Chapter 5
Mechanical and morphological properties of chlorobutyl rubber nanocomposites

Abstract

The morphological analysis and mechanical properties of chlorobutyl rubber based nanocomposites with reference to filler loading has been investigated. The morphological analysis was conducted using XRD, TEM, AFM and SEM. The mechanical properties such as tensile strength, elongation at break, modulus and tear strength have been investigated with reference to filler loading. The variations in properties can be attributed to the extent of intercalation/exfoliation which was highly influenced by the type of organic modification of the layered silicate.

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5.1 Introduction

At present nanocomposites based on polymer matrices and organo-layered silicates represent an interesting opportunity for the design of high characteristic materials mainly from the mechanical properties and thermal stability points of view [1]. While clay nanocomposites have been investigated in combination with many thermoplastics and thermosetting polymers, much less attention has been paid to the elastomers as matrices [2–5]. Besides increased modulus and strength, other factors such as tear properties, fracture toughness and abrasion resistance are claimed to be improved as a result of addition of clay to rubber [6–8]. Polymer-clay nanocomposites can be prepared by several methods [9], such as in situ polymerization or intercalation via solution, while in the case of rubber nanocomposites intercalation of rubber via latex compounding can also be used [10]. Besides changing the properties of vulcanized rubber compositions, the nano fillers affect the chemistry of the vulcanization process also [11]. A substantial reduction of optimum vulcanization time was observed in the presence of organoclay [12]. The effect is explained by the presence of amino groups which act as accelerators of the curing process. The incorporation of organoclay into rubber leads to a slight increase in glass transition temperature, obviously resulting from a restricted motion of the rubber chains on the intergallery space. Similar reasoning may be used to explain certain increase in temperature of thermal decomposition, although this effect may not be a consequence of higher thermal stability of the material decomposing at higher temperature but just due to a prevention of diffusion of volatile remnants immobilized between galleries [12, 13]. Properties of rubber/organoclay nanocomposites were investigated for a number of rubber matrices, e.g. natural rubber (NR) [12, 13], EPDM [14, 15], SBR [16], nitrile rubber [16], silicon rubber [16] and polybutadiene rubber [17]. An increase in tensile strength was usually observed as expected; in most cases the increase was substantial. However, surprisingly also elongation values rose, e.g. for EPDM with organoclay [14]. Important improvement was reported regarding an increase in tear strength originated
from an increased resistance to crack growth [14, 18]. Similar to thermoplastic matrices, a decrease in gas permeability [14, 18] and increased solvent resistance [19] were reported for rubber nanoclay composites. The introduction of organic ions into the interlayer spacing not only render more organophilic phyllosilicates but also results in a larger interlayer spacing depending on functionality, packing density and length of organic molecule [20].

5.2 Results and Discussion

5.2.1 Evaluation of cure kinetics

The cure time of the nanocomposites containing all the different clays was found at different temperatures and the maximum and minimum torque values were tabulated.

According to first order kinetics

\[
\ln (a-x) = -Kt + \ln a
\]

The torque values obtained are proportional to the modulus of rubber

\[
a-x = M_{H} - M_{t}
\]

\[
a = M_{H} - M_{L}
\]

\(M_H\) is the maximum torque

\(M_L\) is the minimum torque

\(M_t\) is the torque at time t

\(\ln M_{H} - M_{t}\) when plotted against time a straight line is obtained whose slope gives the value of \(K\) the rate constant at a particular temperature \(T\). Arrhenius equation is used to calculate the activation energy of the mixes. Since \(t_90\) is a measure of the cure rate, it is taken as a measure of the rate of cure reaction.

\[
1/ t_{90} = Ae^{-E/RT}
\]

\[-\log t_{90} = \log A - E / 2.303 RT\]
A plot of $-\log t_{90}$ vs $1000/T$ gives a straight line (figure 5.1) and from the slope of this curve, the activation energy can be calculated.

