Chapter 5

Morphology, Mechanical, Viscoelastic and Transport Behaviours of Nitrile Rubber/Natural Rubber Blend Membranes

Abstract

A new variety of membranes from blends of nitrile rubber (NBR) and natural rubber (NR) was prepared and their morphology, transport, miscibility and mechanical properties were studied. These blend membranes find application in the dairy industry where good mechanical properties and swelling resistance are required. The morphology of the blends indicated a two-phase structure in which the minor phase is dispersed as domains in the major continuous phase. The transport properties of substituted benzenes (aromatics) through NBR/NR blend membranes have been investigated in the temperature interval 28-70°C. Network characterisation was done using phantom and affine models. The viscoelastic behaviour of crosslinked nitrile rubber/natural rubber blends was studied with reference to the effect of blend ratio, frequency and temperature. The glass transition behaviour of the blends is affected by blend ratio and frequency. Attempts were made to correlate the properties with the morphology of the system. The Arrhenius relationship was used to calculate the activation energy for transition. Various theoretical models were used to predict the modulus and permeability of the blends. The static mechanical properties of the blends were also investigated. NBR/NR blends are useful for producing milking inflation, which is the part of a milking machine. A special formulation, which conform to food contact regulations, was developed for making the milking inflation and the transport properties of this blend was investigated by using ghee as the penetrant.

Part of the results of this chapter have been accepted for publication in Journal of Membrane Science and the other part is communicated for publication in Polymer
As preparation of polymer blends ranks among the most cost effective ways of upgrading existing polymers¹, it is desirable to anticipate the blend properties such as morphology, mechanical and viscoelastic behaviours. Also, permeability of various penetrants may play an important role in many applications of polymer blends. The permeability of blends will depend not only on the permeability of constituents, but also on the actual phase structure in a blend. The correlation of experimental data on permeability with model predictions might be an efficient tool in the blend structure analysis.²

Miscibility, thermal, mechanical, gas permeation, morphological and surface properties of poly (vinyl chloride) (PVC) blends containing 1-10% triblock polycaprolactone-poly (dimethylsiloxane)-polycaprolactone (PCL-PDMS-PCL) copolymer were investigated by Karal and co-workers.³ An experimental method to determine interphase composition profiles generated by diffusion in amorphous polymer pairs and polymer-solvent pairs is reported.⁴ The method is based on the measurement of dynamic mechanical properties of slender composite beams, and well-established properties of amorphous polymer homogeneous blends and solutions. The mechanical and dynamic mechanical properties of blends of poly(ethylene-co-acrylic acid) (PEA) and epoxidised natural rubber (ENR-50) have been studied by Mohanty et al.⁵

The objective of this chapter is to investigate the morphology, transport behaviour, mechanical and viscoelastic properties of nitrile rubber/natural rubber blend membranes. The transport and viscoelastic behaviours have been correlated with the morphology of the blend. Attempts have also been made to predict the experimental
permeation and mechanical properties using existing theoretical models. In order to find out the practical application of NBR/NR blends in the development of milking inflation, a special formulation is developed and the transport of ghee through this blend is also studied.

5.1. Results and Discussion

5.1.1. Cure characteristics

The compositions of NBR/NR blends are designated as N₀, N₃₀, N₅₀, N₇₀ and N₁₀₀ where N₀ and N₁₀₀ are pure components. The rheographs of the mixes are given in Figure 5.1 and cure characteristics in Table 5.1. In the rheograph, torque is plotted against time. The minimum torque in the rheograph is presented as minimum viscosity value (M₁) and is a measure of the extent of mastication. The lowest value of N₇₀ indicates its higher extent of mastication during mixing. The maximum torque in the rheograph is presented as maximum viscosity. The highest value is for N₃₀ composition. From the formulations it can be seen that in the present study the membranes were vulcanised with conventional vulcanising system. The high sulphur/accelerator ratio results in predominantly polysulphidic linkages.

**Table 5.1 Cure characteristics**

<table>
<thead>
<tr>
<th>Cure characteristics</th>
<th>N₁₀₀</th>
<th>N₇₀</th>
<th>N₅₀</th>
<th>N₃₀</th>
<th>N₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum torque (Nm)</td>
<td>0.03</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Maximum torque (Nm)</td>
<td>0.24</td>
<td>0.25</td>
<td>0.30</td>
<td>0.35</td>
<td>0.33</td>
</tr>
<tr>
<td>Scorch time (min)</td>
<td>2.17</td>
<td>2.40</td>
<td>2.93</td>
<td>3.55</td>
<td>8.31</td>
</tr>
<tr>
<td>Optimum curetime (min)</td>
<td>5.78</td>
<td>7.70</td>
<td>8.03</td>
<td>9.80</td>
<td>20.40</td>
</tr>
<tr>
<td>CRI (min⁻¹)</td>
<td>27.68</td>
<td>18.87</td>
<td>19.62</td>
<td>16.00</td>
<td>8.27</td>
</tr>
</tbody>
</table>
The rheometric scorch time $t_2$, (premature vulcanisation time) is the time taken for minimum torque value to increase by two units. It increases from $N_{100}$ to $N_0$; i.e. the $N_0$ composition shows maximum scorch safety. Optimum cure time ($t_{90}$) is the vulcanization time to get optimum physical properties and it is the time corresponding to the optimum cure torque. The sample $N_0$ shows maximum cure time while $N_{100}$ shows minimum cure time. Cure rate index (CRI) is calculated using the equation\(^6\).

$$CRI = 100 / t_{90} - t_2$$ (5.1)

The higher the CRI values the higher will be the vulcanization rate. From Table 5.1 it can be seen that NR has the highest cure rate and NBR the minimum.
Among the blend compositions, N\textsubscript{50} has the highest cure rate. The high CRI value of NR is due to its high degrees of unsaturation.

5.1.2. Morphology of blend membranes

The polymer blend properties are strongly influenced by the morphology of the system. The morphology of NBR/NR blend is shown in Figure 5.2(a-c). In N\textsubscript{30} and N\textsubscript{70}, the minor phase is dispersed in the major continuous phase. The N\textsubscript{50} shows a co-continuous morphology, where both the phases are continuous. The size characteristics of the dispersed phase (\( \bar{D}_{\text{m}}, \bar{D}_{w}, \bar{D}_{a} \) and \( \bar{D}_{c} \)) and its distribution (polydispersity index values) in the different blend compositions are presented in Table 5.2.

