Thermal Characterisation of Nylon 6/NBR Composites

Chapter 7

Thermal Characterisation of Nylon 6/NBR Composites

Abstract

The thermal behaviour of nylon 6 /NBR composites has been studied by thermo gravimetry (TG) and differential scanning calorimetry (DSC). The degradation temperatures of fibre filled composite systems have been observed to be higher than that of NBR. The percentage weight loss at different temperatures during thermal scanning has been found to be decreased with fibre loading. Composite samples cured by DCP exhibit a higher decomposition temperature compared to the sulphur cured samples indicating that the vulcanisation routes can significantly affect the thermal features of fibre filled polymer systems. The addition of bonding agents enhances the thermal stability of the composites. The DSC studies indicate that the fibre filled systems possess higher glass transition temperatures ($T_g$) than the gum. The bonding agent added composite shows higher $T_g$ compared to the other composite systems, which has been attributed to the higher interaction between the fibres and the matrix in the former.

Contents of this chapter have been communicated to:
Polymers and Polymer Composites
7.1 INTRODUCTION

Thermal analysis is an important tool in the characterisation of polymeric materials. During the fabrication of new products from polymer composites, a knowledge of the thermal stability of their components is essential\(^1\). The threshold temperature for break down determines the upper limit of temperature in fabrication. Optimisation of the processing temperature and time with an understanding of the matrix, the reinforcing element and the interface can lead to a best balance of composite properties.

Thermogravimetry (TG) can help in understanding the degradation mechanism and thus to assist any effort to enhance the thermal stability of a polymeric material\(^2\). This analysis needs only a small quantity of the sample. It is possible to quantify the amount of moisture and volatiles present in the composites which have a deteriorating effect on the properties\(^3\).\(^4\). Thermogravimetric data provides 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.

Differential scanning calorimetry (DSC) helps us to obtain quantitative information about the melting and phase transitions by measuring the heat flow rate associated with a thermal event as a function of time and temperature. This technique can explore the heterogeneous nature of polymeric composites and can provide information about the glass transition temperature (\(T_g\)). Miscible systems will show a single and sharp transition peak intermediate between those of the components. Separate peaks are generally obtained for heterogeneous systems\(^5\).
Chapter 7: Thermal Characterisation

The thermal stability of individual polymers can be enhanced to a greater extent by blending it with other polymers or by reinforcing with fibres. The synergism so obtained is usually attributed to the interfacial adhesion of the components. Various researchers have previously studied the thermal behaviour of rubber blends and composites in detail \(^6\), \(^7\). Corre\'a et al.\(^8\) examined the influence of short fibres on the thermal resistance of the matrix, its \(T_g\) and kinetic parameters of the degradation reaction of thermoplastic polyurethane. They also found that the thermal resistance of aramid fibre-reinforced composites was greater than that of carbon fibre-reinforced composites. The degradation characteristics of Kevlar fibre-reinforced thermoplastics were reported by Kutty et al.\(^9\). TG has been used by Faud et al.\(^{10}\) to determine the filler content of wood-based composites. Suhara et al.\(^{11}\) reported the thermal degradation of short polyester fibre-polyurethane elastomer composites. They observed that incorporation of short fibres enhanced the thermal stability of the elastomer. George et al.\(^{12}\) characterised the thermal behaviour of pineapple fibre reinforced polyethylene composites. Ahmed et al.\(^{13}\) reported the thermal studies on sulphur, peroxide, and radiation cured NBR and SBR gum vulcanisates and also with fillers such as carbon black and silica. It was found that the radiation cured NBR and SBR vulcanisates possessed better thermal stability. Seema and Kutty \(^{14}\) investigated the thermal degradation of short nylon 6 fibre reinforced SBR composites.

