Chapter 6

Stress Relaxation Behaviour of Organically Modified Montmorillonite Filled Natural Rubber/Nitrile Rubber Nanocomposites

Abstract

To reduce material consumption, it is important to have reinforced material with longer life time. Incorporation of nanoparticles to reinforce and compatibilize polymer blends is one of the widely undergoing research areas in polymer science technology. A series of natural rubber and nitrile rubber (NR/NBR) nanocomposites vulcanizes, reinforced with two different organically modified clay (OC) were prepared. To predict the performance of a material over long periods of time, stress relaxation studies with both the reinforced systems were done. The effects of loading, blend composition, filler polarity and temperature on stress relaxation of OC reinforced NR/NBR nanocomposites were carefully measured. Based on the stress relaxation measurements, it was observed that due to its polarity difference, O1Mt (Mt modified with dimethyl, benzyl, HT modification provided by Southern Clay Products) was preferentially located at the NBR phase, while, O2K (Kaolin clay modified with mercapto silane provided by English India Clay) had more affinity with natural rubber in the NR/NBR nanocomposites. The preferential localization of OC has been analyzed by HRTEM. The nature of interaction of the nanoclay was found to influence the stress relaxation rate. NR/NBR nanocomposites with higher filler loading showed higher rates of relaxation rate due to the presence of more filler-filler interactions. At 70°C, the viscosity ratio was found to influence the reinforcement, and consequently relaxation rate of the 50/50 NR/NBR nanocomposites. It was found that the rearrangements of the polymer chains are dependent on the blend composition, temperature, filler/polymer interactions etc. To explain and predict the observed phenomena, the stretched - exponential Kohlrausch equation and Maxwell - Weichert model were used. For both models, the experimental curve fitted well with the theoretical models.¹

¹ The results of this chapter has been published in Applied Clay Science, Volume 87, January 2014, Pages 120–128
6.1. Introduction

Blending existing polymers is a very advantageous means of developing new materials, tailored to specific market segments. The philosophy of mixing materials involves combining good properties of the individual materials, while mitigating their respective detrimental characteristics. Predominantly, polymers are incompatible in mixtures. Thus, a compatibilizer is often added to improve the compatibility of different polymers. Nanoparticles are added as nanocompatibilizers to improve the interfacial strength of blends, by exploiting the concept of polymer polymer nanocomposites. Organoclay (OC) mineral has been used as a compatibilizer for incompatible polymers and it was pointed out by Rafailovic et al.\(^1\) that it could be added into polymer blends in order to improve the compatibility between two incompatible polymers, and to develop a more homogeneous system. The use of montmorillonite (Mt) as a reinforcing and as compatibilizing material for nitrile butadiene rubber (NBR) and styrene butadiene rubber (SBR) nanocomposites has been studied. At higher clay mineral concentration, the OC mineral was not homogeneously distributed in the matrix and agglomeration of the clay mineral causes phase separation\(^2\). The influence of clay mineral modification on the structure and mechanical properties of Mt/EPDM nanocomposite showed that the OMt layers were fully exfoliated in the EPDM matrix and has good mechanical properties\(^3\).

The determination, of mechanical properties like tensile strength and elongation at break, provides us with a fundamental understanding about the behavior of a material and these experiments are time-independent. However, these experiments are not enough to predict its long term behavior. Therefore to design a material which has good durability, it is very important to analyze the time- dependent viscoelastic nature of polymers such as stress relaxation, creep, dynamic mechanical properties etc. The stress relaxation experiment is conducted in order to characterize the time-dependent reinforcement of polymer nanocomposites\(^4\). For the viscoelastic rubber, when strained at a constant rate to a fixed deformation, the stress required to maintain that strain
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decays with time. This is referred to as stress relaxation. The stress relaxation rate depends on the probability of transition of the system from one stage of equilibrium to another\(^5\). It may be a one-stage or two-stage mechanism in multiphase systems\(^6\). The processes that can occur during stress relaxation of a typical rubber vulcanizate include physical relaxation, (which occurs due to the rearrangement of the polymer chains and the fillers when subjected to deformation), and the chemical effect (which is more prominent at higher temperature and at longer durations), due to the aging of rubber by oxidative chain scission, crosslink breakage, or crosslink formation\(^6\). There are comparatively less studies reported in this area on polymer nanocomposites. However there are some recent reports\(^7\)-\(^9\) which shows the importance of these properties.