![Scanning electron micrographs of NBR/NR blends](image)

(a) NBR/NR 70/30 (N\textsubscript{30})
(b) NBR/NR 50/50 (N\textsubscript{50})
(c) NBR/NR 30/70 (N\textsubscript{70})

*Figure 5.2(a-c) Scanning electron micrographs of NBR/NR blends*
Table 5.2. Dimensions of dispersed phase of NBR/NR blends

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>( N_{70} )</th>
<th>( N_{30} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bar{D}_n ) (( \mu )m)</td>
<td>3.38</td>
<td>2.12</td>
</tr>
<tr>
<td>( \bar{D}_w ) (( \mu )m)</td>
<td>3.66</td>
<td>2.61</td>
</tr>
<tr>
<td>( \bar{D}_d ) (( \mu )m)</td>
<td>3.52</td>
<td>2.35</td>
</tr>
<tr>
<td>( \bar{D}_v ) (( \mu )m)</td>
<td>3.89</td>
<td>2.54</td>
</tr>
<tr>
<td>PDI</td>
<td>1.23</td>
<td>1.08</td>
</tr>
</tbody>
</table>

It is clear from the table that the values of \( \bar{D}_n, \bar{D}_w, \bar{D}_d \) and \( \bar{D}_v \) decrease from \( N_{70} \) to \( N_{30} \). The PDI values show more uniform particle distribution for \( N_{30} \). The particle size distribution curve is drawn by measuring 300 particles from the SEM photomicrographs and it is exhibited in Figure 5.2. The normal and cumulative distribution curves are shown in the figure. In the normal distribution curve, particle diameter is plotted against number of particles and in the cumulative curve, cumulative percentage is plotted. It can be seen from the figure that \( N_{70} \) shows broader distribution than \( N_{30} \).

Figure 5.2. The normal and cumulative distribution curves of NBR/NR blends
5.1.3. Viscoelastic properties

The dynamic mechanical properties such as storage modulus (E'), loss modulus (E'') and damping (tan δ) of NBR, NR and their blends were evaluated from -70 to 30°C. The variation of tan δ with temperature at five frequencies of NR and NBR is shown in Figures 5.3 & 5.4. The tan δ curve of NR at a frequency of 0.1Hz shows a peak at -50°C due to the α-transition arising from the segmental motion. This corresponds to the glass transition temperature (T_g) of natural rubber. At the same frequency, nitrile rubber shows the glass transition temperature at -15°C, in the tan δ curve. Natural rubber shows higher damping than nitrile rubber. The values of tan δ_max and T_g corresponding to NR and NBR transitions at five frequencies are tabulated in Table 5.3.

![Plot of tan δ against temperature for natural rubber](image-url)
Table 5.3. Effect of frequency on \( \tan \delta_{\text{max}} \) and \( T_g \) of NBR and NR

<table>
<thead>
<tr>
<th>Frequency (Hz)</th>
<th>( \tan \delta_{\text{max}} )</th>
<th>( T_g ) (°C) (from ( \tan \delta_{\text{max}} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NBR</td>
<td>NR</td>
</tr>
<tr>
<td>0.1</td>
<td>1.43</td>
<td>2.34</td>
</tr>
<tr>
<td>1</td>
<td>1.49</td>
<td>2.28</td>
</tr>
<tr>
<td>10</td>
<td>1.56</td>
<td>2.05</td>
</tr>
<tr>
<td>50</td>
<td>1.65</td>
<td>1.97</td>
</tr>
<tr>
<td>100</td>
<td>1.76</td>
<td>2.02</td>
</tr>
</tbody>
</table>

Figure 5.4. Plot of \( \tan \delta \) against temperature for nitrile rubber

The \( T_g \) of NR is shifted progressively from -50 to -36 and that of NBR changed from -15 to -2 as the frequency increased from 0.1 to 100 Hz. The \( \tan \delta_{\text{max}} \)
also varied with frequency. The viscoelastic properties of a material are dependent on time, temperature and frequency. If a material is subjected to a constant stress, its elastic modulus will decrease over a period of time. This is due to the fact that the material undergoes molecular rearrangement in an attempt to minimise the localised stress. Modulus measurements performed over a short time (high frequency) result in higher values whereas measurements taken over long times (low frequency) result in lower values. The storage modulus value of NR was high at low temperature and decreased after the transition to rubbery phase around -40°C. In the case of NBR, the storage modulus shows a high value up to the transition temperature (±20°C) and thereafter the value decreases.

The effect of blend ratio on the dynamic mechanical behaviour of NBR/NR blends was also studied. Dynamic mechanical investigation was used to predict the miscibility of the polymer/polymer systems. Generally, for an incompatible blend, the tan δ vs. temperature curve shows the presence of two tan δ or damping peaks corresponding to the glass transition temperatures of individual polymers. For a highly compatible blend, the curve shows only a single peak in between the transitions temperatures of the component polymers, whereas broadening of transition occurs in the case of partially compatible system. In the case of compatible and partially compatible blends the Tgs are shifted to higher or lower temperatures as a function of composition. The variation of tan δ with temperature of NBR/NR blends and homopolymers are exhibited in Figure 5.5. The blends show two tan δ peaks corresponding to the Tgs of nitrile rubber and natural rubber, which indicates that the blends are not compatible. The Tg
corresponding to NR component is shifted to a lower temperature upon the addition of NBR and that corresponding to NBR component is shifted to a higher temperature upon the addition of NR. This suggests that the crosslink densities of the rubber phases in the blends show heavy biasing towards the NBR phase. Similar results are reported earlier in the literature.  

![Graph](image)

**Figure 5.5.** The variation of tan $\delta$ with temperature of NBR/NR blends and homopolymers at 10 Hz

The variation of tan $\delta_{\text{max}}$ of the blends as a function of NR content is shown in Figure 5.6. It can be seen that the tan $\delta_{\text{max}}$ due to NR phase increases as the NBR content decreases, i.e., the damping increases as the NR content increases. The damping due to NBR phase decreases because of the lower
concentration of NBR phase. The variation in tan $\delta_{\text{max}}$ can be explained in terms of the morphology of the blends. The tan $\delta_{\text{max}}$ due to NR phase increases sharply after 50 wt% because of the higher contribution of tan $\delta_{\text{max}}$ due to the continuous NR phase. But tan $\delta_{\text{max}}$ of NBR decreases as the NR content increases and the decrease is much sharper when the NR content is 50% or above, where NR forms a continuous phase.

