Chapter 5

Mechanical properties of maleated natural rubber organoclay nanocomposites developed through masterbatch technique

Exploiting the ‘nanoreinforcement’ effect of layered silicates (clays), property improvement can be achieved even by adding small amounts of organoclay [1-6]. Properties enhancement is a consequence of both higher specific surface area and higher aspect ratio, in comparison to conventional fillers [7-9]. Key aspect of the ‘nano-concept’ is to intercalate and exfoliate the layers of the silicate [10]. For that purpose, the inherent ‘incompatibility’ between the polymer and the clay has to be circumvented. In order to facilitate, the penetration of the chains in between the galleries and thus to form a nanocomposite, different strategies are followed. They include the modification of the surface of the clay layers and/or the polymeric chains [11-15]. Further important factors are the length of the organophilic intercalant [16] and its number of alkyl tails [17], the molecular mass of the polymer matrix [18] and its polarity [19,20], as well as, the type of the layered silicate [21,22]. Although systems with intercalated structures are also termed as nanocomposites, the ultimate goal is to reach full exfoliation of the clay. Intercalation is also shown to be affected by the type and content of clay [23-25] and the type of clay intercalant, i.e. clay organic modification [26]. In general, improved intercalation is obtained at relatively low clay loading and high coupling agent-to-clay ratio. To support intercalation and exfoliation, the interlayer distance should be greater than 1.5nm [27] and the layered structure should be broken down [28]. The most commonly used approach to further aid compatibilization and dispersion of organoclays in PP is by melt compounding with maleic anhydride grafted PP (MA-g-PP) [28-32]. This method is found to
be effective to a great extent, but leads to loss of properties, as a result of high concentrations of MA-g-PP required for complete exfoliation of nanoclays. It is believed that the polar character of the anhydride causes an affinity for the silicate surface such that the maleated polypropylene can serve as a compatibilizer between the matrix and filler. This approach has been well developed for polypropylene-based systems; however, only a few studies have reported how the ratio of MA-g-PP to organoclay affects morphology and the related performance of PP-based nanocomposites [33, 34]. Lopez-Manchado et al. [35-37] prepared organoclay nanocomposites based on natural rubber and noticed an increase in the crosslink density, degree of curing, structure, order and glass transition temperature. Cis-1,4-Polyisoprene and epoxidized natural rubber were studied by Vu and coworkers [38]. Masterbatch technique of PP/MA-PP cloisite 30B organoclay was also reported by Perrin-Sarazin et al. [39].

In this chapter, the mechanical properties and cure characteristics of layered silicate reinforced 10% maleated natural rubber (10MA-g-NR) nanocomposites developed through masterbatch technique are proposed to be investigated.

5.1 Experimental

5.1.1 Preparation of maleated natural rubber-clay nanocomposites developed through masterbatch technique

5.1.1 A Preparation of maleated natural rubber/clay masterbatch

Natural rubber of grade ISNR-5 obtained from Rubber Research Institute of India, Kottayam, India was used for preparing maleated natural rubber. The organically treated montmorillonite from Southern clay products, USA, was used as the nanofiller for composite preparation. The nanoclay used was Cloisite 30B [MT2EtOH: methyl tallow, bis 2- hydroxyethyl, quaternary ammonium chloride] which is having an interlayer distance of 18.4Å. Other chemicals used were of commercial grade. Nanoclay was blended using (10MA-g-NR) at a level of 20-
50phr to prepare a masterbatch. 10MA-g-NR nanocomposites cannot be prepared by direct method because there occurs retardation in cure due to the presence of the excess acid group in 10MA-g-NR. In order to overcome this problem and to obtain better strength and properties the masterbatch technique is preferred. The masterbatch is prepared by mixing 20-50phr nanoclay with 10MA-g-NR for 6 minutes in a Brabender Plasticorder in order to get a proper dispersion. Nanocomposites using different clay loading up to 7 weight percentage were prepared by mixing calculated amounts of the masterbatch and virgin NR. Then the above mix after 12 hours is used for rubber compounding.