To this date, only few studies reported about the time and temperature dependent reinforcement of polymer clay nanocomposites, especially in rubber blend systems\(^10\)-\(^12\). The stress relaxation behavior of short-jute-fibre reinforced acrylonitrile butadiene rubber composites, studied by Bhagawan \textit{et al.}\(^13\) reported that a two-stage relaxation pattern existed in these composites. Flink and Stenberg\(^14\) reported that stress relaxation studies could provide insight into the interfacial adhesion in NR composites reinforced with short cellulose fibers. Varghese \textit{et al.}\(^15\) studied the stress relaxation behavior of acetylated short-sisal-fiber-reinforced NR composites. Recently, from this laboratory, Meera \textit{et al.}\(^16\) investigated the tensile stress relaxation behaviour of natural rubber reinforced with titania and nanosilica. The rate of stress relaxation was found to increase with increase in filler loading for both the filled system and the silica-filled system, showing a higher rate of stress relaxation compared to the TiO\(_2\)-filled NR. Thus it is understood that the relaxation mechanism in nanocomposites is dependent on many factors, such as, the nature of the polymers, filler and interface, strain level, strain rate, and temperature.

The rate of stress relaxation of rubber chains can be influenced by its surrounding structure and will be different from other chains even in a
homogeneous, unfilled rubber compound. When one compares a polymer/polymer blend nanocomposite and a polymer nanocomposites, a major difference is observed between both morphological and thermomechanical properties. As with the behavior during the deformation stage, the behavior will be different during the relaxation stage also. The complexity is increased by the presence of nanoparticles. Different types of relaxation process can take place under loading, which will vary with the different types of interfaces in the material. Naturally, this variation in deformation was expected to result in different modes of stress relaxation behaviour. Two OCs were used for the blend preparation. One was cloisite 10A which is polar (O1Mt) and the other was Nanocaliber 200m which is nonpolar (O2K).

In this chapter the effect of filler loading, blend composition and nature of OC material on the stress relaxation behaviour of NR/NBR nanocomposites is discussed. We have reported here the stress relaxation behaviour of the OC filled elastomer blends of natural rubber and nitrile rubber. Both NR and NBR have specific individual properties like good mechanical properties for NR and good oil resistance for NBR. Incorporation of OC into this elastomeric blend was done as an attempt to make the two rubbers compatible. OC was found to be effective in compatibilizing elastomer blends. It appears, no work has been reported explaining the effect of OC on the stress relaxation behaviour of NR/NBR blend nanocomposites.

6.2. Results and discussion

6.2.1 Effect of nature of filler

Two types of blend compositions (70/30 and 50/50 NR/NBR) were taken for the study to differentiate the interaction of fillers, O1Mt and O2K with the two elastomers. The stress relaxation plots of 70/30 and 50/50 NR/NBR nanocomposites with O1Mt and O2K are given in Fig.6.1. For better understanding of the slope of each system, a plot of slope vs different fillers is shown in the inset.
Figure 6.1  

a) Effect of nature of filler on the relaxation behaviour of NR/NBR blend nanocomposite. Schematic representation shows the preferential migration of the two organically modified clay towards the polymers. The figure in the inset shows the plot of slope vs filler loading. 