![Activation energy plots for the nanocomposites containing cloisite 15A](image)

**Fig 5.1** Activation energy plots for the nanocomposites containing cloisite 15A. As the clay loading increases, the value of activation energy decreases as shown in table 5.1, indicating that the aliphatic MMT clay is acting as a catalyst towards the vulcanization of CIIR.
To show the accelerating effect of the aliphatic group of the organic surfactant the nanocomposites prepared using different clays were subjected to a cure kinetic study. The cure kinetics followed a first order reaction. The rate constant K was obtained at different temperatures and the value of K is found to be increasing with increase in temperature for all the nanocomposites. Figure 5.2 shows the variation of the rate constant of the nanocomposites containing different clays at different temperatures. From the figure it is evident that cloisite 15 A and 20 A containing aliphatic modifiers are more effective in the acceleration of the cure rate of chlorobutyl rubber nanocomposites. This is further confirmed in figure 5.3 which shows the variation of torque with time during the curing of the nanocomposite. Aliphatic MMT show a maximum value of torque as indicated in figure 5.3. This shows that a higher cross linking degree is obtained with aliphatic MMT clays. So these clays are better dispersed in the polymer matrix and a higher torque is necessary for this composite to flow. Thus aliphatic MMT behaves as a catalyst for the vulcanization of CIIR. Increase in the value of K indicates the fastness of a reaction.

Table 5.1 Activation energies of the nanocomposites containing different loadings of cloisite 15 A

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation energy KJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIIR/15C₂</td>
<td>34.09</td>
</tr>
<tr>
<td>CIIR/15C₅</td>
<td>30.05</td>
</tr>
<tr>
<td>CIIR/15C₁₀</td>
<td>21.03</td>
</tr>
<tr>
<td>CIIR/15C₂₀</td>
<td>19.35</td>
</tr>
</tbody>
</table>
Fig 5.2  Plots of rate constant vs temperature of chlorobutyl rubber nanocomposites containing various clays.

Fig. 5.3  The effect of torque against time of the different clays
5.2.2 Mechanical properties

The properties of rubber clay nanocomposites depend on

(a) The type of organic modification.

(b) Structure of the organic modifier.

(c) Length of the organic modifier. (No. of carbon atoms)

(d) Cation exchange capacity (CEC) or modifier concentration.

Layered silicate filled nanocomposites show enhanced mechanical properties when compared to other inorganic filler systems. The figure 5.4 shows the stress strain behavior of the clay filled CIIR nanocomposites. The mechanical properties of the nanocomposites are depicted in table 5.2 and figure 5.5 depict the mechanical properties of the chlorobutyl rubber nanocomposites containing cloisite 15 A. It is interesting to note that the tensile strength increases around 4 times when the clay loading goes to 10 phr. Similar is the trend shown by other mechanical properties like tear strength and hardness. When the filler loading increases to 20 phr, the tensile strength as well as tear strength decreases. This can be attributed to the agglomeration of the clay platelets as seen from the XRD profiles which will be discussed later in this chapter.

Table 5.2 Mechanical properties of the nanocomposites containing cloisite 15 A

<table>
<thead>
<tr>
<th>Sample</th>
<th>Strain at break (%)</th>
<th>Tensile strength (MPa)</th>
<th>Tear strength (KN/m)</th>
<th>Hardness (Shore A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIIR</td>
<td>423</td>
<td>3.5</td>
<td>16.7</td>
<td>35</td>
</tr>
<tr>
<td>CIIR/15 C&lt;sub&gt;2&lt;/sub&gt;</td>
<td>430</td>
<td>4.2</td>
<td>18.4</td>
<td>48</td>
</tr>
<tr>
<td>CIIR/15 C&lt;sub&gt;5&lt;/sub&gt;</td>
<td>538</td>
<td>12.1</td>
<td>24.1</td>
<td>50</td>
</tr>
<tr>
<td>CIIR/15 C&lt;sub&gt;10&lt;/sub&gt;</td>
<td>578</td>
<td>13.6</td>
<td>28.8</td>
<td>54</td>
</tr>
<tr>
<td>CIIR/15 C&lt;sub&gt;20&lt;/sub&gt;</td>
<td>601</td>
<td>12.7</td>
<td>22.4</td>
<td>57</td>
</tr>
</tbody>
</table>
Fig 5.4 Stress strain curves of the CIIR nanocomposites containing cloisite 15A

(a)
Rubber clay nanocomposites show remarkable enhancement in tensile strength and strain at break. This phenomenon seemed to be caused by the slippage of rubber molecules due to the plasticizing effect of clay layers and orientation of the intercalated silicate layers under stress as shown in figures 5.6 and 5.7.