5.1.1 B Preparation of nanocomposites

The 10MA-g-NR clay masterbatch should be diluted with natural rubber in order to make the nanoclay loading in the range of 1, 3, 5&7 weight percentages. The ingredients were added to the masterbatch in the Brabender Plasticorder at 50 rpm for 10 minutes according to the recipe given in table 5.1 for preparing nanocomposies. Maleic anhydride concentration of 10% was used throughout the study in masterbatch technique. For 10% MA concentration the masterbatch technique is preferred because; above 5% maleic anhydride concentration there occur retardation in cure due to the excess acid concentration of MA during nanocomposite preparation. The mixed compounds were matured for a period of 24hrs and the cure characteristics like cure time, scorch time, maximum and minimum torque were determined using rubber process analyzer at a temperature of 150°C and a pressure of 200kg cm⁻² pressure up to their respective cure times.
### Table 5.1 Compound formulation

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Sample Code</th>
<th>20 phr</th>
<th>30 phr</th>
<th>40 phr</th>
<th>50 phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>10MA-g-NR+Y+NR</td>
<td></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>ZnO</td>
<td></td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td></td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Diethylene glycol</td>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>CBS</td>
<td></td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>TMTD</td>
<td></td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Sulphur</td>
<td></td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Y = 1, 3, 5 & 7 parts of Cloisite 30B for hundred parts of rubber

#### 5.1.2 X-ray diffraction

X-ray diffraction (XRD) was used to study the nature and extent of dispersion of the clay in the nanocomposite.

#### 5.1.3 Transmission electron microscopy

The transmission electron microscopy was performed using a JEOL, JEM -2010 (Japan), TEM operating at an accelerating voltage of 200 kV.

#### 5.1.4 Cure characteristics of the compounds

The processing characteristics of the compounds were monitored using a Rubber Process Analyzer. The die type used was biconical and the die gap was 0.487 mm. The cure time; $T_{90}$, scorch time; $T_{10}$, maximum torque; $T_{\text{max}}$ and minimum torque;
\( T_{\text{min}} \) values were determined at 150°C at a frequency of 50.0 cpm and a strain of 0.20 deg.

5.1.5 Mechanical properties

Mechanical properties of the nanocomposites are done according to the ASTM standards mentioned in Chapter 2.

5.1.6 Strain sweep measurements

The strain sweep measurements on unvulcanized samples were conducted to study the rubber-filler interactions using the Rubber Process Analyzer (RPA 2000-Alpha Technologies).

5.2 Results and discussion

5.2.1 Characterisation of maleated natural rubber-clay nanocomposites using X-ray diffraction technique

Figure 5.1 (a), (b), (c), (d), & (e) shows the X-ray diffraction patterns of the cloisite 30B, nanocomposites with 1, 3, 5 and 7 wt% cloisite 30B respectively for 40 phr masterbatch which is having higher d-spacing among the mentioned masterbatches. For 20, 30 and 50 phr loading also the XRD patterns shows the same trend and closer values with 40 phr masterbatch. The cloisite 30B clay shows a diffraction peak at \( \theta = 4.81 \text{Å} \) that is assigned to an interlayer platelet spacing (001 diffraction peak) of 18.4 Å. The first, second and third peak corresponds to the d001, d002 and d003 spacing respectively. It is also seen in figure 5.1 (b), (c), (d) and (e) that d-spacing is increased from 18.4 Å to 27, 27.56, 27.67 and 26.33 Å respectively owing to the intercalation of maleated natural rubber in the nanocomposites. This increase in interlayer distance of the clay by approximately 9.27 Å confirms the formation of intercalated nanocomposites.
Figure 5.1 XRD patterns of: (a) cloisite 30B and (b), (c), (d) & (e) nanocomposites with 1, 3, 5 and 7wt% cloisite 30B loading respectively for 40phr masterbatch.

