Chapter 8

Thermal analysis of Nanocomposites

Abstract

This chapter deals with the various types of thermal analyses of chlorobutyl rubber nanocomposites like TGA, DSC and DTA. The thermal degradation behaviour of the organically modified layered silicate nano composites have been analysed with respect to various filler loadings as well as surfactant types.
8.1 Introduction

Polymeric materials are subjected to various types of degradation ranging from thermal degradation to biodegradation. Thermal degradation studies involve the measurement of the changes in weight of the material as a result of heating in presence of an inert atmosphere or in presence of air/oxygen. One of the most well accepted methods for studying the thermal properties of polymeric materials is the thermogravimetric analysis. The integral (TGA) and derivative (DTG) thermogravimetric curves provide information about thermal stability and extent of degradation of the polymeric material. Dispersion of layered silicates into a polymer matrix results in the formation of intercalated and/or exfoliated nanostructures that can dramatically change the thermal behavior [1-6] of the resulting polymer-clay nanocomposites. The quaternary ammonium ion is nominally chosen to compatibilize the layered silicate with a given polymer resin. However, the molecular structure, such as alkyl chain length, number of alkyl chains and unsaturations, is also the determining factor of the thermal stability of the polymer/MMT nanocomposites [7]. Although these modification agents have been gaining significant success in the preparation of polymer/ MMT nanocomposites, their common shortcoming is the poor thermal stability. If the processing temperature is higher than the thermal stability of the organoclay, then decomposition occurs, and the interface between the filler and the matrix polymer is effectively altered. The degradation process of intercalated montmorillonite reveals significant differences. For instance, pure montmorillonite do not exhibit any significant mass loss due to decomposition processes in a temperature up to 300 °C.

Early investigations by Greene-Kelly [8] considered the MMT differential thermal curve in two parts: the free water and interlayer water region in the temperature range 100–300 °C and the structural water (bonded hydroxyl groups that undergo dehydroxylation) region in the temperature range 500–1000 °C. Studies by Xie et al. [7,9] reported the thermal stability of MMT modified by long carbon-chain alkyl quaternary ammonium ions and found that the onset decomposition temperature of the resultant organically modified layered silicates (OLS) was approximately 180 °C and
thermal decomposition of organic substances between silicate layers was mainly in the range 200-500°C. In another study, the improvement of thermal stability of the epoxy/clay nanocomposites was attributed to the presence of the clay nanolayers, which acted as barriers to minimize the permeability of volatile degradation products out from the material [10]. Most recently, Tang et al. [11] found out that PP/clay nanocomposites showed both a decrease in 5% temperature loss and improved char formation. It was suggested that the probable reason was that in nanocomposites the intimate contact between the polymer molecules and the atoms of the inorganic crystalline layers was more extensive than that in a microcomposite, and at the same time, there was a catalytic role played by the layered silicates deriving from the Hofmann reaction of hexadecyltrimethyl ammonium bromide, which accelerated the charring process at the beginning of the degradation as proposed earlier on by Zanetti et al. [12]. The shift in glass transition temperature ($T_g$) and improvement in the thermal stability of NBR/Na-MMT nanocomposites were reported by Kader et al. [13]. Kim et al. [14] investigated the thermal properties of nitrile rubber layered silicate nanocomposites with silane coupling agent. It is usually well accepted that the improved thermal stability for polymer–clay nanocomposites is mainly due to the formation of char which hinders the out-diffusion of the volatile decomposition products, as a direct result of the decrease in permeability, usually observed in exfoliated nanocomposites [15-18]. At low clay loading (1 wt. %), exfoliation dominates but the amount of exfoliated nanoclay is not enough to enhance the thermal stability through char formation [17]. The present study focuses on the thermal behavior of chlorobutyl rubber nanocomposites which has not been much previously reported in the literature. It also deals with a comparison of the thermal behavior of the layered silicate nanocomposites containing different types of surfactants.

8.2 Results and Discussion

8.2.1 Analysis of thermograms

The thermal behaviour (TGA) at a heating rate between $30^\circ$ C and $600^\circ$ C of the neat polymer and the layered silicate filled samples are shown in figure 8.1. At
lower temperature, there is no considerable change in the material behaviour of the filled samples and CIIR gum.

![TGA curves of chlorobutyl rubber nanocomposites containing cloisite 15 A](image)

**Fig 8.1** TGA curves of chlorobutyl rubber nanocomposites containing cloisite 15 A

The degradation of CIIR starts at 250 °C whereas that of cloisite 15 A filled nanocomposites starts after 310°C. This can be attributed to the intercalation/exfoliation of the polymer matrix with the silicate particles, which resulted in a strong barrier effect preventing the thermal degradation to a certain extent and this observation is an indication of the fact that the nanocomposites are stable up to a temperature of 362°C in nitrogen atmosphere. As a general trend, thermal stability increases with the increase in filler loading but at higher loadings, the nanocomposites exhibit almost same trend towards thermal stability. Degradation temperatures of chlorobutyl rubber nanocomposites containing cloisite 15 A at different loadings is given in table 8.1.