b) Normalised graph of the stress relaxation plot blend nanocomposites with two different OC
It is understandable from Fig. 1 that the initial and final stress value for both 70/30 and 50/50 NR/NBR nanocomposite with O2K modified clay mineral is higher, compared to the other NR/NBR nanocomposites (Fig. 6.1). The slope of the relaxation curve of 50/50 and 70/30 NR/NBR (Fig. 6.1) is found to be steeper for O1Mt loaded NR/NBR nanocomposites than that for O2K filled NR/NBR nanocomposites (Fig 6.1 inset). The improved mechanical property and the slow stress relaxation of O2K filled NR/NBR filled nanocomposites is due to the strong interaction between O2K and NR. Due to its non polar nature, O2K goes to the NR phase preferentially. Modifications such as mercapto and organofunctional silane can act as molecular bridges between NR molecules and clay mineral particles. Thus O2K creates strong crosslinks with the NR phase during vulcanization. The intercalated O2K results in good dispersion and enhances the polymer/filler interactions. Additionally, the electron microscopy data for the 70/30 NR/NBR/O2K also support the fact that, O2K preferentially goes to the NR phase. (Fig 6.2). Fig.6.3 represents the hypothesis of interaction between O2K and the two rubbers.

**Figure 6.2**  SEM images of the 70/30 NR/NBR blend nanocomposites with 5phr O2K showing the preferential localization of O2K in the NR phase
The viscosity of the NR phase will increase as more number of O2K goes to this phase. It is generally accepted that viscosity ratio [i.e., the ratio of viscosity of the dispersed phase to the viscosity of the matrix (λ)] is one of the most critical variable for controlling blend morphology. Researchers\(^{17-19}\) reported that low viscosity ratio is more favourable for a finer morphology, because high viscous matrix enhances droplet break up by exerting an efficient shear stress transfer towards the dispersed phase, leading to finer diameter of the dispersed phase. Also, it has been already reported that once the viscosity of the matrix phase is increased, the domain size of the dispersed phase will be decreased due to rheological reasons\(^{20}\). For a viscoelastic dispersion, the critical condition for droplet breakup is given by\(^{21}\) (Eq 6.1)

$$W_e \geq \frac{F(\eta_{\text{dispersed}}/\eta_{\text{matrix}})}{\sin(2\Phi)} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots
Lower the viscosity ratio larger is the deformation of NBR domains i.e. when the viscosity ratio is smaller than unity, the domain size of the dispersed NBR phase is finer and its distribution is more uniform. Thus for 70/30 NR/NBR, the preferential localization of O2K in the NR phase will increase the NR phase viscosity, leading to a fine and uniform distribution of NBR domain in the NR continuous phase. Since the molar mass of the NR phase is extremely high, the complete migration of the platelets of the clay mineral into NR phase will be restricted by diffusional constraints. Therefore, it is reasonable to believe that a substantial portion of the clay mineral will stay at the interface. Fig.6.3 explains the type of interactions in O2K NR/NBR nanocomposite. The slow relaxation behaviour of NR/NBR nanocomposites for the 70/30 NR/NBR containing O2K system is thus due to the strongly bonded O2K to the NR phase. For the 50/50 NR/NBR with O2K system too, the clay mineral is localized at the NR and at the interface. Interestingly, this system also shows very slow relaxation process as explained earlier.

On the other hand, O1Mt shows affinity towards NBR predominantly. This can also be established from the TEM images (Fig.6.4a, b &c). The polar interaction between NBR and O1Mt, localizes the O1Mt, predominantly in the NBR phase. This results in the increase of NBR phase viscosity, which ultimately decreases the polymer chain mobility and suppresses the coalescence of the NBR domains, leading to a fine morphology in the NR matrix for the 70/30 NR/NBR system. (Fig.6.4). According to viscosity ratio, the increase in viscosity of the dispersed NBR phase will not favour a fine morphology. However, in this situation the decrease in dispersed domain size is also attributed to the comparable viscosity of NR and NBR phase as a result of the localization of O1Mt in the NBR phase (the pure NR viscosity is much higher than NBR viscosity). The presence of O1Mt at the interface of the two elastomers, (Fig. 6.4 a,b&c) shows the partial interaction of O1Mt towards NR phase. The alkyl rich HT present in O1Mt imparts the interaction between NR and O1Mt. The presence of HT in O1Mt slightly
weakens the polar interaction between O1Mt- NBR\textsuperscript{22-24}. Consequently, the O1Mt acts as an amphiphile holding the two rubbers. The strength of interaction to both or each of the elastomer is thus estranged. As a result of these weak bonds, the relaxation takes place extremely fast in the case of O1Mt filled systems. The mechanical property shown in Table 6.1 confirms the presence of comparatively stronger interaction in the case of O2K filled NR/NBR nanocomposites.

