Chapter 6

Stress Relaxation Studies

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The development of polymer based products requires a deep knowledge on the mechanical response of the material as a function of time and temperature. To assess the service life of any product, accelerated tests can be carried out so that the effect of both temperature and time can be obtained within a short time interval. Generally creep and stress relaxation measurements are the widely employed standard test methods for this purpose. The long-term characteristics of the polymer based products can be predicted from the results of stress-relaxation experiments because they represent the basic time dependent response of the material.\textsuperscript{1} According to Denby,\textsuperscript{2} it is possible to correlate creep, stress relaxation and recovery for both textile polymers and other viscoelastic polymers.

Mijovic\textsuperscript{3} studied the effect of physical ageing on the viscoelastic properties of compatible PMMA/SAN polymer blends. It was found that the slope of the stress relaxation curve does not change with change in composition, ageing temperature or ageing time. The stress-relaxation behaviour of polyacetal-thermoplastic polyurethane elastomer blends has been reported by Kumar\textit{et al.}\textsuperscript{4}

Till date no systematic studies have been reported on the stress relaxation behaviour of natural rubber/polystyrene blends although this blend can be used in dynamic applications. In the present chapter, the stress-relaxation behaviour of natural rubber/polystyrene blends with and without the addition of the compatibiliser, i.e., natural rubber-graft-polystyrene has been reported. The relaxation behaviour was also studied with special reference to the effects of strain level, blend ratio and ageing.
6.1 Results and discussion

The results of stress relaxation experiments are presented as linear plots of $\sigma_t/\sigma_0$ vs. log time, where $\sigma_t$ is the stress at a particular time $t$ and $\sigma_0$ is the stress at $t = 0$.

6.1.1 Effect of strain level

Linear plots of $(\sigma_t/\sigma_0)$ vs. log $t$ of 60/40 natural rubber/polystyrene blends at different strain levels (50, 100 and 150%) are given in Figure 6.1. In all the cases, the rate at which the initial strain attained is kept constant. The relaxation patterns of the samples were studied at different strains. There is only marginal variation in the rate of relaxation at all extensions. It is seen that in all cases, the experimental points fall on two intersecting straight lines. Two different straight lines will intersect at a point at which the relaxation mechanism changes from one mode to another. The time corresponding to this point is known as the cross over time. The values of crossover time are 1819, 622 and 2411 sec for samples, C, I and J, respectively. The slopes and intercepts of the two straight lines are given in Table 6.1 which were obtained by the linear regression analysis method. The difference in the values of slopes and intercepts indicate that the mechanism of relaxation operates in two ways; one that operates at shorter time and another that is prominent at the later stages of relaxation. Initial slope (i.e., relaxation rate) is nearly the same for all the 3 strain levels. The slope and location of the second process depend on strain level. The contribution by the earlier process of relaxation has been calculated as reported by Mackenzie and Scanlan\(^5\) by dividing the differences of the two intercepts by the intercept of the first line at $t = 1$ sec. From Table 6.1 it is seen that as the strain level increases from 50% (sample J) to 150% (sample C) the contribution of the early process increases from 13.1 to 26.9% in the case of non-compatibilised blend and this can be attributed to the high interfacial tension across the phase boundary.
Figure 6.1. Effect of strain level on the stress relaxation pattern of 60/40 NR/PS blend: (C) 150%, (I) 100% and (J) 50%.