![Graph showing variation of tan $\delta_{\text{max}}$ of NBR/NR blends with volume fraction of NR.](image)

*Figure 5.6. Variation of tan $\delta_{\text{max}}$ of NBR/NR blends with volume fraction of NR*

The tan $\delta$ peak height is a measure of damping. Usually it gives an indication of phase continuity of the system, the phase exhibiting the higher peak representing the more continuous phase, whereas two transition peaks of the same height may be an indication of dual phase continuity. From Table 5. 4 it is clear that as the NBR content increases from 0 to 100%, the NBR damping peak height increases
and NR peak height decreases. The peak width at half height for the NR and NBR transitions was measured and the values are also given in Table 5.4. It decreases as the blend composition changes from 70 to 30 wt%. The height of the region between the tan δ peaks (inter transition height) is a measure of the phase mixing. The inter transition height was determined for NBR/NR blends and the values are included in Table 5.4. They are very low and it decreases with decreasing NR content in the blends. The low value is an indication of very limited phase mixing and little interface area in the blend.

**Table 5.4.** Values of peak height, peak width at half height and inter transition height

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Relative peak height (cm)</th>
<th>Relative peak width at half height (cm)</th>
<th>Inter transition height (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NBR</td>
<td>NR</td>
<td>NBR</td>
</tr>
<tr>
<td>N100</td>
<td>2.4</td>
<td>7.0</td>
<td>15.8</td>
</tr>
<tr>
<td>N70</td>
<td>5.8</td>
<td>2.7</td>
<td>10.4</td>
</tr>
<tr>
<td>N50</td>
<td>8.7</td>
<td>1.0</td>
<td>10.4</td>
</tr>
<tr>
<td>N30</td>
<td>10.4</td>
<td>-</td>
<td>10.4</td>
</tr>
<tr>
<td>N0</td>
<td>-</td>
<td>15.8</td>
<td>-</td>
</tr>
</tbody>
</table>

The variation of storage modulus $E'$ of NBR/NR blends and homopolymers as a function of temperature is shown in Figure 5.7. The two steps in the storage modulus-temperature curve of the blends are characteristic of an immiscible two-phase system. As in the case of blend components, the modulus of the blends decreases with rise in temperature due to the decrease in stiffness of the sample. It can be seen from the figure that in the glassy region, the modulus of the blends increases with
increase in the NR content. This behaviour can be attributed to the better glass forming characteristics of NR with a higher degree of modulus value.

Figure 5.7. The variation of storage modulus $E'$ of NBR/NR blends and homopolymers as a function of temperature

Figure 5. 8 shows the variation of storage modulus at $-30^\circ$C and at a frequency of 1Hz as a function of NR content. The modulus decreases with increase in NR concentration. The curve shows a positive deviation from the additivity line. The curve shows a slope change from $N_{30}$ to $N_{50}$ due to the phase inversion of NR from the dispersed to continuous phase.

The variation of loss modulus $E''$ with temperature (Figure 5.9) also shows the same trend as that of tan $\delta$, i.e., the curves show two maxima corresponding to
the glass transition temperatures of NR and NBR. The loss modulus decreases with an increase in the NR content. Thus the dynamic mechanical analysis established the two-phase nature of NBR/NR blends.

**Figure 5.8.** Variation of storage modulus with weight % of NR at −30°C and at 1Hz

**Figure 5.9.** Variation of loss modulus of NBR/NR blends with temperature
The dynamic mechanical properties of NBR/NR blends were analysed from −70 to 30°C at different frequencies (0.1, 1, 10, 50 and 100 Hz). The influence of frequency on storage modulus, loss modulus and tan δ of N50 as a function of temperature are given in Figures 5.10-5.12. Storage modulus increased with increasing frequency whereas it decreased with increasing temperature. Loss modulus decreased initially with increase of frequency and after passing through the transition region an increase was observed. At low temperature region, tan δ values decrease with increase of frequency and at high temperature region, just the reverse has happened. The glass transition temperature is shifted towards higher temperature region with increasing frequency.

Figure 5.10. The effect of frequency on the storage modulus of N50 with temperature
Figure 5.11. The influence of frequency on the loss modulus of $N_{50}$ with temperature

Figure 5.12. The effect of frequency on the tan $\delta$ of $N_{50}$ with temperature
The activation energy, $\Delta H$ for the glass transition of the blends can be calculated from the Arrhenius equation$^{10}$

$$f = f_0 \exp\left(-\frac{\Delta H}{RT}\right)$$  \hspace{1cm} (5.2)

where $f$ is the measuring frequency, $f_0$ is the frequency when $T$ approaches infinity and $T$ is the temperature corresponding to the maximum of loss modulus $E''$ curve. The $\Delta H$ values obtained are given in Table 5.5. It may be noted that the activation energy for NBR transition is higher than that for NR transition.

### Table 5.5. Activation energy of NR and NBR glass transitions

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Activation energy $\Delta H$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NBR</td>
</tr>
<tr>
<td>$N_{100}$</td>
<td>-</td>
</tr>
<tr>
<td>$N_{70}$</td>
<td>296.11</td>
</tr>
<tr>
<td>$N_{50}$</td>
<td>442.61</td>
</tr>
<tr>
<td>$N_{30}$</td>
<td>404.49</td>
</tr>
<tr>
<td>$N_0$</td>
<td>399.93</td>
</tr>
</tbody>
</table>

The integral of the loss modulus versus temperature curve is characterised to develop a relationship between the extent of damping and the contribution for each group towards the damping performance. Fay et al. suggested five methods, namely, tan $\delta = 0.03$, straight line, height $\times$ width, integral area and constant $E''$ for the evaluation of the area under the linear loss modulus versus temperature curve (LA).$^{11}$ Comparatively, the integral method includes the area under the loss modulus versus temperature curves over a well-defined temperature range without neglecting any area directly beneath the $E''$ transition. Hence in this
system the integral method is made use of. The area under the linear loss modulus-temperature curve can be derived via a phenomenological treatment.¹²

\[
LA = \int_{T_G}^{T_R} E'' dT \equiv \left( E'_G - E'_R \right) \frac{R}{(E_a)_{avg}} \frac{\pi}{2} T^2
\]

where \( E'_G \) and \( E'_R \) represent the storage moduli in the glassy and rubbery states, respectively, \( T_G \) and \( T_R \) are glassy and rubbery temperatures just below and just above the glass transition, \( (E_a)_{avg} \) is the average activation energy of the relaxation process, and \( R \) is the gas constant.