It is also important to point out that in all the cases, a two stage relaxation process is observed. The relaxation at the initial phase relates to the filler- filler rupture and the second phase corresponds to breakage of the polymer /filler and polymer/polymer interactions. That is, interaction with different interfaces in the NR/NBR nanocomposites relaxes at different rates.

**Table 6.1.** Tensile properties of NR/NBR blend nanocomposites with the two different fillers.

<table>
<thead>
<tr>
<th></th>
<th>70/30(0)</th>
<th>70/30(5)</th>
<th>70/30(5)</th>
<th>50/50(0)</th>
<th>50/50(0)</th>
<th>50/50(0)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O1Mt</td>
<td>O2K</td>
<td>O1Mt</td>
<td>O1Mt</td>
<td>O2K</td>
<td>O2K</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>12.9</td>
<td>21.3</td>
<td>10.9</td>
<td>3.28</td>
<td>13.42</td>
<td>5.7</td>
</tr>
<tr>
<td>Elongation at break(%)</td>
<td>226</td>
<td>530</td>
<td>496</td>
<td>333</td>
<td>416</td>
<td>331</td>
</tr>
<tr>
<td>Modulus at 100% (MPa)</td>
<td>1.68</td>
<td>1.23</td>
<td>0.78</td>
<td>0.67</td>
<td>1.23</td>
<td>0.88</td>
</tr>
<tr>
<td>Modulus at 200%(MPa)</td>
<td>9.78</td>
<td>4.46</td>
<td>1.57</td>
<td>1.30</td>
<td>2.32</td>
<td>1.81</td>
</tr>
</tbody>
</table>
Figure 6.4  TEM image showing the localization of O1Mt in 50/50 (2) blend nanocomposites a) & b) in the NBR phase and at the interface c) & d) the intercalated and exfoliated morphology of O1Mt