Table 6.1. Results of Stress Relaxation Measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Slope (–ve)</th>
<th>Intercept</th>
<th>Contribution to initial mechanism (%)</th>
<th>Cross-over time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Intermediate</td>
<td>Final</td>
<td>Initial</td>
</tr>
<tr>
<td>A</td>
<td>0.0979</td>
<td>-</td>
<td>0.0572</td>
<td>0.9893</td>
</tr>
<tr>
<td>B</td>
<td>0.0978</td>
<td>-</td>
<td>-</td>
<td>0.9937</td>
</tr>
<tr>
<td>C</td>
<td>0.1285</td>
<td>-</td>
<td>0.2253</td>
<td>1.0126</td>
</tr>
<tr>
<td>D</td>
<td>0.1147</td>
<td>-</td>
<td>0.0367</td>
<td>0.9316</td>
</tr>
<tr>
<td>E</td>
<td>0.0943</td>
<td>-</td>
<td>0.1035</td>
<td>0.9458</td>
</tr>
<tr>
<td>F</td>
<td>0.1182</td>
<td>0.8089</td>
<td>0.0989</td>
<td>0.9403</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>0.1191</td>
<td>-</td>
<td>0.0671</td>
<td>0.9412</td>
</tr>
<tr>
<td>H</td>
<td>0.9698</td>
<td>-</td>
<td>9.0641</td>
<td>0.0997</td>
</tr>
<tr>
<td>I</td>
<td>0.1086</td>
<td>-</td>
<td>0.0725</td>
<td>0.9437</td>
</tr>
<tr>
<td>J</td>
<td>0.1200</td>
<td>-</td>
<td>0.1865</td>
<td>0.9318</td>
</tr>
</tbody>
</table>

*Second cross overtime.
The stress relaxation behaviour can be related to the morphology of the blend. In 60/40 NR/PS blends where NR is the continuous matrix and PS is the dispersed phase, the initial stage relaxation is due to the continuous NR matrix which is slow compared to the relaxation due to PS dispersed phase.

### 6.1.2 Effect of composition

Figure 6.2 shows the stress relaxation curves of different NR/PS blends of varying composition. In the case of 50/50 blend, the experimental points fall on a single straight line, whereas in the other two cases, (i.e., curve A - 40/60 NR/PS and curve C - 60/40 NR/PS blends) the experimental points fall on two intersecting straight lines, indicating that the relaxation process follows two different mechanisms. In the case of 40/60 NR/PS blend, it was shown that NR is the dispersed phase and PS forms the continuous phase. In the case of sample C (60/40 NR/PS blend) the reverse is true and hence the relaxation due to NR increases. From Figure 6.2 it is observed that the behaviour of 50/50 blend is different from the others.

![Figure 6.2](image.png)

**Figure 6.2.** Effect of composition on the stress relaxation pattern of different NR/PS blends at a strain level of 150%: (A) 40/60, (B) 50/50 and (C) 60/40 NR/PS blend.
The relative stress decay is found to be a linear function of log T over the time scale studied. This indicates a single relaxation mechanism for the 50/50 blend, unlike 60/40 and 40/60 blends. The difference in behaviour can be understood in terms of the morphology of the blend.

Figure 6.3 shows the morphology of different NR/PS blends varying in composition. Figures 6.3a and 6.3c represent 40/60 and 60/40 NR/PS blends where NR and PS forms the dispersed phase, respectively. In Figure 6.3a, the dispersed rubber domain size is higher compared to the dispersed plastic domains in Figure 6.3c and this is due to the coalescence of the rubber domains (Table 6.2).

Figure 6.3. Optical microphotographs of (a) 40/60, (b) 50/50 and (c) 60/40 NR/PS blends.
Due to the low viscosity of PS phase as compared to NR, the coalescence of the NR domains is favoured. For the 50/50 NR/PS blend, there is a tendency for the components to form a co-continuous morphology and this accounts for the single phase relaxation mechanism shown by the 50/50 NR/PS blend (Figure 6.3b). The 50/50 NR/PS blend shows a partial co-continuous morphology, i.e., both dispersed and co-continuous phases exist.

Table 6.2. Polydispersity Index (PDI) of Different NR/PS Blends

<table>
<thead>
<tr>
<th>Samples</th>
<th>Polydispersity index</th>
<th>Average domain diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40/60</td>
<td>1.24</td>
<td>17.14</td>
</tr>
<tr>
<td>50/50*</td>
<td>1.14</td>
<td>14.11</td>
</tr>
<tr>
<td>60/40</td>
<td>1.09</td>
<td>13.45</td>
</tr>
</tbody>
</table>

*The size has been measured based on the available domains in the semi-co-continuous structure.