The present chapter deals with the thermal analysis of short nylon fibre reinforced NBR composites by thermogravimetry and differential scanning calorimetry. The effects of fibre loading, vulcanising systems and the bonding agents on the thermal features of the composites have been examined.
7.2 RESULTS AND DISCUSSION

7.2.1 Thermal analysis of nylon 6

Figure 7.1 represents the TG and DTG curves of nylon 6 fibre. The onset temperature ($T_{\text{onset}}$) and the temperature of maximum decomposition ($T_{\text{max}}$) are 408 °C and 454 °C respectively. The major decomposition step of nylon, which occurs in the range 330 °C - 480 °C, is due to volatilisation. In this stage, probably a crosslinked structure is also formed. Because of the formation of a thermally more stable structure the rate of degradation slows down after 480 °C. On further heating, the crosslinked structure decomposes and yields 1.1% thermally stable char at 800 °C. The DTG curve of nylon 6 fibre shows a degradation peak at 454 °C corresponding to the major decomposition step.

![TG and DTG curves of nylon 6 fibre](image-url)
7.2.2 Thermal analysis of composites

Figures 7.2 and 7.3 show the thermal degradation behaviour (TG and DTG curves) of gum (NBR) and fibre filled composite system consisting of 24 phr fibres cured by DCP (Mix M). In the case of NBR gum sample, a two stage degradation is observed (Figure 7.2). This is due to the presence of both acrylonitrile and butadiene units in nitrile rubber\textsuperscript{16}. The first step of degradation is from 365 °C to 425 °C and the second step is from 426 °C to 530 °C. Mass losses during the first and second stages of degradation are 70\% and 13.7 \% respectively. Only 6 \% of the sample remains at 800 °C.

![TG curves of DCP cured gum and fibre filled sample](image)

**Figure 7.2 TG curves of DCP cured gum and fibre filled sample**

The DTG curve (Figure 7.3) of NBR shows two peaks; one at 425.8 °C and the other at 452.5 °C. The first peak is mainly due to the degradation of butadiene segments and the second one corresponds to the degradation of acrylonitrile units.
From the TG curve of fibre filled composite (Figure 7.2) it is clear that the onset of thermal degradation is shifted to a higher temperature (370 °C). The major decomposition occurs in the range of 370-460 °C and at 800 °C the weight loss observed is about 90% compared to 94% in the case of gum sample. The DTG curve of fibre filled composite (Figure 7.3) shows only one major decomposition peak. It can be seen that there is only one major decomposition step which occurs at 456.5 °C. The temperature of maximum degradation is higher than that of the gum sample. Thus it is evident from the thermo-gravimetric scan that the thermal stability of fibre reinforced NBR system is higher than that of the gum sample. This is reflected in the weight losses of NBR (gum) and nylon-NBR composite systems at different temperatures (Table 7.1). It can be seen from the table that the weight losses are lower in the case of composite systems compared to the gum sample.

Figure 7.3 DTG curves of DCP cured gum and fibre filled sample
Table 7.1 Thermal degradation of various mixes at different temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percentage weight loss at various degradation temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300 °C</td>
</tr>
<tr>
<td>H</td>
<td>4.46</td>
</tr>
<tr>
<td>J</td>
<td>4.40</td>
</tr>
<tr>
<td>L</td>
<td>3.88</td>
</tr>
<tr>
<td>M</td>
<td>3.78</td>
</tr>
<tr>
<td>Q</td>
<td>3.60</td>
</tr>
<tr>
<td>R</td>
<td>3.57</td>
</tr>
<tr>
<td>A</td>
<td>4.76</td>
</tr>
<tr>
<td>F</td>
<td>3.86</td>
</tr>
</tbody>
</table>

7.2.2.1 Effect of fibre loading

Figures 7.4 shows the TG curves and Figures 7.5 represents the DTG curves of composite samples consisting of 0, 12, 18 and 24 phr fibres respectively (Mixes H, J, L and M). On comparing the thermograms, it is clear that the increment in the loading of short nylon fibres has a retarding effect on the extent of degradation of fibre reinforced NBR composites. From Table 7.1, it is obvious that, at each temperature, the percentage of weight loss decreases with increase in fibre loading. As fibre loading increases, the degradation temperature also increases as indicated in Figure 7.5. Thus the resistance to degradation increases with fibre loading due to the enhanced interaction between the fibres and rubber at higher loading.
Figure 7.4  TG curves of short nylon 6 fibre reinforced NBR composites at different fibre loadings

Figure 7.5  DTG curves of short nylon 6 fibre reinforced NBR composites at different fibre loadings
Chapter 7: Thermal Characterisation

The degradation temperatures evaluated from the thermograms of nylon 6-NBR composites at different fibre loading are tabulated in Table 7.2. From the table it is clear that the onset temperature \( (T_{\text{onset}}) \), temperature at which 50% weight loss takes place \( (T_{50}) \) and the temperature of maximum degradation \( (T_{\text{max}}) \) increase as the fibre loading increases (Mixes H to M). The increase in decomposition temperature confirms the increased interaction between the fibres and the matrix, which enhances the overall thermal stability of the composites.