6.2.2 Effect of filler loading

As the filler loading is increased the relaxation rate also was found to increase. The rate of stress relaxation will be more when there is more number of interactions that leads to rupture, resulting in an increase in entropy. As reported earlier\textsuperscript{25}, the conditions favoring an increase in entropy will enhance the rate of stress relaxation. So an increase in slope corresponds to rupturing or relaxation of these interactions. The initial stress value was found to be increasing with increase in O1Mt loading (Fig. 6.5). This can be due to the
more number of filler/filler interactions in the case of higher filler loaded samples corresponding to an improved reinforcing effect. However, as the filler content is increased, an increase in slope of the stress relaxation curve was observed. Although an improved reinforcement is shown initially due to a higher number of interactions, most of these filler-filler interactions ruptured easily. The lower residual stress value observed in the case of 10 phr O1Mt loaded NR/NBR nanocomposites may also be associated with the breakage of these weak filler/filler and polymer/filler networks during the course of relaxation process. It was interesting to note that 2 phr NR/NBR nanocomposite have better reinforcement than 5 phr loaded sample, as the former showed higher initial and residual stress value. The SEM images given in Fig 6.6 also shows a decrease in domain size of the dispersed phase. This was supported by the XRD, (Fig 6.7) where we can observe a fairly better intercalated and exfoliated morphology for 2 phr NR/NBR nanocomposites with O1Mt as the filler, while higher filler loaded samples indicated the presence of intercalated aggregate structure. The fact that 1 phr polymer/polymer nanocomposite shows an intercalated aggregate structure, may be because of the isolated clay mineral aggregates in the rubber matrix with low filler loading. Also 1phr O1Mt loading shows low initial reinforcement compared to higher filler loading because in this bad dispersion state, the contact area between rubber and clay mineral is insignificant, and therefore, clay mineral shows only a minimal reinforcement effect. Agglomeration at higher concentration should have resulted in a higher relaxation rate due to more and more filler/filler rupturing. Intercalation of polymers between the O1Mt layers (Fig. 6.4) and the subsequent rupturing of this interaction on stress relaxation is represented in Fig. 6.4.
Figure 6.5  a) Effect of filler loading on stress relaxation behavior of 50/50 NR/NBR blend nanocomposite with O1Mt. The schematic representation shows the intercalated aggregates of the O1Mt at different filler loading. In the inset the plot of slope vs filler loading is given. b) Normalised graph of the stress relaxation plot for blend nanocomposites with varying filler loading
The two stage mechanism observed in this case also suggests the different types of interfaces existing in the polymer/polymer nanocomposites. The initial portion represents breakage of the filler/filler interactions, which can be observed clearly from the curve of 10phr NR/NBR nanocomposite, where the slope of the initial portion is higher. It should also be pointed out that the relaxation for NR/NBR blend without O1Mt is lower than that for NR/NBR nanocomposites. This may be explained based on the effect of orientation of OC and polymer chains. However, this has to be re-examined further using techniques like Small angle X-ray diffraction studies and will be a subject matter of future study. The TEM results (Fig. 6.4) also supports the above argument.

Figure 6.6: SEM images showing the decrease in domain size of NBR dispersed phase with filler loading for 70/30(2) and 70/30(5) NR/NBR (O1Mt) blend nanocomposites.
6.2.3 Effect of temperature

The stress relaxation behaviour at higher temperature was studied by comparing the stress relaxation plot of 50/50 and 70/30 NR/NBR, loaded with 2 phr O1Mt at room temperature (30°C) and an elevated temperature (70°C) (Fig 6.8). In addition to that, a plot showing variation in slope value with temperature for different nanocomposites is shown in the inset. At 70°C, even though a higher initial stress value was shown by 50/50 (2) NR/NBR nanocomposite, the slope of the curve for 70/30(2) was found to be lower (Fig. 6.8). Variation in slope value with temperature for different polymer/polymer nanocomposites is shown in the inset. This can be explained on the basis of the irreversible changes occurring in the system and of viscosity. Irreversible changes occurring in the system, like increased bonding between clay mineral and polymer, increased crosslinks etc can make the interactions more stable. It has been reported earlier, that when the viscosity of the matrix is very high (\(\eta_d/\eta_m \ll 1\)), then the viscosity factors outweighs the interfacial
tension\textsuperscript{19} and the presence of OC at the interface will not affect the viscosity ratio. In this context, if we analyze the 70/30 and 50/50 NR/NBR O1Mt system, in the former case, at room temperature, majority of O1Mt may be in the NBR phase due to polarity factors, and slightly at the interface due to its affinity towards NR, as a result of the alkyl groups in hydroxy tallow (i.e. $\eta_d>>>\eta_m$). At 70\textdegree C, a major change in viscosity can be shown only by the matrix phase, as variation in the viscosity of the highly filled dispersed phase is difficult at this temperature. This decrease in viscosity of NR matrix phase can pull the O1Mt from the interface towards it, resulting in a better interaction between NR and O1Mt at 70 \textdegree C. It is important to note that polar interaction between polymer and clay mineral\textsuperscript{29} will weaken at higher temperature and drive the migration of O1Mt towards the NR phase. This new interaction between NR and O1Mt causes a decrease in relaxation rate for both the composition at higher temperature. At higher temperature, there is the possibility of additional crosslinks for both the phases, due to aging processes. This also could have resulted in the decreased relaxation rate at higher temperature.
6.3 Modelling

