Dynamic mechanical analysis is a useful technique for characterization of polymer layered silicate nanocomposites. The extent of intercalation and exfoliation of layered silicates in polymer can be obtained from the storage modulus and glass transition temperature. A large number of rubber articles like automobile tyres, springs and dampers are subjected to cyclic deformation or loading during their service life. Rubber is used as the base material in a product if it requires rubber-like elasticity and flexibility. Since rubber products generally undergo dynamic loading during service, their dynamic mechanical analysis is very important. Thus it is particularly useful for evaluating the mechanical properties of viscoelastic materials like polymeric composites whose properties exhibit time, temperature and frequency dependence. The dynamic mechanical properties of polymer layered silicate nanocomposites depend highly on the separation of the silicate layers. As the spacing between the silicate layers increases the storage modulus (E') increases and the damping peak corresponding to the glass transition temperature broadens. The viscoelastic behaviour of polymer nanocomposites has been studied by many scientists for analyzing the change in glass transition temperature, damping behaviour (tan δ), storage and loss modulus (E'') with addition of nanofillers [1-9]. Arrighi et al. [7] observed a second relaxation dynamics due to interaction of the polymer with filler surface. Varghese et al. [10, 11] studied the damping behavior of layered silicates reinforced natural rubber nanocomposites. The frequency sweep of the
NR and NR/clay composite at 60°C under 0.58 strain is reported [12]. The
dynamic mechanical properties of NBR/clay [13], MA-g-EPDM/clay [14] have
been studied. Dynamic mechanical studies have considerable practical
significance for several reasons, particularly if they are analyzed over a wide
range of frequencies and temperatures. The dynamic properties are also of direct
relevance to a range of unique polymer applications, concerned with the isolation
of vibrations or dissipation of vibrational energy in engineering components.

Dielectric property analysis of filled polymers and polymer-polymer blend
contribute to a better understanding of the structure-property relationships at the
morphological level [15-18]. The dielectric properties of polymeric material
depend on the additives, fillers and impurities present in it. The effect of filler on
the electrical properties of polymeric material has been investigated by many
researches [19, 20-24]. The most widely used fillers in polymeric material are
carbon black, graphite particles and conducting fibers. The properties of these
composites depend on three phases, namely, the phase of organic polymer, the
phase of filler content and the phase of interaction between the polymer and the
blend.

The dynamic mechanical analysis and dielectric properties of nanoclay
reinforced maleated natural rubber nanocomposites by direct method and
masterbatch technique are proposed to be investigated with reference to the
maleic anhydride content, organoclay content and frequency using the frequency
sweep method.

8.1 Experimental

8.1.1 Dynamic mechanical analysis

In dynamic mechanical analysis the frequency is proposed to be varied from 1 to
50Hz under frequency sweep mode at a rate of 2Hz/min and at a temperature of
60°C.
8.1.2 Dielectric studies
The dielectric permittivity was measured in alternating current at room temperature using HP 4285 A LCR Hi-tester by varying the frequencies (0.1-8 MHz).

8.1.3 Heat build-up
The Ektron flexometer conforming to ASTM D 623-1999 was used for measuring the heat build-up.

8.2 Results and discussion

8.2.1 Dynamic mechanical properties (DMA)

8.2.1.1 Maleated natural rubber clay nanocomposites
The dynamic mechanical response of the maleated natural rubber (MA-g-NR) containing layered silicate is measured to examine the degree of filler-matrix interaction. Maleic anhydride concentration in direct method is taken as 1, 3, 5 percentages. The elastomer chains get intercalated into the layered structures of silicate resulting in the change in modulus and damping behaviour. The interaction of polymer chain into silicate layers will enhance the contact surface area of filler and matrix. Figure 8.1 is the $E'$ vs weight percentage of nanoclay curves at different frequency of 5MA-g-NR. The $E'$ connects with the elastic modulus of the material. The $E'$ of nanocomposite is higher than unfilled system. Due to the aggregation of filler at higher concentration, the clay filled MA-g-NR shows reduced modulus. The enhancement in modulus with the addition of filler is associated with the stiffness of the material. Up to 5 weight percentage nanoclay there shows an enhancement in storage modulus and this may be due to better interaction between the polar rubber and polar filler. Figure 8.2 is the $E'$ verses weight percentage of nanoclay curves at different frequency of 3MA-g-NR. For 3MA-g-NR system, the $E'$ is higher for filled system. 3MA-g-NR nanocomposites show the same trend as that of 5MA-g-NR. But the storage modulus is decreased by 18% in the case of 3MA-g-NR nanocomposites. From
this it is evident that by increasing the maleic anhydride concentration the storage modulus can be improved and may be due to the better polarity of the matrix. Higher storage modulus indicates better dispersed and more exfoliated system. In case of intercalated structures, the contact surface area between polymer and the silicate layers are relatively low and as a result the change in $E'$ with frequency are not very predominant as compared to virgin polymers.