5.2.2 Transmission electron microscopy

The Transmission electron microscopy (TEM) imaging for rubber nanocomposites was carried out using a Transmission Electron Microscope CM-200 of Philips Technology. TEM was used in order to visualize the morphology of the clay layers in the nanocomposites. Figure 5.2 (a), (b), (c) & (d) shows TEM micrographs of 10MA-g-NR at 5wt% nanoclay loading for 20, 30, 40 and 50phr masterbatch. Even though, X-ray diffraction indicated all intercalated structures, exfoliated layers can also be observed in the TEM pictures.
Figure 5.2 (a) TEM micrograph of 10MA-g-NR nanocomposites with 5wt% nanoclay loading for 20phr

Figure 5.2 (b) TEM micrograph of 10MA-g-NR nanocomposites with 5wt% nanoclay loading for 30phr
Figure 5.2 (c) TEM micrograph of 10MA-g-NR nanocomposites with 5wt% nanoclay loading for 40phr

Figure 5.2 (d) TEM micrograph of 10MA-g-NR nanocomposites with 5wt% nanoclay loading for 50phr
5.2.3 Cure characteristics of the compounds

The use of rubber products always involves vulcanized materials because crosslinked elastomers present better mechanical properties. The cure characteristics of 5MA-g-NR compounds and NR compounds were discussed in the previous chapter. Here in this chapter the cure characteristics of 10MA-g-NR compounds developed through the masterbatch technique is discussed. The cure characteristics of the mixes are given in figure 5.3(a) - 5.3(d). Rubber compounds with organoclay showed an accelerating effect on the cure characteristics [40,41].

![Figure 5.3(a) Variation of cure time with nanoclay loading](image)

Figure 5.3(a) Variation of cure time with nanoclay loading
Figure 5.3 (b) Variation of cure rate index with nanoclay loading

The cure rate index is found to be high for 10MA-g-NR at 5wt% nanoclay loading in the case of 40phr than all other masterbatches with same amount of organoclay as seen in figure 5.3 (b). The cure time was reduced and cure rate index is increased for 5 weight percentage filler loading for 10MA-g-NR compound in 40phr batch when compared with pure NR gum. But the cure time was reduced and cure rate index is increased when compared with 5MA-g-NR compound at 5 weight percentage filler loading. This might have resulted in high rubber filler interaction through the anhydride group and is very high in the case of master batch technique.
Figure 5.3 (c) Variation of scorch time with nanoclay loading

Scorch time is the time required for the torque value to reach 10% of maximum torque. It is a measure of the processing safety- the time available for safe processing before the onset of vulcanization reaction. Scorch time is lower for grafted rubber in the case of master batch as shown in figure 5.3 (c) indicating
better processing safety. The reduction in scorch time for organoclay is due to some catalytic effect of the silicates on the crosslinking reaction [40].

Figure 5.3 (d) shows that the torque development $T_{(\text{max-min})}$ with filler content is higher at 5wt % for 10 MA-g-NR when compared to the 5MA-g-NR system. The increased $T_{(\text{max-min})}$ may be arising from the formation of more extensive crosslink. These results are attributed to the intercalation of the rubber with in the silicate galleries. Consequently, a better interaction between the rubber and the filler is obtained. The minimum torque; $T_{\text{min}}$, represents the effective viscosity of the mixtures before vulcanization. It is found to increase with filler loading for both grafted and ungrafted rubber. In the case of polymer nanocomposites filled with various particulate fillers the minimum torque in rheographs is considered to be a direct measure of the filler content. $T_{\text{min}}$ can be considered as a measure of stiffness of the unvulcanized compound. The increase in viscosity with the addition of filler suggests a reduced mobility of the rubber chains caused by the incorporation of these fillers.