Two models were applied to compare the theoretical value with experimental results. One is a two component stretched exponential Kohlrausch equation and the other is three elements Maxwell-Weichert model with three relaxation times. It was found that both models fitted well with the experimental stress relaxation curves. The stretched exponential Kohlrausch equation (Eq.6.2) used to fit the experimental curves of the nanocomposites is given by

$$\frac{\sigma_t}{\sigma_0} = \frac{\sigma_\infty}{\sigma_0} + \frac{\sigma_1}{\sigma_0} e^{-\left(\frac{t}{\tau}\right)\beta}$$

where $\sigma_\infty/\sigma_0$, $\sigma_1/\sigma_0$, $\tau$ and $\beta$ are the fitting parameters. The relaxation time $\tau$, the stretching parameter $\beta$, transient stress $\sigma_1/\sigma_0$, and limiting stress $\sigma_\infty/\sigma_0$ are...
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given in Table 6.2. The extent of fit was made from the $\chi^2$ and R value, given in the table (Table 6.2) to assess the quality of the fits.

Figure 6.9. Time dependence of normalized stress for a) different NR/NBR blend nanocomposites with O1Mt and b) different concentration of O1Mt loaded 70/30 NR/NBR blend (solid line indicates the curve fitting with Kohlrausch model.)
Table 6.2. Curve fitting results for stress relaxation data according to figure 9a and 9b.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\sigma_\infty/\sigma_0$</th>
<th>$\sigma_1/\sigma_0$</th>
<th>B</th>
<th>$10^3\gamma$/sec</th>
<th>$\chi^2$</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0(5)</td>
<td>0.659</td>
<td>0.277</td>
<td>0.135</td>
<td>0.057</td>
<td>1.365</td>
<td>0.985</td>
</tr>
<tr>
<td>70/30(5)</td>
<td>0.641</td>
<td>0.261</td>
<td>0.144</td>
<td>0.145</td>
<td>1922</td>
<td>0.983</td>
</tr>
<tr>
<td>50/50(5)</td>
<td>0.537</td>
<td>0.293</td>
<td>0.142</td>
<td>0.184</td>
<td>4.367</td>
<td>0.975</td>
</tr>
<tr>
<td>0/100(5)</td>
<td>0.445</td>
<td>0.311</td>
<td>0.165</td>
<td>0.222</td>
<td>2.153</td>
<td>0.990</td>
</tr>
<tr>
<td>70/30(0)</td>
<td>0.855</td>
<td>0.175</td>
<td>0.092</td>
<td>0.010</td>
<td>1.160</td>
<td>0.940</td>
</tr>
<tr>
<td>70/30(1)</td>
<td>0.794</td>
<td>0.231</td>
<td>0.093</td>
<td>0.041</td>
<td>3.120</td>
<td>0.930</td>
</tr>
<tr>
<td>70/30(2)</td>
<td>0.767</td>
<td>0.230</td>
<td>0.110</td>
<td>0.042</td>
<td>2.070</td>
<td>0.960</td>
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<tr>
<td>70/30(3)</td>
<td>0.641</td>
<td>0.261</td>
<td>0.1455</td>
<td>0.145</td>
<td>1.920</td>
<td>0.980</td>
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<tr>
<td>70/30(10)</td>
<td>0.535</td>
<td>0.291</td>
<td>0.1453</td>
<td>0.193</td>
<td>3.440</td>
<td>0.980</td>
</tr>
</tbody>
</table>

The experimental curves fitted to the above equation (2) are shown in Fig. 6.9a and 6.9b for varying composition of NR/NBR nanocomposites and for different concentration of O1Mt loaded 70/30 NR/NBR nanocomposites, respectively. It is clear from the data (Table 6.2) that the limiting stress value $\sigma_\infty/\sigma_0$ decreases as the filler content is increased. One reason may be the higher structural changes occurring in the blend nanocomposites with higher filler loading. This can be explained by the fact that, as the filler concentration is increased, higher scale structural rearrangements occur by rupturing of more and more of these filler/filler and polymer/filler networks. For the NR/NBR nanocomposites with different O1Mt loading, this can be determined from the fitting parameter values. As the filler loading is increased, the transient stress $\sigma_1/\sigma_0$ and the characteristic relaxation time were found to be increasing, while the limiting stress value $\sigma_\infty/\sigma_0$ decreases. This can be attributed to the increased structural relaxation caused by the rupturing of a higher content of polymer/filler and agglomerated filler/filler networks.