Table 7.2 Degradation temperatures of different mixes

<table>
<thead>
<tr>
<th>Mix</th>
<th>( T_{\text{onset}} ) (^\circ\text{C})</th>
<th>( T_{50} ) (^\circ\text{C})</th>
<th>( T_{\text{max}} ) (^\circ\text{C})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>366.0</td>
<td>404.3</td>
<td>452.5</td>
</tr>
<tr>
<td>J</td>
<td>368.2</td>
<td>443.6</td>
<td>453.2</td>
</tr>
<tr>
<td>L</td>
<td>369.5</td>
<td>444.0</td>
<td>456.0</td>
</tr>
<tr>
<td>M</td>
<td>370.1</td>
<td>446.8</td>
<td>456.3</td>
</tr>
<tr>
<td>Q</td>
<td>371.0</td>
<td>447.2</td>
<td>458.2</td>
</tr>
<tr>
<td>R</td>
<td>370.8</td>
<td>447.0</td>
<td>457.0</td>
</tr>
<tr>
<td>A</td>
<td>365.2</td>
<td>403.1</td>
<td>451.3</td>
</tr>
<tr>
<td>F</td>
<td>367.6</td>
<td>446.1</td>
<td>455.5</td>
</tr>
</tbody>
</table>

Figure 7.6 shows the plot of onset temperature, temperature at which 50% weight loss takes place, and the temperature of maximum degradation against fibre loading. From the figure it is clear that the degradation temperatures increase with fibre loading.
7.2.2.2 Effect of curing systems

The thermal degradation behaviour of nylon 6 fibre–NBR composites cured by different vulcanising systems is found to be different. This can be seen from the TG (Figure 7.7) and DTG (Figure 7.8) curves of samples containing 24 phr fibre cured by sulphur and DCP (Mixes F and M). The onset temperature and temperature of maximum decomposition are highest for DCP cured samples indicating their higher thermal stability (Table 7.2). This can be explained on the basis of the difference in the type of crosslinks produced by sulphur and DCP. The C-C linkages in peroxide cured system are less flexible with higher bond energy (85 kcal mol\(^{-1}\)) compared to the polysulphidic linkages in sulphur cured system. From Table 7.1 it can be seen that the mass loss observed at a particular temperature is lesser for DCP cured system.

Figure 7.6 Variation of different degradation temperatures with fibre loading
Chapter 7: Thermal Characterisation

Figure 7.7 TG curves of mixes cured by sulphur and DCP systems

Figure 7.8 DTG curves of mixes cured by sulphur and DCP systems
7.2.2.3 Effect of bonding agents

The incorporation of bonding agents, namely hexa-resorcinol and phthalic anhydride plays a significant role on the thermal degradation of nylon fibre reinforced NBR composites. This is evident from the TG (Figure 7.9) and DTG (Figure 7.10) curves of unbonded and bonding agent added composite systems. The extent of degradation is comparatively lesser in both hexa-resorcinol and phthalic anhydride bonding agent added systems (Mixes Q and R) than that of the unbonded one (Mix M). This is also evident from the weight losses at different temperatures given in Table 7.1. It has been found that the onset temperature, temperature at which 50% weight loss takes place, and the temperature of maximum degradation of bonding agent added composites are higher than that of the corresponding unbonded one (Table 7.2). The effect of bonding agents on the increased thermal resistance of the composites can be attributed to the strengthening of the interface.

