Chapter 10
Thermogravimetric Properties of Gr, GZ and GCZ Reinforced EPDM Rubber Nanocomposites

Summary: This chapter outlines the thermogravimetric studies of the nanocomposites with respect to different filler additions. The effect of various nano fillers on the thermogravimetric properties of the nanocomposites has also been studied. The studies show that the thermal stability of the coupling agent grafted EPDM rubber is significantly enhanced due to the good reinforcement of nano fillers. The hybrid nano fillers provided the better thermal stability compared to pristine graphene due to the excellent synergistic effect. The thermal stability of the coupling agent grafted EPDM is significantly shifted to the higher temperature due to the strongest interaction with GCZ layers. The EGCZ-5 shows the superior thermal stability than others. The activation energy for the degradation is calculated from the Coats – Redfern equation. The results show that GCZ and GZ reinforced nanocomposites show the highest activation energy than pristine graphene reinforced nanocomposites.
10.1 Introduction

The incorporation of nano fillers results in the considerable improvement in the thermal degradation stability of the nanocomposites\textsuperscript{1-3}. Various factors such as molecular surface slippage\textsuperscript{5}, molecular segmental arrangement\textsuperscript{6}, inter particle displacement\textsuperscript{7-8} and binding forces\textsuperscript{9-10} between the filler and polymer chains are mainly controlled the thermal stability\textsuperscript{11-14} of the nanocomposites. In addition, the good dispersion and interaction between the filler and polymer matrix mainly results the good thermal stability. Most of the processing method mainly controls the good interaction between the filler and polymer.

The investigation of thermal stability of graphene reinforced nanocomposites is very valuable for technological applications. In graphene reinforced nanocomposites, the increased surface area and the layer like structure effectively performed the good adhesion between graphene and the polymer chains\textsuperscript{15-18}. In addition, the particle size, particle morphology and surface area of the graphene layers also affected by the functionalisation of graphene layers. Thus the functionalised graphene layers can more interact with the polymer chains. The interaction between graphene – polymer chains is the major key role to control the mobility of the polymer chains. These parameters are also the prime influential factor to control the physico – chemical properties of the nanocomposites\textsuperscript{19-20}.

In this work, the effect of filler additions on the thermogravimetric properties of the nanocomposites has been investigated. Different additions of various fillers such as pristine Gr, GZ and GCZ are used for this study. The thermogravimetric properties of the nanocomposites have also been correlated with coupling agent grafted EPDM rubber. Furthermore, the activation energy for the thermal degradation has also been investigated.

10.2 Results and Discussion

10.2.1 Thermogravimetric Analysis

The thermal stability of the coupling agent grafted EPDM rubber and the nanocomposites are analysed using thermogravimetric analysis (TGA). The
corresponding TGA curves of the coupling agent grafted EPDM rubber and the nanocomposites are depicted in Figure 10.1(a) – (e). The thermal stability is related to the free movement of the C – C chains in the rubber molecules. The temperature for the onset degradation, temperature at which 50% degradation ($T_{50}$), 90% degradation ($T_{90}$) and temperature for the maximum degradation and are calculated from the TGA curves and shown in Table 10.1. It is observed that the addition of nano fillers significantly increased the thermal stability of the nanocomposites.

As shown in Table 10.1, the onset temperature of the coupling agent grafted EPDM is 405°C. However, the onset temperature of the nanocomposites is gradually increased with increasing filler additions. The onset temperature of EGr-0.5 is 427°C and is gradually increased to 440°C by the additions of 2phr Gr. While the EGr -5 shows the decreased onset temperature. In the case of GZ-0.5, the onset temperature is found to be 440°C. The onset temperature of GZ reinforced nanocomposites is gradually increased with increasing GZ additions. The EGZ-2 and EGZ-5 show the onset temperature of 459 and 460°C. Moreover the onset temperature of the EGCZ-0.5 is 470°C which is superior to other nanocomposites. This indicates that the addition of GCZ effectively produced the thermal properties of the nanocomposites than others.

The addition of Gr on the maximum thermal stability of the nanocomposites is also shown in Figure 10.1 (a). The coupling agent grafted EPDM rubber shows the maximum thermal stability at 450°C. It is observed that the maximum thermal stability of the nanocomposites is slowly increased due to the additions of pristine Gr. The thermal stability of the nanocomposites is attained at 476°C with the 2 phr Gr additions. In addition, the $T_{50\%}$ and $T_{endset}$ temperature of the nanocomposites is also slightly increased with increasing Gr additions till 2 phr. This result can be attributed the fact that substantial improvement of the nanocomposites are due to the addition of pristine Gr. The agglomerated graphene layers at 5 phr addition are also reduced the thermal stability of the nanocomposites. Thus the EGr-5 shows the reduced thermal stability at 460°C.

