Chapter 7
Dynamic Mechanical Analysis of Nanocomposites

Abstract
The dynamic mechanical properties of chlorobutyl rubber nanocomposites are discussed in this chapter. The viscoelastic properties such as storage modulus, damping behaviour and loss modulus of polymer composites depends on matrix filler interaction, crystallinity and extent of crosslinking. It has been observed that the storage modulus of the composites increased with the addition filler due to the enhancement in stiffness of the material. The damping behaviour was found to decrease with the addition of filler and this was attributed to the restricted movement of the polymer segments. The higher surface area to volume ratio of the layered silicate resulted in the better interaction between the polymer matrix and filler.

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7.1 Introduction

Dynamic mechanical analysis (DMA) measures the response of a given material to an oscillatory deformation as a function of temperature. DMA results are composed of three parameters: (1) storage modulus (G’) (2) loss modulus (G”) (3) tan delta is useful for determining the occurrence of molecular mobility transitions, such as glass transition temperature (Tg). Elastomeric nanocomposites form an important class of technologically important materials mainly because of their thermo mechanical and dynamic mechanical behavior. Especially, polymers at the transition region from glassy to rubbery state have the great potential for vibration damping. In general, the damping capacity of a polymer is determined by the intensity and breadth of the loss tangent (tan δ) peak and the value of the loss modulus at the use temperature. Great many efforts have been devoted to develop new materials with high damping capacity. Relaxation phenomena arising in rubber nanocomposites include contributions from both the elastomeric matrix and the presence of nano filler, and in many cases reflect the interactions between matrix and filler. Relaxations originate from molecular dynamic effects, interfacial phenomena and phase changes. Nanocomposites can be classified according to the aspect ratio of the used filler. Suitably selecting the type and the amount of nano inclusions, the performance of nanocomposites can be tailored. Binary and ternary blends of polymers having different glass transition temperatures (Tg) are often used as damping materials [1–5]. When a moderate miscibility is achieved, a wide temperature range with high loss tangent is generally obtained. The interpenetrating polymer network (IPN) restricts the domain size to very small phase and enhances the degree of formation of a micro-heterogeneous structure, which results in a broad glass-transition region [6–11]. Interactions between polymer chains and the highly charged nanoparticle surface lead to the formation of polymer nanolayer close to the nanoparticle surface and it is this interfacial nanolayer that determines the glass transition temperature. The nanoparticle polymer interactions can be attractive, repulsive or neutral and depending on this behavior Tg can increase, decrease or
remain constant. An increase in Tg has been reported in a few cases [12] but a decrease has also been cited in certain cases when nano fillers are added to polymers [13]. This behavior of Tg in nanocomposites have been suggested by Tsagopoulos et al. in his dual nanolayer theory [14]. It is suggested that polymer nanoparticle interactions actually lead to the formation of 2 nanolayers around the nanoparticle. The first nanolayer close to the particle surface is tightly bound restricting the motion of polymer chains. The second layer which is slightly thicker than the first which contains loosely bound polymer chains. At higher filler concentrations the inter particle distance decreases which results in an overlap of the immobile polymer region around the nanoparticles. This will lead to an increase in the volume of the immobile polymer regions in the nanocomposite which in turn will cause an increase in Tg.

7.2 Results and discussion

7.2.1 Variation of tan delta of the nanocomposites

Nanocomposites generate a great deal of interest from material scientists because of their potentially novel properties. It is important to study the mobility of polymers inside the fillers and also how the presences of nano fillers affect the mobility of the surrounding polymers. Dynamic mechanical analysis (DMA) was used to study the chain mobility. During the glass transition, the long range polymer chain gains mobility and this dissipates a great amount of energy through viscous movement. This is shown in the tan δ peak as depicted in figure 7.1. The tan delta curve decreases with increase in filler loading in the case of cloisite 15 A filled CIIR nanocomposites. There is a slight increase in tan delta values also. Therefore, any depression in the tan δ indicates the reduction of the number of the mobile chains during the glass transition. CIIR shows a broad tan delta peak, in which the efficient damping (tan δ> 0.5) has a wide temperature range more than 70 °C. The tan δ value of CIIR nanocomposites comes from the contribution of both CIIR and filler materials. The adding of nanoclay reduces the volume percentage of the CIIR in composites, which lowers hysteresis loss of rubber composites under a dynamic
condition. This can be beneficial for the actual application of some rubber products, such as tires. It is well known that the smaller the tan delta peak, the higher is the reinforcing efficiency of the related filler. Reduced chain mobility owing to physical and chemical adsorption of the CIIR molecules on the filler surface causes a height reduction of the tan delta peak during dynamic mechanical deformation.

