Chapter 3

Microcomposites vs Nanocomposites of chlorobutyl rubber

Abstract

This chapter deals with the comparison of the microcomposites of chlorobutyl rubber containing titanium dioxide as the filler with the nanocomposites containing calcium phosphate as well as organically modified layered silicate (cloisite 15 A) prepared by melt mixing. The calcium phosphate nanoparticles were synthesized and characterized in the laboratory by polymer precursor method. The surface morphology of the nanocomposites has been analyzed by SEM, and TEM. The mechanical properties have also been compared. It is seen that the layered silicates with a high aspect ratio is superior to the other fillers in chlorobutyl rubber.

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3.1 Introduction

Among the several reasons to incorporate fillers into polymers (cost reduction, improvement of some physical properties such as flame retardancy or barrier properties) the enhancement in mechanical reinforcement is gaining top priority [1]. Traditional fillers display average characteristic sizes in the range of several microns. However, due to the development of nanosized fillers, the specific influence of the nanometric size in the reinforcement mechanisms has to be addressed. Composite materials based on nano-sized fillers, the so called nanocomposites, are presently studied especially because they may have unusual combinations of properties [2–6]. These unusual properties may be a consequence of the extremely large specific interfacial area. They may be also related to the very short distances between the reinforcing fillers (about 10−8 m), that may become close to the characteristic size of the macromolecular coils. In addition, some years ago, it was showed that drastic reinforcing effects may be observed at very low volume fractions for fillers with very large aspect ratio, when the percolation of the fillers occurs [7]. The presence of these nanoparticles improves the elastic modulus without decreasing the elongation at break and does not worsen the rheological and processing behavior and the optical properties of the polymer matrix.

The main problem in the preparation of nanocomposites in the molten state [8-10] is the good filler dispersion in the polymer matrix. Recently much attention was devoted to the synthesis of nano calcium phosphate and the incorporation of nano calcium phosphate in various polymer matrices by Thomas et.al. [11]. Here we attempt to develop nano calcium phosphate by a much cheaper method using PEG as the polymer precursor. Generally, inorganic materials neither have good interaction with organic polymers to achieve good dispersion nor adequate adhesion, and, as a result, surface treatments are common (12-16). Due to their nanometer phase dimensions, polymer nanocomposites (PNCs) exhibit unique properties even by the addition of just a low weight percentage (<5 wt %), not shared by their micro counterparts or conventional filled polymers. In recent years
nanocomposites have attracted a great deal of interest, both in academia and in industry, because they often exhibit remarkable improvements in material properties when compared with virgin polymer or conventional macro and micro composites. These materials exhibit behavior different from conventional composite materials with micro scale structure due to small size of structural unit and high surface to volume ratio. As compared to micron size filler particles the nano size filler particles are able to occupy substantially greater number of sites in the polymer matrix. The significant increase in specific surface area of filler particles contributes to the enhanced physical property of the polymer matrix.

3.2 Characterization of nano calcium phosphate

The elegant approach of in situ deposition technique was used for the synthesis of nano calcium phosphate using polyethylene glycol and calcium chloride as starting materials. The particles thus prepared were subjected to XRD, TEM and SEM to analyse the particle size and to confirm that they are in the nano regime.

From the TEM micrographs, as shown in figure 3.1, it is evident that the calcium phosphate particles have size within the nano regime. Figure 3.1 (a), (b) and (c) shows the TEM images of nano calcium phosphate at different scales like 10nm, 20 nm and 100 nm. Further calculation of particle size was carried out by XRD.

![Fig 3.1 TEM images of calcium phosphate nano particles](image)
The most prominent peak in the XRD (figure3.2) corresponds to all the three states \( \text{Ca}_3(\text{PO}_4)_2, \text{Ca}_3(\text{PO}_3)_2 \cdot 3 \text{H}_2 \text{O}, \beta \) Calcium orthophosphate being the major phase. Since calcium chloride is first complexed with PEG, only certain crystalline phases of calcium phosphate is allowed to grow as compared to the number of phases getting developed in normal free precipitation. The particle size has been analysed by Scherrer equation \( L = \frac{0.9\lambda}{\beta \cos\theta} \), where \( \lambda \) is the wavelength of X-ray used and \( \beta \) is the full width at half minimum. The mean particle size calculated was 22.83 nm which is in agreement with TEM images.