The effect of GZ on the maximum thermal stability of the nanocomposites is also shown in Figure 10.1(b – c). It is observed that the thermal stability of the nanocomposites is significantly increased with increasing GZ additions. The maximum thermal stability of the nanocomposites gradually increased from 490 – 502°C as the GZ
addition increased from 0.5 to 5 phr. The enhanced thermal stability of the nanocomposites is due to the interacted structure of the nanocomposites. Moreover the $T_{50\%}$ and $T_{\text{endset}}$ temperatures show the highest values than pristine Gr reinforced nanocomposites.

Table 10.1: Decomposition temperature of coupling agent grafted rubber and nanocomposites at different weight losses

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{onset}}$</th>
<th>$T_{\text{max}}$</th>
<th>$T_{50%}$</th>
<th>$T_{\text{endset}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-EPDM</td>
<td>405</td>
<td>450</td>
<td>465</td>
<td>484</td>
</tr>
<tr>
<td>EGr - 0.5</td>
<td>427</td>
<td>468</td>
<td>483</td>
<td>500</td>
</tr>
<tr>
<td>EGr - 2</td>
<td>442</td>
<td>476</td>
<td>496</td>
<td>517</td>
</tr>
<tr>
<td>EGr - 5</td>
<td>410</td>
<td>460</td>
<td>476</td>
<td>493</td>
</tr>
<tr>
<td>EGZ – 0.5</td>
<td>440</td>
<td>490</td>
<td>506</td>
<td>526</td>
</tr>
<tr>
<td>EGZ - 2</td>
<td>459</td>
<td>499</td>
<td>512</td>
<td>531</td>
</tr>
<tr>
<td>EGZ - 5</td>
<td>460</td>
<td>502</td>
<td>514</td>
<td>536</td>
</tr>
<tr>
<td>EGCZ – 0.5</td>
<td>457</td>
<td>509</td>
<td>526</td>
<td>545</td>
</tr>
<tr>
<td>EGCZ - 2</td>
<td>468</td>
<td>517</td>
<td>532</td>
<td>551</td>
</tr>
<tr>
<td>EGCZ - 5</td>
<td>470</td>
<td>520</td>
<td>538</td>
<td>559</td>
</tr>
</tbody>
</table>

To evaluate the effect of GCZ addition on the thermal stability of the nanocomposites, the corresponding TGA curves are shown in Figure 10.1(d – e). The GCZ reinforced nanocomposites show the superior maximum thermal stability than others. The maximum thermal stability of the nanocomposites is dramatically increased from $509 - 520^\circ C$ with respect to the increased GCZ additions. The $T_{50\%}$ and $T_{\text{endset}}$ temperatures show the dramatic improvement in the values reveal the strong interaction between GCZ and rubber chains.

The increased thermal stability of the nanocomposites is depends on the dispersion of the nano fillers. In the case of Gr reinforced nanocomposites, there is a poor
dispersion and interaction in between the Gr layers and the rubber chains. Due to this weak interaction, the rubber chains can easily slipped from the surface of pristine graphene layers. Therefore the thermal stability of Gr reinforced nanocomposites shows the decreasing trend at higher loading of pristine Gr.

The thermal stability of the hybrid nano fillers reinforced nanocomposites shows better thermal stability than pristine Gr. This is mainly depends on the synergistic effect. In addition, there is some good interaction existed in between GZ and rubber chains due to the intercalated structure of GZ. Thus the volume of constrained region increases, which results the restriction of the free movement of rubber chains. Thus the thermal stability gradually enhanced due to the additions of GZ.

The excellent thermal stability of GCZ reinforced nanocomposites are explained by the following facts. The introduction of GCZ can significantly improve the thermal stability of the nanocomposites. The well exfoliated GCZ layers can easily prevent the quick expansion of heat which effectively lowers the further degradation. In addition, there is a strong interaction existed between the GCZ layers and rubber chains.
Thus the superior volume of constrained polymer resulted in the nanocomposites. Therefore, there is a strong restriction on the movement of rubber chains which lead the
higher thermal stability of the nanocomposites.