![Figure 7.9 TG curves of unbonded and bonding agent added composites](image-url)
Figure 7.10 DTG curves of unbonded and bonding agent added composites

7.2.3 Energy of activation for thermal degradation

The activation energy for the process of thermal degradation has been calculated using the basic Arrhenius relationship:

$$\log X = \log X_0 - \frac{E_D}{2.303 RT}$$  \hspace{1cm} (7.1)

where $X$ is the percentage loss of weight of composite at temperature $T$, $X_0$ is the pre-exponential factor and $E_D$ represents the activation energy for the thermal degradation, obtained from the slope of the typical Arrhenius plots of $\log X$ versus $1/T$. The calculated values of $E_D$ at different fibre loadings are given in Table 7.3.

From the table it can be seen that the $E_D$ is least for the gum sample. This indicates that the degradation occurs easily in the absence of fibres without consuming much energy. However, as the fibre loading increases the process of degradation takes place only at higher temperatures, consuming more energy. These observations parallel with the higher thermal stability of the composite systems at higher fibre loading.
Table 7.3 Activation energy at different fibre loadings

<table>
<thead>
<tr>
<th>Fibre loading (phr)</th>
<th>Energy of activation (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>24.76</td>
</tr>
<tr>
<td>12</td>
<td>25.46</td>
</tr>
<tr>
<td>18</td>
<td>26.07</td>
</tr>
<tr>
<td>24</td>
<td>26.94</td>
</tr>
</tbody>
</table>

7.2.4 Differential scanning calorimetric studies

Figure 7.11 shows the DSC curves of gum (NBR) and nylon 6 fibre reinforced NBR composite containing 24 phr fibres (Mix M) cured by DCP. Unlike the gum
Chapter 7: Thermal Characterisation

sample, the composite system shows two endothermic peaks, indicating two
different transitions and also the heterogeneity of the system. The $T_g$ value of gum
compound is found to be -24.8 °C and is very close to that of uncrosslinked NBR
(-26 °C). The $T_g$ value increases with fibre loading (Table 7.4). The $T_g$ value of the
sample containing 24 phr fibres is found to be -22.3 °C. The increment in $T_g$ is due
to the stiffness and rigidity provided by the fibres. The change in $T_g$ of the
composites upon the incorporation of fibres has been reported by several
authors\textsuperscript{17,18}.

<table>
<thead>
<tr>
<th>Mix</th>
<th>$T_g$ of matrix (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>-24.8</td>
</tr>
<tr>
<td>J</td>
<td>-23.3</td>
</tr>
<tr>
<td>L</td>
<td>-23.0</td>
</tr>
<tr>
<td>M</td>
<td>-22.3</td>
</tr>
<tr>
<td>Q</td>
<td>-21.8</td>
</tr>
<tr>
<td>R</td>
<td>-22.0</td>
</tr>
</tbody>
</table>

Table 7.4 $T_g$ of matrix of various mixes

Figure 7.13 shows the DSC curves of hexa-resorcinol and phthalic anhydride
bonded composite samples (Mixes Q and R). It is observed that the $T_g$ value
Corresponding to the matrix increases on the addition of the bonding agent. The
bonding agent added composite systems show higher $T_g$ values compared to the
others (Table 7.4). The higher interaction between the fibres and matrix, in the
presence of bonding agent, provides higher stiffness to the resultant composite
system and as a result the $T_g$ value increases.
7.3. CONCLUSIONS

The thermal behaviour of nylon 6 fibre, and nylon/NBR composites has been studied by TG and DSC with special reference to the effects of fibre loading, curing systems and the incorporation of bonding agents. The degradation temperatures of fibre filled composite systems were observed to be higher than those of the gum. As the fibre loading increased, the decomposition temperature has been shifted to higher temperature range. The percentage weight loss at different temperatures decreased with fibre loading. The decomposition temperature of DCP cured sample was higher than that of sulphur cured one. The extent of degradation was comparatively lower for bonding agent added fibrous composite systems compared to the unbonded one. The activation energy for thermal degradation of the composites increased with fibre loading. The DSC studies of composites indicated that the fibre filled systems possessed higher $T_g$ values than the pure gum due to the

Figure 7.13 DSC curves of unbonded and bonded composite samples
higher rigidity and stiffness of the matrix provided by the fibres. The bonding agent added fibrous composite systems showed higher $T_g$ values compared to the others due to improved fibre-matrix interaction. These results have been found to be complementary to those obtained from the evaluation of the mechanical properties of nylon 6/NBR system.

References