Figure 8.1 Storage modulus vs nanoclay curves of 5MA-g-NR nanocomposites

Figure 8.2 Storage modulus vs nanoclay curves of 3MA-g-NR nanocomposites
Up to 30Hz the storage modulus gradually increases at 5 weight percentage nanoclay but at 50Hz the increase is very fast. For 1MA-g-NR nanocomposites the storage modulus shows the same trend as that 5MA-g-NR and 3MA-g-NR. But the storage modulus is very low compared to the above two matrices.

Figure 8.3 Storage modulus vs nanoclay curves of NR nanocomposites

The dynamic mechanical properties of pristine natural rubber and its composites with clay were investigated over a wide frequency range as shown in figure 8.3. A 400% increase in storage modulus is observed for 5MA-g-NR at 5wt% compared to pure NR at 5wt% nanoclay loading for a frequency of 30Hz. Storage modulus $E'$ shows linear increase with frequency for all the composites irrespective of the matrix.

Figures 8.4-8.6 shows the $E''$ vs nanoclay curves of layered silicate filled 5MA-g-NR, 3MA-g-NR and NR. At lower concentration of filler the $E''$ increases. The $E''$ relates to the energy loss due to viscous dissipation. It is the viscous modulus of polymeric material. $E''$ shows a high value for gum sample compared to the filled nanocomposites. Up to 5wt% of nanoclay loading the loss modulus shows a decreasing trend and above that the loss modulus is increased. The $E''$ is decreased by 11.09% by the addition of 5wt% nanoclay in 30Hz for 5MA-g-NR when compared to the NR nanocomposite. It was seen that, $E''$ of the
composite at any frequency is lower than that of gum compound. Clay incorporation decreases the $E''$, which indicates the lower heat dissipation (heat build-up) in the clay reinforced MA-g-NR nanocomposites compared to that of gum compound. But an increment in loss modulus is observed at 7wt% nanoclay loading irrespective of the frequency. At 50Hz the loss modulus is increased which means high heat dissipation which may be explained in terms of the friction between the filler particles and the matrix. The nanoclay loading have also a significant effect on the frequency-dependency of the $E'$ and $E''$.

![Loss modulus vs nanoclay curves of 5MA-g-NR nanocomposites](image)

**Figure 8.4** Loss modulus vs nanoclay curves of 5MA-g-NR nanocomposites
Figure 8.5 Loss modulus vs nanoclay curves of 3MA-g-NR nanocomposites

Figure 8.6 Loss modulus vs nanoclay curves of NR nanocomposites
The damping behaviour of nanocomposites is displayed in figures 8.7-8.9. It is seen that the nanofiller reinforcement caused a decrease in tan δ value; increase in concentration of layered silicate results in a consistent decrease in loss tangent. This can be interpreted in terms of the restricted mobility of polymer chains due to their confinement in the layers of the silicates.

Figure 8.7 Tan δ vs nanoclay curves of 5MA-g-NR nanocomposites

Figure 8.8 Tan δ vs nanoclay curves of 3MA-g-NR nanocomposites
By the addition of clay, the tan δ becomes smaller. It is known that the height of the dynamic transition of a composite apparently reflects the relative quantity of the component itself. The decrease in tan δ is the result of the reduction of the amount of polymer being deformed during strain oscillation and thus reduces the amount of dissipated energy in the dynamic transition and this may be due to the greater amount of polymer in the intercalated stacks. It is often believed that the mechanical loss factor at 60°C has apparent relation with rolling resistance when the rubber is used for tire. The lower value of mechanical loss factor at 60°C indicates lower rolling resistant. The frequency sweep of the NR and MA-g-NR/clay composites at 60°C under 0.5146 strains is studied. The results show that pure NR [12] slightly decreases the mechanical loss factor under experimental conditions because of the weak interaction between the clay and matrix. In 5MA-g-NR organoclay nanocomposites decrease in the mechanical loss factor is high compared to pure NR nanocomposites due to the better interaction between the filler and polar matrix. It is interesting to point out that the decrement is much more in the case of 5wt% organoclay and when more clay is incorporated the storage modulus increases again, but still lower than 5MA-g-NR vulcanizate. A decrement of 351% and 223% in tan δ by the addition of
5wt% nanoclay in 30Hz for 5MA-g-NR and 3MA-g-NR when compared to the NR nanocomposites. From these results, it can be deduced that 5MA-g-NR reinforced with 5wt% organoclay has the lowest rolling resistant. It is assumed that at the experiment conditions the organoclay gets the best dispersion and morphology in the rubber matrix, which lead to best dynamic mechanical properties. When adding more inorganic fillers in the matrix, the dynamic mechanical properties become worse because the superabundant filler cannot deform and absorb energy during strain oscillation.