By examining the area under the glass transition, a quantitative analysis of group contributions can also be made. The group contribution analysis for LA is based on the assumption that the structural groups in the repeating units provide a weight fraction additive contribution to the total loss area. The basic equation for the group contribution analysis of LA is¹³

\[
LA = \sum_{i=1}^{n} \frac{(LA)_i M_i}{M} = \sum_{i=1}^{n} \frac{G_i}{M}
\]

where \( M_i \) is the molecular weight of the \( i^{th} \) group in the repeating unit, \( M \) is the molecular weight of the whole mer, \( G_i \) is the molar loss constant for the \( i^{th} \) group, \((LA)_i\) is the loss area contributed by the \( i^{th} \) group, and \( n \) represents the number of moieties in the mer. Equation (5.4) provides a predictive method for LA values via the structure of the polymer.
Table 5.6. Experimental and theoretical values of loss area (LA)

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Experimental LA \times 10^{11} \text{ Pa.K}</th>
<th>Theoretical LA \times 10^9 \text{ Pa.K}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NR</td>
<td>NBR</td>
</tr>
<tr>
<td>N_{70}</td>
<td>37.48</td>
<td>0.77</td>
</tr>
<tr>
<td>N_{50}</td>
<td>28.98</td>
<td>6.33</td>
</tr>
<tr>
<td>N_{30}</td>
<td>9.81</td>
<td>12.69</td>
</tr>
</tbody>
</table>

The theoretical and experimental values of LA for different blend compositions are given in Table 5.6. The experimental values are larger than those obtained by group contribution analysis. The experimental values of LA are influenced by the morphology, crosslink density, interaction between the polymer components and phase continuity. There is no possibility of any specific interaction between the NR and NBR phases. Dual phase and co-continuous morphology was observed through SEM studies. For certain compounds there must be the possibility of intercrosslinking between the phases. Therefore, we believe that the higher values of LA are due to co-crosslinking of the two phases during vulcanisation.

The Cole-Cole plots were drawn by plotting loss modulus (E'') against storage modulus (E'). Generally homogeneous polymeric systems exhibit a semicircle diagram. The Cole-Cole plots of N_{30}, N_{50}, and N_{70} at a frequency of 0.1 are depicted in Figure 5.13. The plots do not have semicircular shape. This suggests the heterogeneous nature of these blends.
In polymeric systems modulus is a function of time as well as temperature. Due to the broad time dependence involved, it is not feasible to directly measure the complete behaviour of the modulus as a function of time at constant temperature. In principle, the complete modulus versus time behaviour of any polymer at any temperature can be measured. This is achieved by a shifting procedure that enables one to construct a "master curve" which is based on the principle of time-temperature correspondence. The master curve thus obtained is identical to that which would be measured at long times at a particular temperature.

Figure 5.13. Cole-Cole plots of $N_{30}$, $N_{50}$ and $N_{70}$
Figure 5.14. Plots of log $E'$ versus log $t$ of NBR/NR blends at different temperatures

The viscoelastic properties at a given frequency $f$ are quantitatively equivalent to those of an experiment carried out over a time $t = 1/2\pi f$. Viscoelastic data collected at one given temperature can be superimposed upon data collected at different temperatures by shifting the curves, i.e., by using the time-temperature superposition principle. The experimental log $E'$ versus log time graph at different temperatures is shown in Figure 5.14. The modulus curve at a particular temperature is then shifted along the time axis until it overlaps with the next curve. The distance between curves gives the value of shift factor, $a_T$. The shift factor characterises the rate of relaxation mechanism at some temperature $T_i$ in comparison with the rate at a higher temperature $T_{i+1}$. In this
way log aₜ values for all temperatures were determined. The master curve was constructed by plotting log (t/aₜ) vs. log (E'T₀/T), where E' is the storage modulus at a particular temperature, T₀ is the reference temperature on the Kelvin scale and T is the temperature of the experiment. The temperature of -30°C is taken as the reference temperature in constructing the master curve. Figure 5.15 shows the master curve for N₅₀. The main advantage of the master curve is that it provides modulus of the blend over a wide range of reduced time.

![Graph](image)

**Figure 5.15 Master curve of N₅₀**

### 5.1.4. Mechanical properties

The stress-strain curves of the unswollen samples are illustrated in Figure 5.16. The nature of deformation characteristic of homopolymers and blends under an applied load are evident from the stress-strain curves. All the
curves show typical elastomeric behaviour. NR shows maximum tensile strength while NBR shows the minimum. The blend compositions occupied intermediate positions. The stress required for deforming the sample increases with increase in NR content. This is mainly due to the strain induced crystallisation behaviour of NR. Figure 5.17 shows the stress-strain curves of samples after reaching equilibrium saturation in toluene. After reaching swelling equilibrium, there is slight difference in the nature of the stress-strain behaviour of NBR/NR blends. With increasing NR content, the stress-strain curve loses its typical elastomeric behaviour. It is also seen that the maximum stress increases with increase in NR content up to 50% and then decreases. This behaviour is due to the lack of strain-induced crystallisation in swollen samples with high NR content. The presence of solvents in the swollen samples restricts the mobility of the polymer chains; hence the orientation is difficult.
Figure 5.16. Stress-strain curves of NBR/NR blends in the unswollen state

Figure 5.17. Stress-strain curves of NBR/NR blends in the swollen state
The mechanical data of homopolymers and blends are presented in Table 5.7. As expected, the tensile strength and elongation at break decrease from \( N_{100} \) to \( N_0 \). The mechanical strength of NBR increases upon blending it with NR. This is due to the increase in crosslink density of NBR phase. The Young’s modulus of a material reflects the stress at low strain while secant modulus values (\( M_{100}, M_{200}, \) and \( M_{300} \)) reflect the stress at higher strains. As can be seen from Table 5.7, secant modulus values of all samples increase from 100 to 300%. In the swollen state, there is an overall reduction in the magnitude of these properties. In the equilibrium-swollen state, the rubber-solvent interaction is maximum while the rubber-rubber interaction is minimum and there is a total change in the conformation of polymer segments and chain entanglements. This results in the decreased values of tensile properties.