5.2.4 Mechanical properties of nanocomposites

As the weight percentage of layered silicates increases the tensile strength also increases as evident from figure 5.4. The improvement in tensile properties is so pronounced in 10MA-g-NR nanocomposites in 40phr batch developed through master batch means when compare to 5MA-g-NR nanocomposites. After 40phr the enhancement in tensile strength is reduced by 3.23% (i.e. in the case of 50 phr). Intercalation of rubber chains into the layers resulted in increase in tensile strength. The enhancement in properties occurs because of the higher polymer-filler interactions than filler-filler interactions. The MA functional groups are incorporated into the polymer; the stress is much more efficiently transferred from the polymer matrix to the inorganic filler, resulting in a higher increase in tensile properties. The driving force for intercalation originates from the strong hydrogen bonding between the maleic anhydride group (COOH group generated from the hydrolysis of the maleic group) and the oxygen groups of the silicates.
An increment of 87.33% in tensile strength is observed for 10MA-g-NR at 5wt% nanoclay in 40phr batch when compared to the pure NR gum sample. While on the other hand 10MA-g-NR nanocomposites when compared to the 5MA-g-NR at 5wt% nanoclay loading shows an increase in tensile strength of 12.14%.

Figure 5.4 Tensile strength of nanocomposites with nanoclay loading

Figure 5.5 is the elongation at break (%) curves of nanocomposites containing varying percentage of nanoclay. The elongation at break of all systems decreases with increase in weight percentage of filler [43]. 10MA-g-NR for 40phr batch at 5wt% nanoclay & 5MA-g-NR with same nanoclay shows a decrement of 26.83 & 7.20% respectively. The decrease at higher loading is due to the enhancement in rigidity of the material and was possibly caused by the reduction in tensile crystallization. All the system shows the same trend. For most of the applications requiring a large initial reinforcement, the ultimate strain is not very crucial.
The dependence of modulus at 300% strain on filler content is shown in figure 5.6. The modulus of all the samples is higher than the gum samples. 10MA-g-NR for 40phr batch with 5wt% nanoclay & 5MA-g-NR with same loading shows an increment in modulus of 162.41 & 78.06% respectively. From the results it is obvious that even with the addition of such a low loading (1-5wt%) of the layered silicates, the modulus increases considerably. The improvement in properties is due to the nanomeric dispersion of silicate layers resulting in efficient reinforcement leading to improved stiffness of the material. The clay platelet aspect ratio has a significant effect on the stiffness of the polymeric material. According to Daniel and co-workers [44] as the matrix modulus increases there is a much higher relative stiffness enhancement in the rubbery state owing to the intercalation of the rubber into the layered silicates.
Figure 5.6 Modulus at 300% elongation of nanocomposites with nanoclay loading

Figure 5.7 Tear strength of nanocomposites with nanoclay loading.

Figure 5.7 is the tear strength curves of the system as a function of weight percentage of nanoclay content. 10MA-g-NR and 5MA-g-NR filled layered silicate exhibit increase in tear strength up to 5wt% nanoclay loading and above that it shows a decrease. 10MA-g-NR for 40phr batch at 5wt% & 5MA-g-NR nanocomposites with 5wt% nanoclay shows an increment in tear strength of
52.57 & 46.32% respectively, indicating the resistance offered in the silicates in order to enhance the crack propagation and the super reinforcement of organoclay. Above all, the finely dispersed silicate layers divert the tear path, which in turn imparts high tear strength to nanocomposites.

Hardness, a measure of low strain elastic modulus, is higher for grafted rubber compared to the ungrafted rubber. From figure 5.8, shows the variation of hardness with nanoclay. 10MA-g-NR for 40phr batch with 5wt% nanoclay & 5MA-g-NR nanocomposites with same nanoclay loading shows an increase in hardness of 76.66% and 30.76% respectively. This is expected because, as more and more nanofiller get into the rubber matrix, the modulus increases and consequently hardness also increases. Here the tensile strength, modulus, tear strength and hardness show the same trend.

As the hardness increases abrasion loss, which is a measure of reinforcement, should decrease and this is reflected in figure 5.9. The increased crosslink density which results in increased hardness and modulus ultimately gives rise to the enhancement of abrasion resistance. It can be observed that 12.5% decrease in
Abrasion loss is observed for 10MA-g-NR nanocomposites at 5wt% for 40phr batch when compared to 5MA-g-NR nanocomposites at same nanoclay loading. This improved abrasion resistance in the organomodified silicate-filled composites is also due to the improved rubber-filler interaction. The intercalation and exfoliation of the modified silicate increased the surface area of the filler, leading to more interaction between the filler and the matrix.