8.2.1.2 Maleated natural rubber clay nanocomposites developed through masterbatch technique

10MA-g-NR masterbatches with 20, 30, 40 and 50phr loading were studied. The maximum property improvement is only up to 40phr and above that a decrement is noticed. So 20phr and 40phr is taken for the study. The mechanical property shows a maximum value at 40phr batch at 5wt% loading for 10MA-g-NR which is mentioned in chapter 5. Figure 8.10 and 8.11 shows the storage modulus verses nanoclay loading of 10MA-g-NR at a frequency of 1, 10, 30 and 50Hz for 20phr and 40phr batch.

![Figure 8.10 Storage modulus vs nanoclay of 10MA-g-NR nanocomposites at 20phr masterbatch.](image-url)
It is seen that the storage modulus increased up to 5wt% nanoclay loading and above that a decreasing trend is observed. At higher levels of clay loading this decrease is due to the poor dispersion of clay. The increase in storage modulus may be due to the stiffness of the material. This is due to the confinement of the macromolecular segments into the organoclay nanolayers and the strong interaction between the filler and rubber matrix. 40phr masterbatch shows the maximum storage modulus when compared to 20phr batch and 5MA-g-NR nanocomposites developed by direct method. An increase of 405% and 519% in storage modulus is observed for 10MA-g-NR at 5wt% nanoclay for 20phr and 40phr batch respectively compared to pure NR nanocomposite at 5wt% loading. And also an increase of 23.52% in storage modulus is observed for 40phr batches when compared to 5MA-g-NR at 5wt% clay loading.

![Figure 8.11 Storage modulus vs nanoclay of 10MA-g-NR nanocomposites at 40phr masterbatch](image)
Figure 8.12 and 8.13 shows the loss modulus verses nanoclay loading of 10MA-g-NR at a frequency of 1, 10, 30 and 50Hz for 20phr and 40phr. The $E''$ relates to the energy loss due to viscous dissipation. It is the viscous modulus of a polymeric material. Decrease in loss modulus is observed for all nanocomposites irrespective of the matrix. This is due to low heat dissipation (heat build up) in nanocomposites. Decrement is higher for 40phr batch at 5wt% clay loading which means low heat built up.

Figure 8.12 Loss modulus vs nanoclay of 10MA-g-NR nanocomposites at 20phr masterbatch
Figure 8.13 Loss modulus vs nanoclay of 10MA-g-NR nanocomposites at 40phr masterbatch

Figure 8.14 and 8.15 shows the tan δ verses nanoclay loading of 10MA-g-NR at a frequency of 1, 10, 30 and 50Hz. The damping behaviour of nanocomposites is lower compared to the gum sample. All matrixes show the same trend. The 40phr batch at 5wt% loading show the lower value in loss tangent compared to all other matrix. The increase in concentration of layered silicates results in a consistent decrease in loss tangent. This can be interpreted in terms of the restricted mobility of polymer chains due to the confinement in the layers of silicates. The decrease in tan δ suggests a strong adhesion between the rubber and filler.
Figure 8.14 Tan δ vs nanoclay of 10MA-g-NR nanocomposites at 20phr masterbatch

Figure 8.15 Tan δ vs nanoclay of 10MA-g-NR nanocomposites at 40phr masterbatch
8.2.2 Heat Build up

Effect of nanoclay in NR and maleated NR nanocomposites were also studied at certain dynamic properties such as the generation of heat under cyclic deformation. We have used the classic test of the Ektron flexometer and the temperature increase was then divided by the hardness of the sample to have a heat index. All the data of this study are reported in figure 8.16-8.19. It can be observed that the heat build up decreases by the addition of nanoclay and the best results are already achieved at 5wt% nanoclay level. The further addition of nanoclay does not affect anymore the heat index. Thus, the nanoclay offers also the beneficial effect of being able to reduce the hysteresis of a rubber compound [25].

![Figure 8.16 Heat build up verses nanoclay loading of nanocomposites](image)

Figure 8.16 Heat build up verses nanoclay loading of nanocomposites
Figure 8.17 Heat index verses nanoclay loading of nanocomposites

Figure 8.18 Heat build up verses nanoclay loading of 10MA-g-NR nanocomposites
Figure 8.19 Heat index verses nanoclay loading of 10MA-g-NR nanocomposites