**Table 5.7. Mechanical properties of NBR/NR blends**

<table>
<thead>
<tr>
<th>Sample</th>
<th>System</th>
<th>Tensile Strength (MPa)</th>
<th>E. B. %</th>
<th>Secant modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( M_{100} )</td>
</tr>
<tr>
<td>Unswollen</td>
<td>( N_{100} )</td>
<td>22.08</td>
<td>1042</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>( N_{70} )</td>
<td>16.64</td>
<td>862</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>( N_{50} )</td>
<td>14.28</td>
<td>685</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>( N_{30} )</td>
<td>11.76</td>
<td>540</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td>( N_0 )</td>
<td>4.68</td>
<td>362</td>
<td>0.93</td>
</tr>
<tr>
<td>Swollen</td>
<td>( N_{100} )</td>
<td>1.22</td>
<td>243</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>( N_{70} )</td>
<td>1.46</td>
<td>187</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>( N_{50} )</td>
<td>1.76</td>
<td>196</td>
<td>1.24</td>
</tr>
<tr>
<td></td>
<td>( N_{30} )</td>
<td>1.16</td>
<td>171</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>( N_0 )</td>
<td>1.18</td>
<td>167</td>
<td>0.60</td>
</tr>
</tbody>
</table>
5.1.5. Model fitting

Applicability of various composite models, such as the parallel model, the series model, the Halpin-Tsai equation, the Kerner model and the Kunori model, were checked to predict the mechanical behavior of the blends.

The parallel model (highest-upper-bound model) is given by the equation\textsuperscript{16}

\[ M = M_1 \phi_1 + M_2 \phi_2 \]  
(5.5)

where \( M \) is the property of the blend and \( M_1 \) and \( M_2 \) are the properties of the components 1 and 2, respectively and \( \phi_1 \) and \( \phi_2 \) are the volume fractions of the components 1 and 2, respectively. In this model the components are considered to be arranged parallel to one another so that the applied stress elongates each of the component by the same amount.

In the lowest-lower-bound series model the components are arranged in series with the applied stress. The equation is\textsuperscript{16}

\[ \frac{1}{M} = \frac{\phi_1}{M_1} + \frac{\phi_2}{M_2} \]  
(5.6)

According to Halpin-Tsai equation\textsuperscript{17}

\[ \frac{M_1}{M} = \frac{1 + AiBi\phi_2}{(1 - Bi\phi_2)} \]  
(5.7)

\[ Bi = \left( \frac{M_1}{M_2} - 1 \right) \left( \frac{M_1}{M_2} + Ai \right) \]  
(5.8)
In this equation the subscripts 1 and 2 refer to the continuous and dispersed phase, respectively. The constant $A_i$ is defined by the morphology of the system. For dispersed elastomer domains, $A_i = 0.66$.

According to Kerner model$^{18}$

$$E_b = E_m \left[ \phi_d E_d \left[ \frac{(7-5v_m)E_m + (8-10v_m)E_d}{(7-5v_m)E_m + (8-10v_m)E_d} \right] + \phi_m / 15(1-v_m) \right]$$

(5.9)

where $E_b$ is the blend property, $v_m$ is the Poisson’s ratio and $\phi$ is the volume fraction. The subscript $m, d$ and $b$ stand for the matrix, dispersed phase and blend, respectively.

Kunori and Geil$^{19}$ reported that the tensile failure of a blend is the result of adhesion failing between the blend components. When there is no adhesive force between the blend components, the tensile strength of the blend $\sigma_b$ may be written as

$$\sigma_b = \sigma_m(1 - A_d)$$

(5.10)

where $\sigma_b$ and $\sigma_m$ are the tensile strengths of the blends and the matrix respectively, and $A_d$ represents the area of fraction occupied by the dispersed phase in transversal cross section. Kunori and Geil$^{19}$ assumed that when a strong adhesive force exists between the blend components, the dispersed phase would contribute to the strength of the blend; therefore, the parallel model may be modified as follows:

$$\sigma_b = \sigma_m(1 - A_d) + \sigma_d A_d$$

(5.11)
If the force propagates mainly through the interface, the above equation may be written as

$$\sigma_b = \sigma_m (1 - \phi_d^{2/3}) + \sigma_d \phi_d^{2/3}$$  \hspace{1cm} (5.12)

And if the force propagates through the matrix, then the equation becomes

$$\sigma_b = \sigma_m (1 - \phi_d) + \sigma_d \phi_d$$ \hspace{1cm} (5.13)

The above equation is the same as the parallel model.

**Figure 5.18.** Comparison of experimental and theoretical tensile strength

Figure 5.18 shows the comparison between experimental and theoretical (parallel model) tensile strength of the NBR/NR blends. Although we have tried all the above-mentioned models, we found that the experimental values were close to the parallel model. Therefore in NBR/NR blends, the applied stress distributes equally in the two phases.
5.1.6. Transport properties

The effect of blend composition on the sorption behaviour of NBR/NR blend membranes in toluene is presented in Figure 5.19. From the figure it is observed that the sorption behaviour varies in the order $N_{100} > N_{70} > N_{50} > N_{30} > N_0$ i.e. the equilibrium solvent uptake decreases with increase in volume fraction of NBR. This is attributed to the inherent solvent resistance behaviour of NBR. The variation in equilibrium solvent uptake ($Q_\infty$) with volume fraction of NR is shown in Figure 5.20. The trend is in accordance with the above observation. It has already been established that the permeability of heterogeneous rubber-rubber blends is intermediate between that of the component polymer.\textsuperscript{20}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{sorption_curves.png}
\caption{Sorption curves of NBR/NR blend membranes in toluene}
\end{figure}
Figure 5.20. The variation in equilibrium toluene uptake ($Q_\infty$) with volume fraction of NR