![Graph showing abrasion loss of nanocomposites with nanoclay loading.](image)

Figure 5.9 Abrasion loss of nanocomposites with nanoclay loading

Compression set values depends strongly on the elastic recovery of the sample. Compression set values which is shown in figure 5.10 is lower for 10MA-g-NR when compared to 5MA-g-NR nanocomposites. It can be observed that 7.2% decrease in compression set values is observed for 10MA-g-NR nanocomposites at 5wt% for 40phr batch when compared to 5MA-g-NR nanocomposites at same nanoclay loading. This can be attributed to higher crosslink density. The lower compression set values indicate a more restrained matrix and elastic deformation is operational.

Resilience, a measure of the elastic component, was found to increase with increase in nanoclay loading. An increase of 11.2% is observed for 10MA-g-NR nanocomposites at 5wt% for 40phr batch compared to 5MA-g-NR at same nanoclay loading. The rebound resilience is increased by the increase in modulus.
This is due to the high reinforcement between the filler and the elastomer as shown in figure 5.11.

![Graph showing compression set of nanocomposites with nanoclay loading](image)

Figure 5.10 Compression set of nanocomposites with nanoclay loading

![Graph showing resilience of nanocomposites with nanoclay loading](image)

Figure 5.11 Resilience of nanocomposites with nanoclay loading

It is seen that the nanocomposite with the clay having higher interlayer distance shows better mechanical properties. This suggests that interlayer distance play a major role in the intercalation of the rubber matrix.
5.2.5 Strain sweep measurements of uncured compounds

The complex modulus ($G^*$) values obtained for the uncured compounds are plotted and shown in figure 5.12. The elastic modulus of a filled rubber is strongly dependent on the deformation and decreases substantially at higher strains. This phenomenon is known as Payne effect and is attributed to the presence and breakdown of the filler network during deformation. But investigations performed with both experimental and theoretical approaches shows that the decrease in $G^*$ with amplitude of deformation (strain) is attributed to the destruction-reformation of a percolating network of filler that can also involve polymer bonded filler [45] i.e. polymer filler links also. The complex modulus values at low strains (15%) are due to polymer networks and hydrodynamic interactions [46]. The limiting values at high strains are due to polymer networks and hydrodynamic effect. Polymer networks are the same for a fixed mass of rubber. But the hydrodynamic effect varies with the filler content and the nature of the filler. The theoretical meaning of hydrodynamic effect is given by the modified form of Guth and Gold equation [47, 48].

The addition of filler increases the shear modulus, $G_f$ for the filled compound

$$G_f = G_0 (1 + 0.67 f_s \phi + 11.62 f_s^2 \phi^2)$$

Where $\phi$ is the volume fraction of the particles and the shape factor $f_s$ represents the ratio of the longest dimension to the shortest dimension of the particle. The modulus as calculated by the equation is independent of the applied strain [49]. The variation of complex modulus ($G^*$) with strain for the composites with clay are presented in figure 5.12. The graph show that the complex modulus values at low strain increases with filler concentration. As the complex modulus values of $G^*$ is due to higher filler-filler or filler polymer interactions. Variation in mechanical properties of the composites explained earlier shows that the network formed are mainly between filler and polymer.
Figure 5.12 Variation of complex modulus with nanoclay content for 10MA-g-NR nanocomposites at 40phr

5.3 Conclusions

Maleated natural rubber-organoclay nanocomposites can be prepared with nanoclay in varying clay loading and the clay content influences the cure characteristics and mechanical properties of maleated natural rubber. In presence of organoclay both the cure time and scorch time are considerably reduced. This reduction in cure time is boosted with the increase in interlayer distance of the clay. A dramatic increase in maximum torque value with increase in clay loading is also observed for the nanocomposites. The mechanical properties of 10MA-g-NR nanocomposites are higher than 5MA-g-NR nanocomposites which are obtained by direct method. Nanocomposites with the clay having higher interlayer distance shows better mechanical properties. The increase in d spacing for these layered clays evident from X-ray results and TEM photographs also confirmed the formation of partially intercalated and exfoliated structure.
References

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