**Table 8.1** Degradation temperatures of chlorobutyl rubber nanocomposites containing cloisite 15 A at different loadings.
The effect of surfactants on the thermal stability of chlorobutyl rubber nanocomposites is depicted in figure 8.2. It can be seen that the nanocomposites containing cloisite 10 A has better thermal stability than the others. In the case of cloisite 10 A filled composites, the degradation occurs only at 325°C. Degradation temperature of chlorobutyl rubber nanocomposites containing different clays at 5 phr loading is given in table 8.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{onset}}$ (°C)</th>
<th>$T_{\text{max}}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIIR</td>
<td>205</td>
<td>305</td>
</tr>
<tr>
<td>CIIR/10 C$_2$</td>
<td>204</td>
<td>312</td>
</tr>
<tr>
<td>CIIR/15 C$_5$</td>
<td>210</td>
<td>318</td>
</tr>
<tr>
<td>CIIR/15C$_{10}$</td>
<td>215</td>
<td>321</td>
</tr>
<tr>
<td>CIIR/15C$_{20}$</td>
<td>217</td>
<td>325</td>
</tr>
</tbody>
</table>

Fig: 8.2 TG curves of chlorobutyl rubber nanocomposites containing different clays.
Table 8.2 Degradation temperatures of chlorobutyl rubber nanocomposites containing 5 phr of different clays.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_{\text{onset}} ) (°C)</th>
<th>( T_{\text{max}} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIIR</td>
<td>205</td>
<td>305</td>
</tr>
<tr>
<td>CIIR/10 C₅</td>
<td>212</td>
<td>325</td>
</tr>
<tr>
<td>CIIR/15 C₅</td>
<td>210</td>
<td>318</td>
</tr>
<tr>
<td>CIIR/20 C₅</td>
<td>208</td>
<td>316</td>
</tr>
</tbody>
</table>

8.2.2 Kinetic parameters of thermal decomposition

The kinetic parameters for the thermal decomposition of chlorobutyl rubber nanocomposites with different filler loadings were analyzed by applying an analytical method proposed by Coats–Redfern [19].

It is an integral method for the calculation of activation energy and the following equation is used

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

(1)

Where \( \alpha \) is the decomposed fraction at any temperature and is given by the expression

\[
\alpha = \frac{C_i - C}{C_i - C_f}
\]

where \( C \) is the weight at the temperature chosen, \( C_i \) is the weight at the initial temperature and \( C_f \) is the weight at final temperature, \( \beta \) is the heating rate, \( E \) is the activation energy for decomposition.
Fig 8.3  Coats – Redfern plots of chlorobutyl rubber nanocomposites at various filler loadings of cloisite 15 A.

The activation energy and the pre-exponential factor (A) were determined from the plot of $\log\left(\frac{-\log(1-\alpha)}{T^2}\right)$ against $1/T$ which is shown in figure 8.3. The activation energy values for the degradation of nanocomposites of the chlorobutyl rubber containing different loadings of cloisite 15 A is given in table 8.3

Table 8.3  Activation energy for the degradation of nanocomposites containing cloisite 15 A

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIIR</td>
<td>324.2</td>
</tr>
<tr>
<td>CIIR/15C_2</td>
<td>335.5</td>
</tr>
<tr>
<td>CIIR/15C_5</td>
<td>347.0</td>
</tr>
</tbody>
</table>
It is evident from the values that the addition of organically modified layered silicate increases the activation energy for thermal degradation of the polymer. The higher value of activation energy is an indication of the relatively better thermal stability of the system. Noticeable increase in the activation energy value is observed in the case of higher loadings of layered silicate and it can be explained on the basis of strong intercalation/exfoliation of the polymer matrix with the filler. The exfoliated/intercalated silicate layers act as a barrier to the thermal degradation of the nanocomposites.

8.2.3 Differential thermal Analysis

The incorporation of clays containing aliphatic modifiers do not improve the thermal stability of the chlorobutyl rubber to a greater extend. Better thermal stability is exhibited by chlorobutyl rubber nanocomposites containing cloisite 10A. The 15A contains a higher amount of intercalants than 20 A which as pointed out earlier has a chance to be expelled during the shear mixing and could remain unbound in the silicate layers and thereby engage in unwanted degradation reactions between the decomposition products and the polymer matrix, which could lead to further matrix degradation and color formation in nanocomposites [20]. DTA curves of nanocomposites containing cloisite 15 A and 10 A as given in figure 8.4 show 2 closely spaced curves. The first one corresponds to the degradation of the excess amine modifier (above Cation Exchange Capacity) in the clay. The second peak corresponds to the degradation of the intercalated surfactants which were stabilized by confinement within the interlayer. In consequence the ammonium surfactants decomposed earlier which paved way for the degradation of the polymer. Figure 8.5 shows the DTA of nanocomposites containing cloisite 15 A at different loadings. It is seen that as filler loading increases the thermal stability increases.
**Fig 8.4** DTA curves of chlorobutyl nanocomposites