The difference in $Q_\infty$ values with blend composition can be correlated with the morphology of the system. In N$_{70}$, NBR phase is dispersed in the continuous NR matrix and in N$_{30}$, NR is dispersed in the continuous NBR matrix. In the N$_{50}$ blend both NR and NBR form continuous phase leading to a co-continuous morphology. Because of the dispersed nature of NR phase in N$_{30}$, the continuous NBR phase acts as a tortuous path for the diffusion process of solvent and hence the uptake is less. This is schematically shown in Figure 5.21. However, as the concentration of NR increases from 30 to 70-wt%, the size of NR domain increases and it forms the continuous phase and the diffusion process is continuous through the NR phase, which leads to the high uptake in N$_{50}$ and N$_{70}$. 
The mechanism of diffusion of NBR/NR blends was analysed using the equation 3.5 (Chapter 3) and the values of $n$ and $k$ were estimated. The results are given in Table 5.8. From the Table it can be seen that the values of $n$ ranges from 0.60 to 0.64, i.e. in NBR/NR blends, the mode of transport is close to Fickian. For the Fickian mode of transport, the rate of diffusion of penetrant molecules is much less than the relaxation rate of the polymer chains. When a
polymer interacts with solvents, two forces are normally generated; they are the mechanical or swelling stress induced by the solvent and chemical potential.\textsuperscript{21} Swelling stresses are either relaxed or dissipated by further swelling and rearrangement of the polymer segment. This process continuous until both mechanical and chemical equilibrium is achieved. It can be seen that there is no definite order in the values of $n$ and $k$. The disturbance in the establishment of mechanical and chemical equilibrium might be the reason for irregular variations of $n$ and $k$.

**Table 5.8. Values of $n$ and $k$ for toluene diffusion through NBR/NR blends**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$n$</th>
<th>$k$ (g/g min$^n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{100}$</td>
<td>0.64</td>
<td>1.21</td>
</tr>
<tr>
<td>$N_{70}$</td>
<td>0.60</td>
<td>1.43</td>
</tr>
<tr>
<td>$N_{50}$</td>
<td>0.60</td>
<td>1.36</td>
</tr>
<tr>
<td>$N_{30}$</td>
<td>0.60</td>
<td>1.31</td>
</tr>
<tr>
<td>$N_0$</td>
<td>0.62</td>
<td>1.44</td>
</tr>
</tbody>
</table>

The permeation of small molecules through polymers generally occurs through a solution diffusion mechanism, i.e. the penetrant molecules are first sorbed by the polymer followed by diffusion through the polymer. The net transport through the polymer depends on the difference in the amount of penetrant molecules between the two surfaces.

The diffusion coefficient $D$ can be calculated using the equation 3.13 (Chapter 3). Although this equation can be solved readily, it is instructive to examine the short-time limiting expression as well.
\[
\frac{Q_t}{Q_\infty} = 4 \left[ \frac{Dt}{\pi h^2} \right]^{1/2}
\] (5.14)

From a plot of \(Q_t\) vs. \(t^{1/2}\), a single master curve is obtained which is initially linear. Thus \(D\) can be calculated from an equation obtained by rearranging Equation 5.14 as

\[
D = \pi \left( h \theta / 4Q_\infty \right)^2
\] (5.15)

where \(h\) is the sample thickness and \(\theta\) is the slope of the initial linear portion of the sorption curves, i.e. before the attainment of 50% equilibrium solvent uptake.

The value of \(D\) depends on the polymer segmental mobility. Equation 5.14 holds for systems without appreciable swelling. For considerable swelling, a correction for the swelling of the polymer can be made by incorporating \(\phi\), the volume fraction of the polymer in the swollen mass, thus giving the intrinsic diffusion coefficient, \(D^*\).\(^{22}\)

\[
D^* = \frac{D}{\phi^{7/3}}
\] (5.16)

The variation in intrinsic diffusion coefficient with volume fraction of NBR in different solvents is illustrated in Figure 5.22. It is observed that the \(D^*\) value decreases with increase in NBR content. The permeation of a penetrant into the polymer matrix depends on the polymer morphology, which controls the propagation of a molecule from one site to another. Any morphological factor that modifies either the structure or the flexibility of the polymer chains will be expected to change the diffusivity of the molecule. Moreover, the diffusivity
values decrease with increase in molecular size of the penetrant. Benzene, toluene and p-xylene were used to study the effect of penetrants. The sorption curves of N$_{50}$ sample for the three solvents are exhibited in Figure 5.23. As expected, as the size of the permeant molecule increases the solvent uptake decreases, i.e. the low molecular weight solvent benzene shows the highest uptake while xylene, the high molecular weight solvent shows lowest uptake.

![Figure 5.22. The variation in intrinsic diffusion coefficient with volume fraction of NBR in different solvents](image)

*Figure 5.22. The variation in intrinsic diffusion coefficient with volume fraction of NBR in different solvents*
Figure 5.23. The sorption curves of N₅₀ sample for the three solvents

The sorption coefficient that is related to the equilibrium sorption of the penetrant is calculated using the equation 3.7 (Chapter 3) and these values are shown in Table 5.9. The sorption coefficient value decreases with increasing NBR content in the blend composition because the solvent resistance increases with increasing NBR content.

Table 5.9. Values of sorption coefficient (S) (g/g)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Benzene</th>
<th>Toluene</th>
<th>p-Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₁₀₀</td>
<td>4.95</td>
<td>4.71</td>
<td>4.5</td>
</tr>
<tr>
<td>N₇₀</td>
<td>4.33</td>
<td>4.27</td>
<td>3.68</td>
</tr>
<tr>
<td>N₅₀</td>
<td>4.14</td>
<td>3.5</td>
<td>3.14</td>
</tr>
<tr>
<td>N₃₀</td>
<td>3.64</td>
<td>3.21</td>
<td>2.65</td>
</tr>
<tr>
<td>N₀</td>
<td>2.34</td>
<td>1.97</td>
<td>1.51</td>
</tr>
</tbody>
</table>
The values of permeability coefficient $P$, which implies the net effect of sorption and diffusion, are given in Table 5.10. Similar trend as that of $D^*$ and $S$ is observed for $P$ values with the change in blend composition. The effect of weight percentage of NR on intrinsic diffusion ($D^*$) and permeation ($P$) coefficients is shown in Figure 5.24. The $D^*$ and $P$ increase regularly up to 50 wt % of NR. Beyond that the properties increase sharply. This can be attributed to the phase inversion in the morphology of the system. In N30, NR phase is dispersed in the continuous NBR matrix and in N50 and N70, NR phase becomes the continuous phase.

![Graph showing the effect of weight percentage of NR on intrinsic diffusion ($D^*$) and permeation ($P$) coefficients.]