The heat build up and heat index of 10MA-g-NR nanocomposites developed through masterbatch technique is lower than the 5MA-g-NR nanocomposites developed by direct method. The first point in the graph of masterbatch method corresponds to the values of pure NR gum. Pure NR gum is taken as the reference material for 10MA-g-NR masterbatch. A decrease in heat build up of 508% is observed for 40phr batch at 5wt% nanoclay loading when compared to pure NR gum. While in the case of 5MA-g-NR nanocomposites at 5wt% nanoclay loading shows a decrease of 200% in heat build up when compared to 5MA-g-NR gum samples. 5MA-g-NR gives lower heat build up values when compared to 3MA-g-NR and 1MA-g-NR nanocomposites. Low heat generated samples are used in tires of automobiles. At the Ektron flexometer the compounds filled with nanoclay show lower heat build up and hence shows lower hysteresis than the reference compound without nanoclay under dynamic conditions. The heat index calculated as the ratio between the temperature jump at the Ektron flexometer and the hardness confirms the trend to lower hysteresis for the nanoclay filled compounds.
8.2.3 Dielectric properties

Figure 8.20 is the dielectric permittivity ($\varepsilon'$) verses frequencies of 5MA-g-NR gum and its organoclay filled nanocomposites at 30°C. It is observed that the filled systems show lower $\varepsilon'$ than pristine polymers. A decrease of 12.19% and 9.21% in $\varepsilon'$ respectively is observed for 5MA-g-NR and 3MA-g-NR at 5wt% nanoclay loading when compared to its gum. This may be due to the formation of ester as result of reaction between OH group of clay and COOH group of maleic anhydride which shows that better interaction at 5wt% of nanoclay loading. At 7wt% of nanoclay loading a noticeable change is not observed and this means that there are no more groups to interact with the OH groups of clay. But when compared to pure NR nanocomposites, the maleated nanocomposites show higher values.

![Dielectric permittivity vs frequency plots of nanocomposites at 30°C](image)

In the case of 3MA-g-NR gum and its nanocomposites the $\varepsilon'$ is lower when compared to 5MA-g-NR nanocomposites and which is shown in figure 8.21. In all systems $\varepsilon'$ decreases with increase in frequency. 3MA-g-NR at 7wt% shows
the same trend as seen in 5MA-g-NR at 7wt% nanoclay loading. 1MA-g-NR shows again lower values of $\varepsilon'$ when compared to the above two maleated matrices. This may be due to the low polarity of 1MA-g-NR and its nanocomposites.

![Dielectric permittivity vs frequency plots of nanocomposites at 30°C](image)

Figure 8.21 Dielectric permittivity vs frequency plots of nanocomposites at 30°C

$\varepsilon'$ decreased up to 5wt% of nanoclay loading in all the case and after that the decrease is not so pronounced as shown in figure 8.22. This shows that further interaction is not possible even after the addition of excess clay and this may be due to the poor interaction between the filler and the matrix which arises due to the lack of acid groups in the maleated rubber matrix for further interaction.
Figure 8.22 Dielectric permittivity vs nanoclay loading at 30°C

Figure 8.23 and 8.24 shows the dielectric permittivity vs frequency plots of 10MA-g-NR nanocomposites at 30°C for 20phr and 40phr batch respectively. Here also $\varepsilon'$ decreases with increase in frequency as that of 5MA-g-NR nanocomposites which is obtained by direct method. And also $\varepsilon'$ shows a decrement as the clay content is increased as shown in 8.25. 40phr batch shows lower $\varepsilon'$ compared to 20phr batch at 5wt% nanoclay loading. This is due to the better dispersion of clay in the matrix. NR nanocomposites show lower $\varepsilon'$ values when compared to the maleated nanocomposites which shows that conductivity is higher in maleated nanocomposites due to the polar nature. A slight increasing trend (23.38%) is observed in the case of NR nanocomposites as the clay content is increased but still lower than the maleated sample which is due to the polar nature of nanoclay.
Figure 8.23 Dielectric permittivity vs frequency plots of 10MA-g-NR nanocomposites at 30°C

Figure 8.24 Dielectric permittivity vs frequency plots of 10MA-g-NR nanocomposites at 30°C
8.3 Conclusions

Storage modulus increases while loss modulus and tan δ decrease with increase in the frequency in frequency sweep method. The storage modulus of nanocomposite is higher than unfilled system up to 5 weight percentage clay loading. This is due to the aggregation of filler at higher concentration, the clay filled MA-g-NR shows reduced modulus. 3MA-g-NR shows the same trend as that of 5MA-g-NR. But the storage modulus is decreased by 18% in the case of 3MA-g-NR nanocomposites. The storage modulus increases as the maleic anhydride concentration in the matrix increases. The loss modulus and damping behaviour is decreased by increasing the clay loading to a particular level. The heat build up is decreased by the addition of nanoclay to a particular loading in all the mixes. The dielectric permittivity is higher for maleated gum samples compared to filled samples. Maleated samples show better dielectric permittivity compared to NR nanocomposites due to hydrogen bonding. In MA-g-NR nanocomposites the dielectric permittivity is decreased by the addition of nanoclay even though the values are higher than that of pure NR nanocomposites.
References