**Figure 5.6.** Slippage of polymer chains due to the plasticizing effect of clay layers in partially intercalated systems (a) partially intercalated system (b) slippage of clay layers towards one direction (c) oriented silicate layers
Figure 5.7. Slippage of polymer chains due to the plasticizing effect of clay layers in fully intercalated systems (a) fully intercalated systems (b) slippage of clay layers (c) oriented silicate layers

The orientation can increase the loading capability of organoclay and the slippage makes it possible for the highly stained molecular chains to relieve tension caused by the stretching so that they will not break prematurely resulting in a higher strain at break and strength. Nano layers have considerable stronger reinforcing effect than micro ones especially for shore A hardness. This can be attributed to two reasons. Nanodispersed clay with high aspect ratio possesses a higher stress bearing capability and efficiency. Moreover stronger interaction between nano layers and rubber molecules associated with larger surface of contact results in more effective constraint of the motion of rubber chains [21,22].

5.3 Characterization of the nanocomposites by XRD

The XRD patterns of the layered silicate nanocomposites were analyzed to study the nature of dispersion of the layered silicates in the chlorobutyl rubber matrix. This helps to identify whether the layered silicates are in exfoliated state or intercalated state in the nanocomposite. The XRD of cloisite 15 A in figure 5.8 shows a peak at 2θ = 2.7. Lower loadings of clay (1 phr) results in the formation of exfoliated nanocomposites as indicated by the absence of any peak in the XRD. At intermediate clay loadings the XRD shows well defined peaks which are shifted towards lower 2θ values (2.7 to 1.9). This indicates that the polymer chains are intercalated into the clay layers resulting in an increase in the d spacing of clay which is substantiated by the shift of XRD peaks. The XRD peaks show an increase in height with increase in clay loading which indicates a higher degree of ordering i.e. intercalation. So as the clay loading increases, the extend of exfoliation
decreases whereas the extend of intercalation increases. At higher loadings (20 phr) the XRD peak shifts to a slightly higher 2θ value than the other loadings showing that agglomeration of clay has occurred.

**Fig 5.8**  XRD of chlorobutyl layered silicate nanocomposites containing cloisite 15 A

From the above XRD profile it is understood that the polymer chains are in a state of exfoliation at lower loadings of clay while as the loading of clay increases the extend of exfoliation decreases and the extend of intercalation increases. At higher loadings the nanocomposites show morphology in between that of intercalated and exfoliated state. Another strong diffraction peak can be observed at about a higher 2θ value in the case of certain nanocomposites. Moreover the trends in mechanical properties can be clearly explained in terms of the XRD profile. The marginal increase or the decrease in mechanical properties found in 20 phr loading of clay can be attributed to slight agglomeration of clay which is evident from the XRD. This probably indicates that there is a bimodal structure for the layered silicates in the polymer matrix when the amount of layered silicates is over 10% [23].
Fig 5.9  XRD plots of the chlorobutyl rubber nanocomposites containing 5 phr of different clays.