**Table 3.1** Calculation of particle size of calcium phosphate

<table>
<thead>
<tr>
<th>( \beta )</th>
<th>Cos( \theta )</th>
<th>L</th>
<th>Mean nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.706</td>
<td>0.9741</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>1.3800</td>
<td>0.9602</td>
<td>20.9</td>
<td>22.83</td>
</tr>
</tbody>
</table>

**Fig 3.2** XRD of the synthesized calcium phosphate nanoparticles
The formation of calcium phosphate was in agreement with the FTIR spectra as shown in figure 3.3. The peak at 3400 cm\(^{-1}\) corresponds to OH group, 1981 cm\(^{-1}\) might be due to P-O stretching and the peak at 1645 cm\(^{-1}\) correspond to P-OH combination band. The peak at 1438 indicates P = O stretching and the various peaks at 1100-1000 cm\(^{-1}\), 927 cm\(^{-1}\), 870 cm\(^{-1}\), 633 cm\(^{-1}\), 600 cm\(^{-1}\) and 583 cm\(^{-1}\) indicate the vibrational modes of phosphate group.

3.3 Results and Discussion

3.3.1 Characterization of chlorobutyl rubber composites

The figure 3.4 (a, b and c) show the TEM images of the titanium dioxide particles. The rutile morphology of the titanium dioxide particles is clearly shown in the figure 3.4.
Fig 3.4 TEM images of titanium dioxide particles.
The SEM images of the morphology as well as fracture surface of the nanocomposites is shown in the figures 3.5-3.7. Figure 3.5 (a) shows the SEM images of the morphology of CIIR gum sample and figure 3.5 (b) shows the morphology of the composites containing 10 phr of titanium dioxide. The figure reveals almost uniform and good dispersion of filler particles in the CIIR matrix. It is evident from the fracture surface of the nanocomposites that the filler particles are reinforcing in nature. It is also clear that the there is a sort of pull out happening on the fracture surface as a result of agglomeration of the filler particles as shown in figure 3.6 in the case of titanium dioxide. Figure 3.6 (a) and 3.6 (b) denote the SEM images of the titanium oxide filled nanocomposites at 10 phr loading. The crevices formed as a result of pull out are microsized and shows bigger aggregates of filler particles. The ridgelines formed as shown in the SEM images of calcium phosphate in figure 3.7 indicate the reinforcing nature of the filler. This is yet again confirmed from the TEM images of the nanocomposites taken after cryosectioning the fracture surfaces.
Fig 3.5  SEM images of the morphology of (a) CIIR and (b) composite containing 10 phr of TiO$_2$

Fig 3.6  SEM images of the fracture surface of composites containing 10 phr of TiO$_2$
Morphology of the filler is found to have a profound influence on the properties of the nanocomposites. Figure 3.8 shows the TEM images of CIIR composites containing 10 phr of titanium dioxide at (a) 20 nm and (b) 50 nm scales. Figure 3.9 shows the TEM images of CIIR nanocomposites containing calcium phosphate at 10 phr loading at (a) 20 nm and (b) 50 nm scales. Due to the particular morphology of the calcium phosphate nanoparticles the polymer chains are rather strongly held and hence upon stretching they show a greater elongation at break. This is evident from the morphology of the nanocomposites obtained from the TEM images in which the surface of the nanocomposites show a sort of pattern formation with all the filler particles arranged in a particular fashion (figure 3.9). In the case of titanium dioxide filled composites (figure 3.8) there is no peculiar pattern formation as in the case of calcium phosphate filled nanocomposites. This paves way to the enhanced properties exhibited by calcium phosphate nanocomposites.

Fig 3.7  SEM images of the fracture surface composite containing 10 phr of calcium phosphate particles

Fig 3.8  TEM images of chlorobutyl rubber nanocomposites containing 10 phr TiO₂

(a)  (b)
Fig 3.9 TEM images of chlorobutyl rubber nanocomposites containing 10 phr calcium phosphate.
3.3.2 Mechanical properties

The mechanical properties of the composites prepared using melt mixing technique was found to be enhanced and this technique proved to be effective in the case of the fillers like titanium dioxide and calcium phosphate. Table 3.2 shows the mechanical properties of calcium phosphate filled chlorobutyl rubber samples. The composites show much inferior properties at lower loadings of titanium dioxide but when the loading rises to around 40 phr the mechanical properties show a steep rise. It is seen that the tensile strength increases by about 2.15 times as the filler loading increases to 20 phr in the case of calcium phosphate filled samples whereas in the case of titanium dioxide filled samples (table 3.3), the filler loading increases only by 1.44 times at 20 phr loading.