Figure 7.2 shows the effect of surface modification on the tan delta values of the chlorobutyl rubber nanocomposites. The tan delta peaks are appearing at almost same positions for the different clay varieties but there is a slight variation in the values of the maxima of the tan delta curves. It is seen that the cloisite 15 A and 20 A show almost similar tan delta values at 5 % loading of the nanoclay in CIIR but a slightly lower value is seen in the case of cloisite 10 A which is due to the presence of the long chain aromatic modifier in the molecule. This can be further attributed to the exfoliation of cloisite 10 A which paves way for the enhanced barrier properties of the nanocomposites especially at higher loadings. Similar trends have been reported in the case of nanocomposites in earlier studies [15].

![Fig. 7.1. Tan delta curves of the cloisite 15 A filled chlorobutyl rubber nanocomposites.](image)
Fig. 7.2  Tan delta curves of the chlorobutyl rubber nanocomposites filled with different clays.

7.2.2. Variation of storage modulus and loss modulus with filler addition

The value of storage modulus, $E'$ signifies the stiffness of the material. From the graph it can be inferred that the incorporation of filler in the polymer matrix increases the storage modulus to a certain extent. This can be attributed to the intercalated state of the elastomer chains into the galleries of the layered silicate and this will bring strong interaction between the matrix and layered silicate [16]. The layered silicate has shown maximum surface contact with the chlorobutyl rubber matrix due to the very high aspect ratio of the filler. A gain in storage modulus with the increase in layered silicate content has been noticed as shown in the figure 7.3. The storage modulus of the nanocomposites increased considerably with the increase in layered silicate content in the temperature range of –50°C to 50°C. The results clearly showed that the addition of layered silicate into CIIR matrix resulted in a remarkable increase in the stiffness of the material indicating a good reinforcing effect of the layered silicate. Specifically, the maximum increase in the storage modulus of these nanocomposites was observed for higher loading of
the layered silicate. This reinforcement, as a result of the addition of layered silicate, increases the thermo-mechanical stability of the material at higher temperature. Moreover, the long alkyl chain in the ammonium salt, which modified the surface of the clay, increased the compatibility between CIIR and the organophilic clay, resulting in an increase in the storage modulus. The results clearly showed that the addition of layered silicate into CIIR matrix resulted in a remarkable increase in the stiffness of material indicating a good reinforcing effect of the layered silicate.

![Graph showing storage modulus of chlorobutyl rubber nanocomposites containing cloisite 15 A against temperature.](image)

**Fig 7.3.** Storage modulus of chlorobutyl rubber nanocomposites containing cloisite 15 A against temperature.

All the curves show three distinct regions representing a high modulus glassy region where the segmental mobility is highly restricted, a transition zone where a considerable decrease in storage modulus is observed with increase in temperature and a rubbery region where modulus value remains almost constant with rise in
temperature. This type of change in storage modulus with temperature has been reported by many researchers in different rubbery systems [17-20].

The peak value of the loss modulus curve when plotted against temperature gives \( T_g \) value of the system. In the present analysis \( T_g \) of pure CIIR is found to be -42\(^\circ\)C whereas 2 phr loading of the nano filler showed \( T_g \) value close to -38.2\(^\circ\)C. In the case of 20 phr the \( T_g \) value increased to -32.5\(^\circ\)C indicating greater restriction of polymer chains in the chlorobutyl rubber matrix (Table 7.1).

Table 7.1  Glass transition temperature of the CIIR nanocomposites containing cloisites 15 A.

<table>
<thead>
<tr>
<th>sample</th>
<th>( T_g )((^\circ)C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIIR</td>
<td>-42</td>
</tr>
<tr>
<td>CIIR/15C(_2)</td>
<td>-38.2</td>
</tr>
<tr>
<td>CIIR/15C(_5)</td>
<td>-37.8</td>
</tr>
<tr>
<td>CIIR/15C(_{10})</td>
<td>-36.5</td>
</tr>
<tr>
<td>CIIR/15C(_{20})</td>
<td>-32.5</td>
</tr>
</tbody>
</table>