In the case of cloisite 10 A filled nanocomposite as shown in figure 5.9 only a small peak is observed at 2θ value 2.5 which shows that the clay layers are in a state of exfoliation than intercalation whereas in the case of cloisite 20 A, a slightly higher peak is observed around 2θ value 2 which suggests intercalation of polymer into the clay layers. A higher amount of intercalation is observed in the case of 15 A because of the increased d spacing of the cloisite 15 A. Moreover the peak is appearing at a much lower 2θ value when compared with the 2θ value of the pristine cloisite 15 A. In this case, the most significant compatibilizing effect was found for the clay modified with tallow only, i.e., C15A and C20A. XRD patterns in Fig. 5.9 indicate a lower degree of exfoliation of clays with less polar treatment (C15A and C20A) in the CIIR matrix, which tends to decrease the strength and stiffness of corresponding nanocomposite. Best exfoliation is obtained with organoclays based on one long alkyl tail apparently owing to the affinity of the polymer for the silicate
surface. Thus organoclays based on one long tail alkyl group (cloisite 10 A) provide more access to the silicate surface of the clay than two or more alkyl tails (cloisite 15A and 20 A). XRD of 20 A composites shows greater d spacing than 15 A composites. This is because the excess amount of surfactant in 15 A could remain unbound in the silicate layers which in their initial state increases the gallery spacing of clays. During shear mixing this excess unbound surfactant could diffuse from the galleries thereby decreasing the d spacing. This combined with the simultaneous intercalation of the polymer molecules could have led to the decrease of d spacing in 15 A when compared to 20 A. similar XRD observations have been reported by Lakshminarayan et.al. [24] in the case of fluoroelastomer and Ranade [25] and coworkers in the case of PETG nanocomposites containing cloisite 15 A and 20 A. Nevertheless 15 A composites have better reinforcement than 20 A nanocomposites. The justification provided was that 15 A nanocomposites were highly oriented compared to 20 A resulting in more platelet-platelet interaction thereby strengthening the composite. As a result, the clay with the best compatibilizing effect does not lead to the best balance of mechanical behavior. Similar results have been reported by Kelnar et.al.[26].
5.4 Effects of physical structure of clay on the mechanical properties of nanocomposites

Keeping the clay same but on changing the concentration of modifier different properties have been observed for the rubber clay nanocomposite system. When cloisite 15 A and 20 A are compared, both have the same organic modifier but the modifier concentration is higher in the case of 15 A.

Fig 5.10. Effect of clay type on the tensile strength of chlorobutyl rubber nanocomposites.

As modifier concentration increases, greater will be the incorporation of amine and more will be the organophilicity of clay. The reason for the enhanced mechanical property of cloisite 15 A when compared to cloisite 20 A as shown in figure 5.10 can be attributed to the following reason. As modifier concentration increases in 15 A, the organophilicity of clay increases. So the polymer chain incorporation will be higher or most facilitated when the modifier concentration is high. This is reflected from the mechanical property analysis of the nanocomposites in which higher tensile strength is exhibited by cloisite 15 A when compared with 20 A though both have the same modifier as shown in figure 5.10. Keeping the clay same but
changing the nature of the surfactant (10 A / 15 A, 20 A) is found to affect drastically the properties of the rubber clay nanocomposite system. During intercalation of the clay with different amines the number of reacting sites in a definite amount of clay will be a constant (5 phr). So the number of amine groups reacting will be a constant. As the molecular weight increases from 10 A to 15 A, the amount of clay in the nano filler (5 phr) would be lower for 15 A than 10 A. The amount of modified clay taken is constant for all the amine modifiers (5 phr). So the number of clay particles added to the rubber matrix is maximum in the case of 10 A than 15 A. At higher filler loadings this effect becomes more pronounced and hence 10 A shows better properties at higher loadings [25]. Moreover the intercalated silicate layers orient in the strain direction thus strengthening the nanocomposites containing 15 A. Thus it can be seen that ordered intercalation in cloisite 15 A filled nanocomposites show very good mechanical properties especially at lower loadings as depicted in XRD. In deciding the modulus of a nanocomposite two factors come to play

1. The number of particles

2. Interaction between the modified clay and the rubber matrix.

The interaction between the nanofiller and the rubber matrix increases with the increase in the number of carbon atoms in the amine chain. This is namely due to nonpolar Van der Waals type of interaction between the filler modifier and the rubber matrix. The variation in tensile strength and modulus is a function of dispersion in addition to filler rubber interaction. Since the amine chain in cloisite 15 A/20A contains two tallow groups, the number of carbon atoms is higher than cloisite 10 A and hence they show enhanced mechanical properties when compared to 10 A as shown in figure 5.11.
Fig 5.11  Effect of clay loading on the elongation at break of chlorobutyl rubber nanocomposites