### 10.2.2 Kinetics of Thermal Decomposition

Kinetics method is generally applied to investigate the thermal stability of the nanocomposites. The kinetic parameters have been determined from the Coats – Redfern method. According to Coats – Redfern method, the activation energy of the samples is calculated from the following equation:

\[
\log \left[ -\log \frac{1-\alpha}{T^2} \right] = \log \left[ \frac{AR}{\beta E} \right] \left( 1 - \frac{2RT}{E} \right) - \frac{E}{2.303RT} \tag{10.1}
\]

Where \( \alpha \) is the fractional mass loss at time \( t \), \( T \) is the absolute temperature (K), \( A \) is the pre-exponential factor, \( R \) is the Universal gas constant, \( \beta \) is the heating rate and \( E \) is the activation energy for decomposition.

Plotting a graph between \( \log \left[ -\log \frac{1-\alpha}{T^2} \right] \) against reciprocal of absolute temperature gives the straight line. The slope of the curve equal to \( (-E / 2.303R) \) and the y – intercept is equal to \( \log (\frac{AR}{\beta E}) \left( 1 - \frac{2RT}{E} \right) \).

Coats – Redfern plots for the coupling agent grafted EPDM rubber and the nanocomposites are shown in Figure 10.2(a) – (c) respectively. The activation energy is analysed from the slope of Coats - Redfern plot and is displayed in Table 10.1. It is found that the activation energy of the nanocomposites is significantly displayed higher values than coupling agent grafted EPDM rubber. Moreover, the activation energy of the nanocomposites is gradually increased with increasing filler additions. This indicates that interaction of nano fillers with the rubber chains easily slow down the chain degradation kinetics. The activation energy of pristine graphene reinforced nanocomposites show lower values than other nanocomposites. The activation energy of GZ reinforced nanocomposites is significantly higher than pristine graphene reinforced nanocomposites. This is because of the good interaction between the rubber chains and GZ. The GCZ reinforced nanocomposites show the superior activation energy than GZ and Gr reinforced nanocomposites. The superior thermal stability of the nanocomposites is due to the better synergistic effect. These results demonstrated that the addition of GCZ plays a crucial role to control the absorption of energy.
Table 10.2: Activation energy for thermal degradation of coupling agent grafted EPDM rubber and nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation Energy (KJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-EPDM</td>
<td>158.12</td>
</tr>
<tr>
<td>EGr - 0.5</td>
<td>272.78</td>
</tr>
<tr>
<td>EGr - 2</td>
<td>301.24</td>
</tr>
<tr>
<td>EGr – 5</td>
<td>244.22</td>
</tr>
<tr>
<td>EGZ – 0.5</td>
<td>284.73</td>
</tr>
<tr>
<td>EGZ - 2</td>
<td>314.16</td>
</tr>
<tr>
<td>EGZ - 5</td>
<td>334.34</td>
</tr>
<tr>
<td>EGCZ – 0.5</td>
<td>309.12</td>
</tr>
<tr>
<td>EGCZ - 2</td>
<td>343.27</td>
</tr>
<tr>
<td>EGCZ – 5</td>
<td>376.32</td>
</tr>
</tbody>
</table>

Figure 10.2(a): Coats – Redfern plot for coupling agent grafted EPDM rubber and Gr reinforced nanocomposites
Figure 10.2(b): Coats – Redfern plot for GZ reinforced nanocomposites

Figure 10.2(c): Coats – Redfern plot for GCZ reinforced nanocomposites
10.3 Conclusions

- The thermal stability of the nanocomposites is found to be higher than that of coupling agent grafted EPDM rubber.
- The thermal stability of the nanocomposites is found to be effectively controlled by the synergistic effect of hybrid nanomaterials.
- The pristine Gr reinforced nanocomposites displayed lower thermal stability than other nanocomposites.
- The GZ reinforced nanocomposites show the higher thermal stability than pristine graphene reinforced nanocomposites.
- The thermal stability of the nanocomposites dramatically increased with increasing GCZ additions and EGCZ-5 displayed superior thermal stability than Gr and GZ reinforced nanocomposites.
- Estimation of activation energy from the Coats-Redfern plot revealed that GCZ reinforced nanocomposites display the superior activation energy than pristine Gr and GZ reinforced nanocomposites.
- The GZ reinforced nanocomposites show the highest activation energy compared to pristine graphene reinforced nanocomposites.
- The pristine graphene reinforced nanocomposites show the poor activation energy.

10.4 References

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