For the understanding of the stress relaxation behavior of NR/NBR/O1Mt nanocomposite, Maxwell-Weichert model with three relaxation times was introduced and it was found that the experimental curve fitted well with the theoretical curve. The expression for stress decay according to this model is given in eq(6.3)
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\[ \sigma(t) = A \exp\left(-t/\tau_1\right) + B \exp\left(-t/\tau_2\right) + C \exp\left(-t/\tau_3\right) \]

where A, B and C are the pre-exponential factors \(A + B + C = 1\) and \(\tau_1, \tau_2, \tau_3\) the relaxation times, \((\tau_1 < \tau_2 < \tau_3)\). As suggested by Xia and Song\(^3\) \textit{et al.}\, the different relaxation times should be related to specific structures. The NR/NBR nanocomposite was expected to have three main relaxation processes, filler/filler disruption, polymer/filler disruption or disentanglement of network of polymer/polymer, and pullout of filler from polymer coils. The first shortest relaxation time is attributed to the breakup of filler / filler interactions, the second relaxation time is due to the disentanglement of the chains in the NR/NBR blend system, and the third longest relaxation time is from the pullout of filler particles from the polymer coils. The values of A, B, C, \(\tau_1, \tau_2\) and \(\tau_3\) were calculated from the curve fitting of experimental data according to Fig. 6.10a &6.10b, and are presented in Table 6.3.

Fig. 6.10 a presents the stress relaxation behavior of NR/NBR nanocomposite with O1Mt at different clay mineral contents. The values of A, B, C, \(\tau_1, \tau_2\) and \(\tau_3\) are presented in Table 6.3. It is seen from Table 6.3 that the value of \(\tau_1\) increases with increase in filler loading, indicating an increase in filler /filler breakage. However, for \(\tau_2\) and \(\tau_3\) although it increased with O1Mt loading, at 5phr a sudden decrease in the values were observed. Since the value of \(\tau_2\) and \(\tau_3\) corresponds to the disentanglement of polymer chains and breakage of polymer/filler interactions respectively, the decrease in value of \(\tau_2\) and \(\tau_3\) can be attributed to the better dispersion and interaction of O1Mt with the polymer chains. The values of the pre-exponential factors A, B & C indicating the fraction of the chains undergoing relaxation, also satisfy to the explanation. The clay mineral particles cannot be elongated during stretching due to high stiffness. Thus, the extension level of polymer matrix in filled NR/NBR nanocomposites was higher than that in unfilled polymer. The same trend was observed in Kohlrausch model also.
Figure 6.10. Time dependence of normalized stress for a) different NR/NBR blend nanocomposites with O1Mt and b) different concentration of O1Mt loaded 70/30 NR/NBR blend (solid line indicates the curve fitting with three element Maxwell-Weichert model.)
6.4 Conclusions