The stress relaxation rate can be analysed by measuring the slope and intercept of the relaxation curve. The slope, intercept, crossover time and the contribution to initial mechanism for different NR/PS blends have been calculated as explained earlier and are given in Table 6.1. It is observed from the table that the rate of stress relaxation is highest in 60/40 NR/PS blend. The relaxation rate decreases as the amount of NR decreases from 60/40 to 40/60 NR/PS blends because the overall relaxation process depends more upon the rubber content. This is further supported by the polydispersity index (PDI) values which are given in Table 6.2. The crossover time changes from 762 to 1819 sec as the matrix phase changes from PS to NR. This is due to the difference in the amount of NR which contributes largely to the relaxation process. It is seen from Table 6.1 that the contribution to initial mechanism changes from 12.5 to 26.9% as the continuous phase changes from PS to NR.
6.1.3 Effect of compatibiliser loading

Figure 6.4 shows the stress-relaxation curves of 50/50 NR/PS blends with varying amounts of the compatibiliser i.e., natural rubber-graft-polystyrene copolymer. It is observed that the relaxation pattern of compatibilised blend is different from that of non-compatibilised one. In the case of non-compatibilised blend, the experimental points fall on a single straight line, indicating that the mechanism of relaxation operates by a single mechanism. For the compatibilised blends (Samples D and E) the experimental points fall on two intersecting straight lines. This is due to the fact that the partially co-continuous morphology is transformed into a matrix-dispersed morphology upon compatibilisation. Compared to non-compatibilised blend, the compatibilised blends show an increase in the rate of relaxation because in these two cases, the compatibiliser added will be located at the blend interface and enhances the interaction between the two phases. Coming to sample F i.e., 50/50 NR/PS blend with 4.5% compatibiliser, the graft copolymer form micelles which reduces the blend properties and thereby a different relaxation pattern is observed. A three stage mechanism is shown at higher loading of compatibiliser. The rate of relaxation is higher compared to blends with lower graft loading. In the case of compatibilised blends (Samples D, E and F) the contribution to early process is nearly constant because of enhanced interfacial adhesion between the blend components. The first cross-over time in the case of sample F is less (1718 sec) compared to that of sample E (2411 sec) and is related to the formation of undesirable micelles. The second cross over time in this case is higher (3383 sec) and leads to a third mechanism which is due to the micelle formation.
Figure 6.4. Effect of compatibiliser loading on the stress relaxation pattern of 50/50 NR/PS blends: (B) 0%, (D) 1.5%, (E) 3% and (F) 4.5% graft copolymer.

6.1.4 Effect of ageing

In order to study the effect of ageing, the relaxation measurements have been made using samples subjected to ageing at 50 and 70°C for 4 days. The dependence of relative stress on log T is shown in Figure 6.5. In the case of unaged 50/50 NR/PS blends, a single relaxation mechanism operates whereas in the case of aged samples operates in two stages (i.e., G and H). The rates of relaxation for the aged and unaged samples are shown in Table 6.1. In the case of aged samples, the rate of relaxation is high in the initial stage compared to later stages. In the aged samples, the initial increase in relaxation rate is due to the degradation of the rubbery phase on ageing. The later stages of relaxation is due to the plastic phase. The slopes and intercepts of these different stages are given in Table 6.1 and show that ageing produces interesting effects on the stress-relaxation of the blends. It was observed that the variation of slope at different stages of relaxation, is gradual both at 50 and 70°C. The slope value indicates that the rate of relaxation is higher for sample aged at 70°C compared to that at 50°C. In the case
of sample G the cross over time is less (87 sec) compared to sample H (171 sec) and it is due to the fact that the former case the matrix phase will undergo degradation at a faster rate compared to the latter one.

Figure 6.5. Effect of ageing on the stress relaxation pattern of 50/50 NR/PS blends: (B) 30°C, (H) 50°C and (G) 70°C.

6.2 References

Chapter 7

Dynamic Mechanical Properties