lt;sub&gt;max&lt;/sub&gt;) %/min</td>
<td>16</td>
<td>16.6</td>
<td>18.4</td>
<td>18.3</td>
</tr>
<tr>
<td>Temp. at 50 % loss (T&lt;sub&gt;50&lt;/sub&gt;), °C</td>
<td>368</td>
<td>350</td>
<td>377</td>
<td>378</td>
</tr>
<tr>
<td>Residue at 600 °C (%)</td>
<td>0.06</td>
<td>0.3</td>
<td>0.07</td>
<td>0.17</td>
</tr>
</tbody>
</table>

The kinetics of the degradation reaction was studied by using the Freeman-Carroll method [28]. According to this method

\[
\Delta \log \left(\frac{dW}{dt}\right) = n \cdot \Delta \log W_r - \left(\Delta E / 2.3 R\right) \Delta (1/T) \quad .................. (6.1)
\]

where \(dW/dt\) is the rate of reaction,

\(n\) is the order of reaction,

\(R\) is the gas constant,
Thermal degradation of blends and composites based on Polystyrene/Natural rubber and Nylon-6 fibre

E is the activation energy,

T is the absolute temperature, and

W_r is proportional to the amount of reactant remaining.

The above equation can be rearranged to

\[
\frac{\Delta \log dW / dT}{\Delta \log W_r} = n - \frac{\Delta (E / 2.3R) \Delta (1/T)}{\Delta \log W_r} \quad \text{................................(6.2)}
\]

The order of the reaction can be obtained from the intercept of the plot of the left hand side of equation (6.2) versus \( \Delta (1/T) / \Delta \log W_r \) and such a plot is given in Figure 6.3. A common line with an intercept of one can be drawn to represent all the data points showing that the degradation of the 85/15 PS/NR blend follow first order kinetics. Freeman-Carroll plot of the dynamically vulcanised is shown in Figure 6.4. The intercept shows that the degradation of the dynamically vulcanised blends also follow first order kinetics.

![Figure 6.3: Freeman-Carroll plot of 85/15 PS/NR blend.](image)
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6.3.2 Effect of short Nylon-6 fibres

The DTG curve of untreated and RFL-coated Nylon fibre composites are shown in Figure 6.5. The corresponding $T_i$, $T_{max}$, $R_{max}$, temperature at 50% loss and residue are given in Table 6.3.
Table 6.3  Thermal degradation characteristics of untreated and RFL-coated fibre composites.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Mix No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Onset of decomposition (T_i) °C</td>
<td>260</td>
</tr>
<tr>
<td>Maximum decomposition Temp. (T_{max}) °C</td>
<td>389</td>
</tr>
<tr>
<td>Peak rate of decomposition (R_{max}) %/min</td>
<td>18.4</td>
</tr>
<tr>
<td>Temp. at 50 % loss (T_{50}) °C</td>
<td>377</td>
</tr>
<tr>
<td>Residue at 600 °C (%)</td>
<td>0.07</td>
</tr>
</tbody>
</table>

The onset temperature of decomposition of the composites is higher compared to that of the unreinforced blends. The temperature at which peak degradation occurs is increased slightly from 380 °C to 383 °C for RFL-coated fibre composites when compared to untreated fibre composites. The T_{max} is, however, slightly lower compared to the blends. The peak rate of decomposition is reduced for RFL-coated fibre composites (18.4 %/min) in comparison to untreated fibre composites (20.1 %/min). This may be due to the better interaction between the fibre and the matrix. The temperature at 50 % loss and the residue remaining at 600 °C remains identical for both the composites.

The Freeman-Carroll plots for the degradation of the composites with 1 wt.% untreated and RFL-coated Nylon fibre given in Figure 6.6 and 6.7 respectively. The intercepts at one indicates that the degradation follows first order kinetics. Similar results have been reported by Kutty et al. [16] and Seema et al. [20] in the case of short Kevlar fibre-thermoplastic polyurethane composite and Nylon-6 fibre SBR composites, respectively.
6.3.3 Effect of surface treated fibre and the use of a compatibiliser

The DTG curve of untreated and surface treated fibre in conjunction with the compatibiliser and its degradation characteristics are given in Figure 6.8 and Table 6.4.
Thermal degradation of blends and composites based on Polystyrene/Natural rubber and Nylon-6 fibre

Figure 6.8: DTG curves of untreated and treated fibre composites containing compatibiliser.

Table 6.4 Thermal degradation characteristics of untreated and treated fibre composites with compatibiliser.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Mix No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E</td>
</tr>
<tr>
<td>Onset of decomposition $(T_i) ^\circ C$</td>
<td>270</td>
</tr>
<tr>
<td>Maximum decomposition Temp. $(T_{\text{max}})$ $^\circ C$</td>
<td>380</td>
</tr>
<tr>
<td>Peak rate of decomposition $(R_{\text{max}})$ %/min</td>
<td>20.1</td>
</tr>
<tr>
<td>Temp. at 50% loss $(T_{50}) ^\circ C$</td>
<td>373</td>
</tr>
<tr>
<td>Residue at 600 $^\circ C$ (%)</td>
<td>0.07</td>
</tr>
</tbody>
</table>

The degradation of untreated and treated Nylon fibre composites in conjunction with compatibiliser starts at a higher temperature in comparison to composites without compatibiliser. Similarly the maximum temperature of decomposition of composites in the presence of compatibiliser increases slightly when compared to the one without compatibiliser.
Figure 6.9: Freeman-Carroll plot of PS/NR composites with untreated fibre and compatibiliser.

Figure 6.10: Freeman-Carroll plot of PS/NR composites with treated fibre and compatibiliser.

The peak rate of decomposition reduces significantly to 16.3 % for treated fibre composites along with compatibiliser. This implies an improved thermal stability of treated fibre composites containing compatibiliser when
Thermal degradation of blends and composites based on Polystyrene/Natural rubber and Nylon-6 fibre compared to untreated one. This may be due to the strong interaction between fibre and matrix in the presence of compatibiliser.

The Freeman-Carroll plots for the degradation of the composites with untreated and surface treated Nylon fibre in conjunction with the compatibiliser are presented in Figures 6.9 and 6.10 respectively. The presence of compatibiliser does not alter the degradation kinetics and both the composites follow first order kinetics.

6.4 Conclusions

The degradation of PS/NR blend, dynamically vulcanised blend and composites with short Nylon fibre, RFL-coated Nylon fibre, untreated and treated composites in conjunction with the compatibiliser follows single step degradation pattern. The dynamically vulcanised blends show improved thermal stability compared to the simple blend. Incorporation of short Nylon-6 fibre in the blend delays the onset of degradation but the maximum decomposition temperature decreases marginally. The peak rate of decomposition decreases in the presence of RFL-coated fibre in comparison to untreated fibre composites. The untreated and partially hydrolysed fibre composites enhances the thermal stability when compared to the one without compatibiliser.

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