The blending of NBR with NR was found to improve the physical and mechanical properties of NBR. The stress relaxation experiment was conducted in order to characterize the time-dependent reinforcement of the clay mineral reinforced NR/NBR nanocomposites. The study of the effect of filler loading showed a noticeable change in the relaxation rate. The rate of relaxation was found to decrease at lower filler loading while at higher filler loading, the rate of stress relaxation is increased. This higher relaxation rate is attributable to the decrease in polymer/filler interactions. At higher loading, the increase in filler-filler interactions accelerates the stress relaxation. The nature of OC was also found to influence the stress relaxation behavior. The O2K clay mineral showed lower relaxation rate compared with O1Mt because of its better interaction with the polymer matrix. Due to its non polar nature, mercapto silane modified clay goes to the NR phase preferentially. Modifications such as mercapto and organofunctional silane can act as molecular bridges between NR molecules and clay mineral particles. This creates strong crosslink formation with the NR phase during vulcanization. While for NBR it is the polar interaction between NBR and O1Mt, that localizes the O1Mt, predominantly in the NBR phase. The presence of additional cross links between the NR and the mercaptan in the case of mercapto silane modified clay thus decreases the relaxation process. Temperature

### Table 6.3. Curve fitting results for stress relaxation data according to figure 6.9 and 6.10

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\tau_1$</th>
<th>$\tau_2$</th>
<th>$\tau_3$</th>
<th>$A$</th>
<th>$B$</th>
<th>$C$</th>
<th>chi$^2$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>70/30(0)</td>
<td>1099.9</td>
<td>0.5218</td>
<td>10.49</td>
<td>0.6216</td>
<td>0.1266</td>
<td>0.0966</td>
<td>0.4741</td>
<td>0.9977</td>
</tr>
<tr>
<td>70/30(1)</td>
<td>1705.7</td>
<td>0.5489</td>
<td>10.75</td>
<td>0.6982</td>
<td>0.1148</td>
<td>0.0803</td>
<td>0.3537</td>
<td>0.9974</td>
</tr>
<tr>
<td>70/30(2)</td>
<td>3524.6</td>
<td>0.8044</td>
<td>14.27</td>
<td>0.8157</td>
<td>0.0664</td>
<td>0.0521</td>
<td>0.3194</td>
<td>0.9946</td>
</tr>
<tr>
<td>70/30(5)</td>
<td>3121.5</td>
<td>0.4927</td>
<td>11.16</td>
<td>0.8636</td>
<td>0.0433</td>
<td>0.0506</td>
<td>0.2621</td>
<td>0.9950</td>
</tr>
<tr>
<td>70/30(10)</td>
<td>6684.5</td>
<td>0.7140</td>
<td>11.62</td>
<td>0.8831</td>
<td>0.0461</td>
<td>0.0320</td>
<td>0.2109</td>
<td>0.9901</td>
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<tr>
<td>100/0(5)</td>
<td>1718.0</td>
<td>0.5328</td>
<td>8.15</td>
<td>0.7178</td>
<td>0.1085</td>
<td>0.0786</td>
<td>0.3252</td>
<td>0.9966</td>
</tr>
<tr>
<td>70/30(5)</td>
<td>1641.6</td>
<td>0.5696</td>
<td>10.82</td>
<td>0.7038</td>
<td>0.1142</td>
<td>0.0791</td>
<td>0.2844</td>
<td>0.9975</td>
</tr>
<tr>
<td>50/50(5)</td>
<td>1162.5</td>
<td>0.8382</td>
<td>12.63</td>
<td>0.6220</td>
<td>0.1302</td>
<td>0.0882</td>
<td>0.5810</td>
<td>0.9967</td>
</tr>
<tr>
<td>0/100(5)</td>
<td>803.14</td>
<td>0.4465</td>
<td>8.34</td>
<td>0.5329</td>
<td>0.1822</td>
<td>0.1148</td>
<td>0.5718</td>
<td>0.9973</td>
</tr>
</tbody>
</table>
also had an effect on the stress relaxation rate. Finally, it is important to add that, in order to design high performance polymer - polymer - OC nanocomposites for dynamic applications, the OC should have a high extent of dispersion in the matrix. The nature of modification in OC determines the polymer - filler interactions. The experimental value of the stress relaxation curve fitted well with the theoretical value of the stretched exponential Kohlrausch equation and the three elements of Maxwell-Weichert model with the three relaxation times.

**References**


29 Meeting of the American Chemical Society, **1914**, (Cleveland, Ohio, April 4).