**Table 3.2** Mechanical properties of chlorobutyl rubber nanocomposites containing nano calcium phosphate

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus at 300 % elongation (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Tear Strength (KN/m)</th>
<th>Hardness (ShoreA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gum</td>
<td>1.98</td>
<td>3.4</td>
<td>16.7</td>
<td>35</td>
</tr>
<tr>
<td>5 phr CP</td>
<td>2.3</td>
<td>3.8</td>
<td>18.1</td>
<td>42</td>
</tr>
<tr>
<td>10 phr CP</td>
<td>2.5</td>
<td>5</td>
<td>20</td>
<td>43</td>
</tr>
<tr>
<td>20 phr CP</td>
<td>3</td>
<td>7.3</td>
<td>23.2</td>
<td>45</td>
</tr>
</tbody>
</table>
Table 3.3  Mechanical properties of chlorobutyl rubber nanocomposites containing titanium dioxide.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Modulus at 300% elongation (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Tear Strength (KN/m)</th>
<th>Hardness (Shore A)</th>
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<td>5 phr TO</td>
<td>2.20</td>
<td>3.6</td>
<td>17.1</td>
<td>37</td>
</tr>
<tr>
<td>10 phr TO</td>
<td>2.27</td>
<td>3.9</td>
<td>18.2</td>
<td>40</td>
</tr>
<tr>
<td>20 phr TO</td>
<td>2.54</td>
<td>4.9</td>
<td>19.4</td>
<td>42</td>
</tr>
</tbody>
</table>

Figure 3.10  Effect of filler type on the tensile strength of chlorobutyl rubber composites

Figure 3.10 shows the effect of filler type on the tensile strength of the nanocomposites. It can be seen that the nanocomposites containing layered silicate (LS) show enhanced properties when compared to the composites containing calcium phosphate and titanium dioxide nanoparticles. This phenomenon seemed to
be caused by the slippage of rubber molecules and orientation of the intercalated silicate layers under stress. The orientation can increase the loading capability of organo-clay and the slippage makes it possible for the highly strained 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 dispersed clay with high aspect ratio possess a higher stress bearing capability and stronger interaction between nanolayers and rubber molecules associated with the larger contact surface results in more effective constraint of the motion of rubber chains [17].

Two specific characteristics of layered silicates are useful for nanocomposite development. The first one is based on the possibility of the high aspect ratio layers to be individually dispersed and the second one on their chemical capacity to be modified through cation exchange reactions. So not only their reinforcing effect may become apparent but their chemical compatibility with the polymer may be considerably improved. The better polymer–filler interaction and the favoring of layered silicate nanocomposite formation can be predicted from the thermodynamic point of view. The free energy change of the system after mixing the clay in halobutyl elastomers may be given as follows:

\[
\Delta G_E = \Delta H_E - T\Delta S_E \quad \text{for elastomers}
\]

(1)

\[
\Delta G_C = \Delta H_C - T\Delta S_C \quad \text{for clays}
\]

(2)

Therefore total free energy change of the system is

\[
\Delta G_S = \Delta H_S - T\Delta S_S = \Delta H_S - T(\Delta S_E + \Delta S_C)
\]

(3)

From the expression, \( \Delta G_S \) value will be negative and hence the most favorable interaction between the clay and the halobutyl elastomer will take place when \( \Delta H_S \) is negative and \( \Delta S_S \) is positive. When polymer chains enter into the gallery of the clay, they reside in a restrained form, i.e. \( \Delta S_E \) is negative. In contrast, the expansion of the gallery by elastomer chains causes the entropy change in the clay, \( \Delta S_C \) to be
positive. If the clays are exfoliated, this may probably compensate the entropy loss associated with the confinement of elastomer chains.

3.3.3 Mechanism of molecular transport in CIIR composites

The swelling experiments were conducted for the chlorobutyl rubber composite samples using cyclohexane as the solvent and the swelling curves were plotted. The swelling curves as shown in figures 3.11-3.13 exhibit two distinguished zones. The first zone shows a high rate of solvent uptake due to the large concentration gradient and the polymer sample is under severe solvent stress. The second zone indicates a reduced swelling rate due to the decrease in concentration gradient, which finally reaches at equilibrium swelling.

![Swelling curves](image)

**Fig 3.11** Variation of mol% uptake of solvent with $t^{1/2}$ for TiO$_2$ filled composites in Cyclohexane
Fig 3.12  Variation of mol% uptake of solvent with $t^{1/2}$ for cloisite 15 A filled composites in cyclohexane

Fig 3.13  Variation of mol% uptake of solvent with $t^{1/2}$ for nano calcium phosphate filled composites in cyclohexane
The permeability of a solvent molecule into a polymer membrane depends on the diffusivity as well as the solubility or sorption of the solvent in the membrane. Therefore, the sorption coefficient has been calculated using the relation [18]

\[ S = \frac{M_\infty}{M_p} \]  

(4)

where \( M_\infty \) is the mass of the solvent taken up at equilibrium swelling and \( M_p \) is the mass of the polymer sample. Sorption coefficient is a thermodynamic parameter which depends on the strength of the interactions in the polymer / penetrant mixture. Permeation can be considered as the combined effect of sorption and diffusion process.