The loss tangent (tan \( \delta \)) curves of the nanocomposite samples with varying filler loading have been analyzed in the case of CIIR cloisite 15 A nanocomposite systems. It has been observed that tan \( \delta \) peak of the nanocomposites representing glass transition were shifted to higher temperatures, which is proportional to the filler loading. Generally, strong interactions between the nanolayers and the matrix polymer can restrict the movement of polymer segments near to the filler surface, thus resulting in an increase of the glass transition temperature of the matrix. The tan \( \delta \) curves of the nanocomposites were very much similar to that of pure CIIR except that there was reduction in the tan \( \delta \) peak height. Upon increasing the level of the filler content, the peak height became small, indicating the restriction in damping characteristics of the nanocomposites. The increase in the \( T_g \) and the reduction in the tan \( \delta \) peak height by the addition of nanoclays are attributed to the
enhanced polymer-nanoclay interaction, which results in restricted segmental mobility of the polymer chains.
The variation of loss modulus ($E''$) with temperature of the CIIR gum sample and the nanocomposites with varying filler loading is displayed in figure 7.4. $E''$ is the viscous modulus of the polymeric material and is related to the energy lost due to viscous dissipation. The increase in $E''$ values as a result of the addition of filler can be explained in terms of the friction between the filler particle and the matrix molecules when the filler particles are uniformly dispersed in the chlorobutyl rubber matrix. It has been noticed that the addition of layered silicate enhanced the loss modulus of the system. This can be attributed to the increase in the availability of surface area per unit volume of the layered silicate resulting in comparatively higher friction between the filler and the polymer matrix. As the filler loading increases there will be considerable increase in the frictional force between the filler and the matrix. The peak point of $E''$ was slightly shifted to higher temperature, compared with pure CIIR, with increasing clay content [21].

**Fig 7.4** Loss modulus of chlorobutyl rubber nanocomposites containing cloisite 15 A against temperature.
7.2.3 Calculation of constrained polymer volume

Nanocomposites generate a great deal of interest from material scientists because of their potentially novel properties. It is important to study the mobility of polymers inside the fillers and also how the presence of nano fillers affect the mobility of the surrounding polymers. Dynamic mechanical analysis (DMA) was used to study the chain mobility. Therefore, any depression in the tan\(\delta\) indicates the reduction of the number of the mobile chains during the glass transition. The relative peak height is proportional to the volume of the constrained chains [22]. The quantitative measurement of constraint chains was developed to study the crystallinity of semi-crystalline polymers. The measurement was used to calculate the constrained polymer volume in a polymer-nano composite. It is calculated using the equation [23].

\[
C = 1 - (1 - C_0) \frac{W}{W_0} \tag{1}
\]

Where \(W_0\) is the energy fraction loss of matrix

\[
W = \frac{\Pi \tan \delta}{\Pi \tan \delta + 1} \tag{2}
\]

It may be noted that the presence of fillers immobilize a significant amount of polymer chains during the glass transition. In this model, the matrix and the filler are bonded each other and form a new phase. This phase reduce the mobility of the surrounding polymers. There is an effective constraint length, and polymers lose their mobility during glass transition when the polymer chain is within this constraint length. The dispersed fillers and the constrained phase form an effective particle with an effective volume much higher than that of the filler. It is assumed that the filler surface is bonded with the segments of the polymer. These polymer segments are embedded between the fillers. As these polymer segments are part of polymer chains, the involved polymer chains are also constrained. The effective constrained polymer volume is much higher because of this extended constraint zone. The constrained polymer chain volume (C) is plotted against filler loading (Figure 7.5). The C values increases with increase of filler loading in the case of CIIR cloisite 15 A.
nanocomposites. This clearly indicates the presence of polymer chain immobilized as a result of interaction between filler and matrix.

**Fig 7.5** Variation of constraint chain volume against filler loading in cloisite 15 A nanocomposites

On plotting the constrained volume against the various filler types it can be seen that the cloisite 15 A and 20 A having the same filler modification shows almost equal values for constrained volume whereas cloisite 10 A having an aromatic group modifier shows enhanced value as shown in figure 7.6. This can be attributed to the presence of a long chain aromatic bulky modifier group in the case of cloisite 10 A which paves way to the reduction in tan delta and subsequently exhibits enhanced value of constrained polymer volume.
**Conclusion**

- The morphological as well as dynamic mechanical analyses of the nanocomposites reveal the presence of intercalation/exfoliation of the CIIR chains within the clay galleries.

- The calculation of constrained volume of the CIIR chains within the clay galleries and the lowering of the tan delta curves further account for the aforementioned observation.

- The increase in the glass transition temperature of the nanocomposites also pave way for the assumption of restriction of CIIR chains within the clay galleries.
References