Of the three clays studied two (15 A and 20 A) are having aliphatic groups in the modifier whereas the clay 10 A is having an aromatic group. The modifiers used in the case of all the clays are shown in figures 5.12 and 5.13

![Structure of the surfactant in cloisite 10 A](image)

**Fig 5.12** Structure of the surfactant in cloisite 10 A
Lower degree of intercalation is obtained with aromatic salts as modifiers due to steric effect of the aromatic rings. The long tallow tails on the amine surfactants are made from natural oil that contains some unsaturation, i.e. double bonds. This unsaturation may lead to undesired chemical reactions particularly at the high temperature used in melt processing. The substituent size (or volume) on a surfactant can affect the dispersion of clay particles in the polymer matrix. The organoclay with a broader d spacing can have much more possibility to be exfoliated in polymer/organoclay nanocomposites because polymer molecules penetrate into the gallery more easily. It is interesting to see that the material with a benzyl group also has a higher elongation at break than do the methyl or hydrogen substituted organoclays as shown by Paul and co workers [27]. The molecular conformation of alkyl ammonium surfactant chains (aliphatic groups) within montmorillonite clay galleries is shown in figure 5.14 as described by Vaia et al. [28]. The figure clearly depicts the reason for the increase in d spacing in the case of virgin cloisite 15 A when compared to cloisite 10 A. Cloisite 10 A which contains an aromatic moiety in the modifier has no possibility to exist in double layer due to steric effect. The increase in gallery spacing is small in the case of cloisite 10 A and therefore the chains are likely not perpendicular to the silicate, but may lie at an inclined angle with respect to the silicate surface facilitating $\pi-\pi$ interactions between the aromatic rings [29].
In addition to the organo clay chemical structure, physical structure may play a role in exfoliation or intercalation in a polymer matrix. Intuitively, one might expect that the further the aluminosilicate platelets are pushed apart by ion exchange with the organic modifier (i.e., the larger the organo clay d-spacing) the easier it will be to obtain intercalation by the polymer. However, study of nylon 6 nanocomposites showed that tensile modulus or yield strength did not increase with the d-spacing of the organo clay; if anything, the opposite trend was found [30]. This study indicated that better exfoliation stems from a good affinity of the polymer for the organo clay rather than larger platelet separation in the pristine organo clay.

5.5 Morphology by SEM and TEM

The morphology of the fracture surface of the nanocomposites was studied by means of SEM. The fracture surfaces of the tensile specimens were gold coated and the micrographs were taken. The SEM images of the fracture surface of CIIR nanocomposites containing different filler loadings are shown in figures 5.15-5.18. The micrograph obtained from the CIIR gum vulcanizates as shown in figure 5.15 reveals very smooth surface with some embedded small particles. These particles are likely to be the metal oxides (ZnO and MgO), which were used for curing of the
rubber. The smoothness of the fractured surface indicates uniform failure of the CIIR matrix without any mechanically weaker region for crack initiation. The fractured surface morphology of CIIR–layered silicate vulcanizate is totally different to that of the gum. It can be seen from figure 5.16 and 5.17 that on the contrary with the gum, the fractured surface of CIIR–layered silicate nanocomposite is very rough with frequent ridgelines indicating the direction of crack propagation. These ridgelines often propagate through the particle polymer interface and these ridgelines of reinforcement indicate the good compatibility of OMMT and the rubber matrix. The ridgelines become clearer in the case of 20 phr loading of organoclay as shown in figure 5.18. Similar observation in the case of chloroprene rubber nanoclay composites with SEM is reported by Amitdas et.al.[31]

![Fig 5.15](image1.png)  
**Fig 5.15**  SEM image of the fracture surface of chlorobutyl rubber vulcanizate

![Fig 5.16](image2.png)  
**Fig 5.16**  SEM image of the fracture surface of chlorobutyl rubber nanocomposite containing 5 phr cloisite 15A
Fig 5.17  SEM image of the fracture surface of chlorobutyl rubber nanocomposite containing 10 phr cloisite 15A