**Figure 5.24.** The effect of weight percentage of NR on intrinsic diffusion ($D^*$) and permeation ($P$) coefficients
Table 5.10. Values of permeability coefficient at 28°C \((P \times 10^5)\) (cm² sec⁻¹)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Benzene</th>
<th>Toluene</th>
<th>p-Xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N_{100})</td>
<td>18.6</td>
<td>15.49</td>
<td>13.41</td>
</tr>
<tr>
<td>(N_{70})</td>
<td>9.14</td>
<td>8.15</td>
<td>6.11</td>
</tr>
<tr>
<td>(N_{50})</td>
<td>7.92</td>
<td>6.51</td>
<td>3.99</td>
</tr>
<tr>
<td>(N_{30})</td>
<td>6.24</td>
<td>4.18</td>
<td>2.02</td>
</tr>
<tr>
<td>(N_{0})</td>
<td>3.64</td>
<td>1.43</td>
<td>0.34</td>
</tr>
</tbody>
</table>

In the case of heterogeneous polymer blends, the permeability can be interpreted in terms of various theoretical models. In addition to the models used in the previous section i.e. parallel and series, Maxwell and Robeson models, are used here.

To describe the effect of permeating component on the overall blend permeability, Maxwell suggested the following equation

\[
P_c = P_m \left[ \frac{P_d + 2P_m - 2\phi_d (P_m - P_d)}{P_d + 2P_m + \phi_d (P_m - P_d)} \right]
\]  \(\text{(5.17)}\)

where the subscripts \(d\) and \(m\) correspond to the dispersed phase and the matrix, respectively.

Robeson et al.\(^{23}\) extended Maxwell's analysis to include the continuous and discontinuous characteristics of both phases at intermediate compositions and expressed the equations as

\[
P_c = x_a P_d \left[ \frac{P_2 + 2P_1 - 2\phi_2 (P_1 - P_2)}{P_2 + 2P_1 + \phi_2 (P_1 - P_2)} \right] + x_b P_1 \left[ \frac{P_1 + 2P_2 - 2\phi_1 (P_2 - P_1)}{P_1 + 2P_2 + \phi_1 (P_2 - P_1)} \right]
\]  \(\text{(5.18)}\)

where \(x_a\) and \(x_b\) are the fractional contributions to the continuous phase so that \(x_a + x_b = 1\).
We have compared the experimental permeation coefficients with various theoretical models. It can be seen from Figure 5.25 that the experimental values are close to the Robeson model up to 50% NBR content; beyond that it is close to the parallel model.

![Graph showing permeation coefficients](image)

**Figure 5.25.** Theoretical modelling for the permeation coefficients of NBR/NR blends in benzene at 28°C

In order to study the effect of temperature on the transport properties, the sorption experiments were carried out at 50, 60 and 70°C in addition to 28°C. Figures 5.26 and 5.27 show the effect of temperature on mol % xylene uptake of N50 and N30 blends. As expected, the solvent uptake increases with increase in temperature. The values of transport coefficients also increase with increase in temperature.
Figure 5.26. Sorption curves of $N_{50}$ in p-xylene at different temperatures.

Table 5.11 Values of activation parameter, $E_D$, $E_P$ and $\Delta H$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_P$ (kJ/mol)</th>
<th>$E_D$ (kJ/mol)</th>
<th>$\Delta H$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{100}$</td>
<td>9.51</td>
<td>7.31</td>
<td>2.20</td>
</tr>
<tr>
<td>$N_{70}$</td>
<td>10.07</td>
<td>8.22</td>
<td>1.85</td>
</tr>
<tr>
<td>$N_{50}$</td>
<td>10.09</td>
<td>8.59</td>
<td>1.50</td>
</tr>
<tr>
<td>$N_{30}$</td>
<td>10.83</td>
<td>10.22</td>
<td>0.61</td>
</tr>
<tr>
<td>$N_0$</td>
<td>10.82</td>
<td>10.95</td>
<td>-0.13</td>
</tr>
</tbody>
</table>
The temperature dependence of transport properties can be used to evaluate the activation energy for the diffusion and permeation process using the Arrhenius relation given in equation 3.9 (Chapter 3). Arrhenius plot of $\log P$ vs. $1/T$ for calculating the activation parameters is given in Figure 5.28. The values of $E_D$ and $E_P$ are presented in Table 5.11. The uncertainty in the values ranges from $\pm 0.001$ to $\pm 0.003$. It is seen that as the concentration of NBR increases both $E_D$ and $E_P$ values increase. The enthalpy of sorption values are also included in Table 5.11. The $\Delta H_S$ is a composite parameter involving the contribution from (i) Henry’s law needed for the formation of a site and the dissolution of the species into that site, the formation of the site involves an endothermic contribution and
(ii) Langmuir's (hole filling) type sorption mechanism, in which case the site already exists in the polymer matrix and sorption by hole filling gives exothermic heat of sorption. The positive $\Delta H_s$ values for NR and the blends suggest a Henry's type sorption and the negative $\Delta H_s$ value for NBR suggests a Langmuir type sorption.

![Figure 5.28 Arrhenius plot of log $P$ vs. $1/T$](image)

**Figure 5.28 Arrhenius plot of log $P$ vs. $1/T$**

5.1.7. **Determination of the network structure**

The investigation of swelling equilibrium can help to elucidate the structure of the polymer network. Diffusion into solid polymers depends on the availability of appropriate molecular size holes in the network, in addition to the attractive forces between the penetrant molecules and the polymer. From the structure and morphology of the polymer, the presence of holes is determined in terms of chain entanglement densities and its dependence on swelling. In order to gain further insight into the sorption process in relation to the morphological characteristics of the
polymer, the molecular weight between crosslinks ($M_c$) has been estimated by using the equation 3.2 (Chapter 3). Whenever a polymer is immersed in an organic liquid, its molecules will diffuse into the solid polymer film to produce a swollen gel. Dissolution is prevented if the attraction between neighbouring polymer molecules is sufficiently great, perhaps due to crosslinking. Swelling equilibrium is approached when the chemical potential of the solvent inside the swollen polymer becomes equal to that of the outside phase. The estimated values of $M_c$ are given in Table 5.12. These values are in the order $N_{100} > N_{70} > N_{50} > N_{30} > N_0$, supporting the solvent uptake behaviour in the blends and the component polymers.