**Fig 8.5** DTA of chlorobutyl rubber nanocomposites containing cloisite 15 A at different filler loadings.
It has been argued that after the early stages of thermal decomposition the stacked silicate layers could hold accumulated heat acting as a heat source to accelerate the decomposition process in conjunction with the heat flow supplied by the outside heat source. The thermal degradation of ammonium salts generally proceeds either by a Hofmann elimination to give a product different from the amine, or an S_N2 nucleophilic substitution reaction to produce the amine. During thermal degradation proceeding according to the Hofmann degradation mechanism the ammonium cation loses an olefin (figure 8.6) and an amine and leaves an acid proton on the surface of the MMT [9]. This acid site on the surface of MMT probably has a catalytic effect during the initial stages of decomposition of organic material within the OLS. Moreover clay itself can also catalyze the degradation of polymer matrices. Thus it becomes obvious that the organoclay may have two opposing functions in the thermal stability of the nanocomposite, a barrier effect (‘labyrinth effect’) which could improve the thermal stability and a catalytic effect on the degradation of the polymer matrix which should decrease the thermal stability as shown in figure 8.6. [21].

![Hofmann elimination reaction of organoclay in chlorobutyl rubber nanocomposites](image)

**Fig 8.6.** Hofmann elimination reaction of organoclay in chlorobutyl rubber nanocomposites

### 8.2.4 Differential scanning calorimetric analysis

In the case of polymer nanocomposites, the differential scanning calorimetric (DSC) measurements are useful for the identification of the extent of intercalation/exfoliation of the nanoparticles in the matrix. The segmental mobility of the polymer matrix is greatly affected by the interactions of the intercalated/exfoliated polymer chains with the nanofillers which enhance the $T_g$ of
the polymer. In the present study, DSC measurements were performed at a temperature range of $-60^\circ$C to $100^\circ$C. The glass transition temperatures increase slightly with the increase in filler loading in the case of cloisite 15 A filled nanocomposites system as shown in figure 8.7. The Tg values of the nanocomposites at different loadings of cloisite 15 A are depicted in table 8.4.

![DSC plot of chlorobutyl rubber nanocomposites containing different loadings of cloisite 15 A](image)

**Fig 8.7:** DSC plot of chlorobutyl rubber nanocomposites containing different loadings of cloisite 15 A

**Table 8.4.** Tg values of chlorobutyl rubber nanocomposites containing cloisite 15 A at different loadings.

<table>
<thead>
<tr>
<th>sample</th>
<th>Tg ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIIR</td>
<td>-59.5</td>
</tr>
<tr>
<td>CIIR/15C₁</td>
<td>-58.9</td>
</tr>
<tr>
<td>CIIR/15C₂</td>
<td>-58.6</td>
</tr>
<tr>
<td>CIIR/15C₅</td>
<td>-58.4</td>
</tr>
<tr>
<td>CIIR/15C₁₀</td>
<td>-57.2</td>
</tr>
</tbody>
</table>
As indicated in figure 8.8, the Tg values of cloisite 15 A and cloisite 10 A filled systems are more than that of cloisite 20 A filled system showing a better interaction between the filler and the matrix in the case of the former layered silicates. It can be seen that there is a substantial difference between the Tg values determined by DSC and DMA. This apparent discrepancy can be explained by the difference in properties measured by the two methods and is often described in the literature [22]. Table 8.5 shows the Tg values of chlorobutyl rubber nanocomposites containing 5 phr of different clays.

![Graph showing DSC plot of chlorobutyl rubber nanocomposites containing 5 phr of different types of cloisite clays](image)

**Fig 8.8** DSC plot of chlorobutyl rubber nanocomposites containing 5 phr of different types of cloisite clays

**Table 8.5.** Tg values of chlorobutyl rubber nanocomposites containing different clays.

<table>
<thead>
<tr>
<th>sample</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIIR/15C_{20}</td>
<td>-56.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>sample</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10A</td>
<td></td>
</tr>
<tr>
<td>15 A</td>
<td></td>
</tr>
<tr>
<td>20A</td>
<td></td>
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<td></td>
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<tr>
<td>----------------</td>
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</tr>
<tr>
<td>CIIR/15 C₅</td>
<td>-58.4</td>
</tr>
<tr>
<td>CIIR/10 C₅</td>
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</tr>
<tr>
<td>CIIR/20 C₅</td>
<td>-65</td>
</tr>
</tbody>
</table>
8.3 Conclusion

- Thermal property is found to be better in the case of chlorobutyl rubber nanocomposites when compared to the virgin chlorobutyl rubber matrix.
- The incorporation of clays containing aliphatic modifiers do not improve the thermal stability of the chlorobutyl rubber to a great extend.
- Better thermal stability is exhibited by chlorobutyl rubber nanocomposites containing cloisite 10 A.
References