Fig 5.18  SEM image of the fracture surface of chlorobutyl rubber nanocomposite containing 20 phr cloisite 15A

From the TEM images it is evident that in the case of nanocomposites containing cloisite 15 A (figure 5.19 (a) the clay layers are in an ordered intercalated state. Whereas in the case of nanocomposites containing cloisite 10 A as shown in figure 5.19 (b) the clay layers are in disordered intercalated state and in the case of cloisite 20 A, a small amount of agglomeration is seen as is evident from figure 5.19 (c). Thus the TEM images support the trend of the mechanical properties as shown in figure 5.19.
5.6. Thermodynamics of chlorobutyl rubber nanocomposites

The energy change with the separation of clay layer plates dispersed in a polymer ΔG can be interpreted to consist of two elements i.e. internal energy ΔE associated with the formation of new molecular interactions and entropy change (ΔS) associated with the formation of nanocomposite constituents.
\[ \Delta G = \Delta H - T \Delta S \] \hspace{1cm} (6)

T is the temperature in Kelvin to describe the energy change accompanying a change in clay gallery spacing from an initial value \( h_0 \) to a new distance \( h_f \). If \( \Delta G \) is less than zero, it suggests that silicate gallery height change is exothermic and favorable. When \( G = 0 \) the system will be in equilibrium with the random distribution of gallery space in between \( h_f \) and \( h_0 \).

\[ \Delta S = \Delta S_{\text{surfactant}} + \Delta S_{\text{polymer}} \text{ (caused by the change in gallery height } h_f - h_o \text{)} \] \hspace{1cm} (7)

Compared to plastics and other elastomers, chlorobutyl rubber has a high molecular weight. Viscosity and shear stress for rubber composites during mixing are very high and molecular chains can be oriented by such shear stress both in internal mixer and particular in two roll mill with a consequent decrease in entropy of polymer. Such shearing of stacked nanoclay plates during mixing will separate the plates with the polymer chains being inserted in them (i.e. silicate gallery spacing).

Liang et.al. [32] reported that this type of structure is thermodynamically unstable. However, if such intercalated structures are formed through mixing of butyl rubber and nano clay, transformation to a more stable structure would be prevented due to a very high viscosity of the nanocomposite at room temperature or rapid initiation of cross link formation, again with increase in viscosity.

When temperature increases with a corresponding rapid decrease in viscosity, then mobility of rubber chains can increase and the energy barrier to structural transformation would be reduced. A new intercalated structure with a lower gallery spacing and reagglomeration of clay can then occur. Extended periods at elevated temperature in a low viscosity unvulcanized state will favor clay plate reagglomeration to the detriment of properties such as permeability [31, 33]. Therefore if such formulated compounds have short vulcanization induction periods and fast cure rates then aggregation phenomenon might be arrested and a wide nanoclay spacing and greater nanoclay plate distribution through the polymer matrix may be maintained. Since the aliphatic modifiers (as seen in the
case of cloisite 15A) increase the cure rate in the nanocomposite systems under study, it is worthwhile explained that the formation of highly ordered intercalated structure is feasible.

5.7 Conclusion

- The mechanical properties of the nanocomposites are far superior when compared to the gum vulcanizates.
- The tensile strength of the layered silicate nanocomposites containing all the different modifiers showed a threefold increase upon the addition of the nano clay.
- The enhancement of mechanical properties of the nanocomposites can be attributed to the high rigidity and aspect ratio together with the favoring affinity between the polymer and organoclay.
- The morphological analysis revealed the interaction of the chlorobutyl rubber matrix with the different layered silicates indicating whether they are in ordered intercalated, disordered intercalated or exfoliated condition.
- The mechanical properties depend to a great extend on the d spacing of the layered silicate, the modifier type and the modifier concentration. Cloisite 15 A with greater d spacing provides easy intercalation of polymer chain into the clay galleries.
- Cloisite 10 A with along aromatic group in the modifier shows higher elongation at break.
References