5.1.8. Model Fitting

Flory and Rehner developed the affine model for a network deforming affinely, where the components of each chain vector transform linearly with macroscopic deformation and the junction points are assumed to be embedded in the network without fluctuations. Then the molecular weight between crosslinks ($M_c$) for the affine limit of the model [$M_c(\text{aff})$] was calculated using the formula

$$M_c(\text{aff}) = \frac{\rho V_s \nu_{2c}^{2/3} \nu_{2m}^{1/3} \left(1 - \frac{\mu}{\nu} \nu_{2m}^{1/3}\right)}{-\ln(1-\nu_{2m}) + \nu_{2m} + \chi \nu_{2m}^{2}}$$

(5.19)

where $V_s$ is the molar volume of the solvent, $\mu$ and $\nu$ are called the number of effective chains and junctions; $\nu_{2m}$, the polymer volume fraction at swelling equilibrium; $\nu_{2c}$, the polymer volume fraction during crosslinking; and $\rho$, the polymer density.
The phantom network model was proposed by James and Guth,\textsuperscript{26} where the chains may move freely through one another. The junction points fluctuate over time around their mean position without being hindered by the presence of the neighbouring chains and are independent of deformation. The molecular weight between crosslinks for the phantom limit of the model \( [M_c(\text{ph})] \) was calculated by\textsuperscript{27}

\[
M_c(\text{ph}) = \left(1 - \frac{2}{\phi}\right) \rho V_s V_{2c}^{2/3} V_{2m}^{1/3} \left[ \ln(1 - V_{2m}) + V_{2m} \chi V_{2m}^2 \right]^{-1/3}
\]

(5.20)

where \( \phi \) is the junction functionality.

\( M_c(\text{aff}) \) and \( M_c(\text{ph}) \) were compared with \( M_c(\text{expt}) \) and these values are also given in Table 5.12. It is observed that \( M_c \) values are close to \( M_c(\text{aff}) \). This suggests that in the highly swollen state, the chains in the blends and in the component polymers deform affinely, i.e., the chains in the network are freely moving without fluctuating the junction points.

**Table 5.12.** Comparison of network structure

<table>
<thead>
<tr>
<th>System</th>
<th>( M_c(\text{expt}) ) g/mol</th>
<th>( M_c(\text{aff}) ) g/mol</th>
<th>( M_c(\text{ph}) ) g/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_{100})</td>
<td>13158</td>
<td>12304</td>
<td>6152</td>
</tr>
<tr>
<td>N(_{70})</td>
<td>7927</td>
<td>7440</td>
<td>3720</td>
</tr>
<tr>
<td>N(_{50})</td>
<td>6036</td>
<td>5680</td>
<td>2840</td>
</tr>
<tr>
<td>N(_{30})</td>
<td>4799</td>
<td>4527</td>
<td>2264</td>
</tr>
<tr>
<td>N(_{0})</td>
<td>2243</td>
<td>2124</td>
<td>1062</td>
</tr>
</tbody>
</table>
5.1.9. Comparison with theory

Figures 5.29 and 5.30 represent the comparison of experimental diffusion results with that of theoretical predictions of $N_{50}$ and $N_{30}$. The total agreement is fairly good. The blend $N_{70}$ also shows a similar trend.

**Figure 5.29.** Comparison of experimental and theoretical diffusion curves of $N_{50}$ in toluene at 28°C

**Figure 5.30.** Comparison of experimental and theoretical diffusion curves of $N_{30}$ in toluene at 28°C
5.2. Application

As an example of a practical use of NBR/NR blends, formulations suitable for use in the manufacture of milking inflations have been developed. Milking inflations are used in the dairy industry and they are the part of the milking machine, which fits on the teat of a cow (Figure 5.31), they come into direct contact with milk.

![Figure 5.31. A milking inflation](image)

Therefore all ingredients must conform to regulations governing food contact. These differ from country to country, but those set by the US Food and Drug Administration (FDA) are particularly pertinent because of both the size of the US market and the use of these regulations elsewhere.

The permitted additives for milking inflation come under the section "Rubber articles intended for repeated use". A wide range of fillers is allowed, but a limit of 10% by weight of the total formulation is imposed on furnace carbon black. This limitation can prove very difficult for NBR, which lacks the inherent high strength of NR, because it is difficult to obtain adequate physical properties
for certain designs of milking inflation. N770 black (SRF) and Insil VN3 (precipitated silica) are selected as the fillers. A wide range of plasticizers is also tolerated, but the total must not exceed 30% w/w. The selection of dibutyl phthalate and dioctyl phthalate as plasticizers in the work considered here is consistent with the work cited in Chapter 4.

In addition to the US specification for a typical milking inflation substantial hot tear resistance is required in order to ensure de-moulding from the injection mould cavity without tearing of the inflation. Resistance to swelling by butter oil is a key requirement of milking inflation. NBR with 34% acrylonitrile content swell very little in butter oil while NR has very poor resistance to swelling in oils.

The carbon black with a loading of 50 phr is added wholly within the NR masterbatch to restrict the swelling arising from rubber-filler interaction. The carbon black is not required to reinforce the NBR phase; the NR phase will impart the necessary strength properties to the blend. The NBR masterbatch is filled with white filler, silica (40 phr). The plasticizers are distributed between the two masterbatches to ensure that the fillers mixed effectively. Separate masterbatches of the NR and the NBR were each prepared by using the two plasticizers DBP and DOP and then cross-blended to give a 50/50 blend ratio and finalised with the curatives on a two-roll mixing mill.

Figure 5.32. illustrates the comparison effect of plasticizer system on the swelling of ghee through NBR/NR blends at 28°C. It shows that the plasticizer
system has little effect on the swelling of ghee. Moreover, the maximum uptake is well below the limit of \( \pm 10\% \) volume change.

\[ \text{Figure 5.32. Swelling of ghee through NBR/NR 50/50 blend} \]

In order to find out the effect of temperature on the ghee transport, we have conducted the swelling experiments at 50 and 70°C in addition to 28°C. Figure 5.33 shows the influence of temperature on the transport of ghee through NBR/NR 50/50 blend. We found that temperature activated the diffusion process.
The physical properties of the blend are summarised in Table1. The plasticizer shows marginal effect on the mechanical properties of NBR/NR 50/50 blend.

**Table 5.13. Physical properties of NBR/NR 50/50 blend**

<table>
<thead>
<tr>
<th>Properties</th>
<th>DBP</th>
<th>DOP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength, MPa</td>
<td>15.02</td>
<td>15.75</td>
</tr>
<tr>
<td>Elongation at break, %</td>
<td>711</td>
<td>735</td>
</tr>
<tr>
<td>Tear strength, kN/m</td>
<td>20.14</td>
<td>19.70</td>
</tr>
</tbody>
</table>
5.3. References