To understand the mechanism of sorption, the values obtained were fitted to the equation [19]

\[ \log \frac{Q_t}{Q_\infty} = \log k + n \log t \]  

(5)

where \( Q_t \) is the mole percent uptake at time \( t \), \( Q_\infty \) the mole percent increase in uptake at equilibrium, \( t \) the time and \( k \) is a constant characteristic of the polymer, which indicates the interaction between polymer and solvent. The magnitude of \( n \) reveals the nature of the sorption phenomena, i.e. Fickian or non-Fickian. If \( n = 0.5 \), the mechanism of sorption is termed as Fickian transport and it happens when the rate of diffusion of the penetrant is smaller than the segmental mobility of the polymer. If \( n = 1 \), the transport is said to be non-Fickian transport (often referred to as case II or relaxation controlled transport) and this situation occurs where the penetrant moves at a faster rate than the polymer relaxation process. If \( n \) lies between 0.5 and 1 then it is called non-Fickian and is anomalous transport and it happens when the mobility of the permeant molecule and the segmental mobility of the polymer are almost similar. The experimentally estimated values of the constants \( n \) and \( k \) are given in table.
Table 3.4 Values of $n$ and $k$ of chlorobutyl rubber nanocomposites (10phr) in cyclohexane.

<table>
<thead>
<tr>
<th>TiO$_2$ content</th>
<th>$n$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIIR</td>
<td>0.47</td>
<td>0.33</td>
</tr>
<tr>
<td>CIIR/TO$_{10}$</td>
<td>0.59</td>
<td>0.018</td>
</tr>
<tr>
<td>CIIR/CP$_{10}$</td>
<td>0.61</td>
<td>0.20</td>
</tr>
<tr>
<td>CIIR/15C$_{10}$</td>
<td>0.65</td>
<td>0.012</td>
</tr>
</tbody>
</table>

The values of $n$ in the present analysis were found to be between 0.5 and 1 revealing the fact that the mechanism of transport is non-Fickian and is anomalous in all the nanocomposite samples. The anomalous mechanism may be due to the leaching out of the additives from the vulcanizates. The magnitude of $k$ signifies the structural characteristics of the polymer and provides an idea about the nature of the interaction between the polymer and the solvent. The values of $k$ in the particle filled systems are lower than the unfilled systems. This indicates that the presence of filler can reduce the interaction between the polymer and the solvent. The overall performance of layered silicate can be attributed to the increased aspect ratio of the layered silicate and better interaction between the filler and the CIIR matrix. Moreover cyclohexane is good solvent for CIIR and hence the CIIR gum sample depicts higher percentage of solvent uptake when compared to filled systems. From figure 3.12 it can be seen that there is a remarkable difference between the solvent uptake characteristics of CIIR gum and the layered silicate filled vulcanizates. Moreover there is a remarkable difference in the solvent uptake behaviour in the case of layered silicate filled samples when compared to composites containing calcium phosphate (figure 3.13) and titanium dioxide (figure 3.11). When filler loading is less there is better exfoliation in the case of layered silicates and the uptake of solvent decreases. When filler loading increases there is a chance of
agglomeration which paves way for a little bit of increase in uptake of solvent. Thus there is no significant difference between the swelling curves at higher filler loadings. Similar results with chlorobutyl nanocomposites were obtained by Sridhar et al.[20,21.]

3.3.4 Mechanism of gas transport in CIIR composites

The gas barrier properties of chlorobutyl rubber composites containing different types of fillers have been analysed. It can be seen that similar trends of liquid transport are repeated in the case of nitrogen permeation values. Figure 3.14 depicts the effect of filler type on the gas permeation characteristics of the chlorobutyl composites. Due to high aspect ratio and effective dispersion of the nano clay platelets the gas barrier properties of cloisite 15 A filled nanocomposites excel that of titanium dioxide and nano calcium phosphate filled composites. Similar reports on the barrier properties of butyl rubber nanoclay filled composites [22].

![Permeability of nitrogen gas through composites at 10 phr filler loading](image)

**Fig 3.14** Permeability of nitrogen gas through composites at 10 phr filler loading

3.4 Conclusions
A comparison of the nanocomposites with different types of fillers was made.

The mechanical properties of the layered silicate reinforced nanocomposites were found to be far superior when compared to that of the composites prepared using titanium dioxide and nano calcium phosphate as fillers.

Nano dispersed clay with high aspect ratio possess a higher stress bearing capability and stronger interaction between nano layers and rubber molecules associated with the larger contact surface results in more effective constraint of the motion of rubber chains thus providing superior mechanical properties.

The CP filled nanocomposites do not exhibit properties up to the mark.

The value of n suggest non Fickian anomalous mechanism in the case of transport of solvent

The CIIR composites containing layered silicate exhibit superior solvent resistance as well as gas barrier characteristics which help the material to function as chemical protective clothing material.
References


