Chapter V

INTERACTION OF CROSSLINKED NATURAL RUBBER WITH CHLORINATED HYDROCARBONS

Results of this chapter have been communicated for publication in *Macromolecules*

The previous chapters have been directed towards the accumulation of transport data of NR in the presence of aliphatic and aromatic hydrocarbons. In these studies, liquid sorption or transport was found to be a function of structure of the network of NR and the diffusant molecule. The present chapter extends these approaches towards the molecular transport characteristics as well as the reduction in mechanical strength of NR with chlorinated hydrocarbons as probe molecules. In this work, another technique has been employed to follow the transport process. After attaining equilibrium in different liquids, the NR samples were desorbed fully. The desorbed samples were exposed to solvents for resorption followed by redesorption. Thus a sorption (S)–desorption (D)–resorption (RS)–redesorption (RD) experiment has
been used for studying the transport phenomenon. This technique has been successfully employed by Aminabhavi and Phayde [1] for investigating the solvent transport into Santoprene thermoplastic rubber samples exposed to n-alkanes.

V.1. Results and discussion

Figure V.1 represents the liquid sorption behaviour of NR samples vulcanized by the four modes viz., DCP, CV, EV and Mixed. The solvent used was CCl₄. It is clear from the figure that the maximum liquid sorption decreases in the order CV > Mixed > EV > DCP. This observation is in qualitative agreement with the experiments using aromatic and aliphatic hydrocarbons.

The plots of S–D–RS–RD experiments with CCl₄ as the solvent, for CV and DCP samples are given in Figures V.2 and V.3, respectively. It is seen that the sorption and desorption curves do not exhibit identical patterns. This clearly indicates the deviation of transport mode from the regular Fickian trend. However, the resorption and redesorption curves exhibit identical patterns. The resorption curves show that the equilibrium uptake values and the time to attain equilibrium are higher, compared to the first sorption process. In a sorption-desorption cycle the available free volume of the rubber might increase due to the rearrangement of rubber chains and the subsequent sorption process is different from that of the original. These effects have been successfully described by the network relaxation in terms of the times required for the molecular rearrangements of the chains and that of the solvent diffusion into the polymer [2]. However, segmental mobility of the polymer might be increased due to solvent ingestion and this depends upon the ability of the solvent molecules to penetrate and thereby weaken the intermolecular forces of the polymer network structure.
Figure V.1. Mole per cent CCl₄ uptake of NR vulcanized by different systems (The samples were cured to a torque of 33.8 dNm).
Figure V.2. S-D-RS-RD curves of CV system.
Figure V.3. S–D–RS–RD curves of DCP system.
The influence of nature of the penetrant on the liquid transport through NR is presented in Figure V.4. Higher Q_v values are observed for NR-CCl_4 system compared to the other two systems, viz., NR-CHCl_3 and NR-CH_2Cl_2. This is in fact, due to the differences in polarity of the probe molecules. The non-polar NR matrix has more affinity towards the non-polar CCl_4 molecules with zero dipole moment value. The liquid sorption decreases with increase in the polarity of the solvent molecules. 

The mechanism of transport in the systems under investigation was followed by using Equation III.3. The estimated values of the constants n and k are compiled in Table V.1. The n values are accurate to ± 0.01 units. The values of n for sorption experiments suggest that the observed diffusion mechanism can be classified as anomalous. However, for resorption experiments the n values are close to 0.5 suggesting Fickian type transport where the rate of polymer chain relaxation is higher, compared to the concurrent solvent diffusion. The change of the transport mode from the anomalous nature to the Fickian trend after a sorption-desorption cycle can probably be due to the leaching out of extra network materials (ENM) [3]. The ENM represent all the unreacted materials left behind in the rubber matrix after vulcanization. The presence of these materials can reduce segmental as well as the overall rubber chain mobility causing the deviation of transport mode from the regular Fickian trend.
Figure V.4. Mole per cent solvent uptake of CV system.
Table V.1. Values of n and k.

<table>
<thead>
<tr>
<th></th>
<th>CH₂Cl₂</th>
<th>CHCl₃</th>
<th>CCl₄</th>
<th>CH₂Cl₂</th>
<th>CHCl₃</th>
<th>CCl₄</th>
<th>CH₂Cl₂</th>
<th>CHCl₃</th>
<th>CCl₄</th>
<th>CH₂Cl₂</th>
<th>CHCl₃</th>
<th>CCl₄</th>
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<tbody>
<tr>
<td>n</td>
<td>0.61</td>
<td>0.62</td>
<td>0.64</td>
<td>0.52</td>
<td>0.52</td>
<td>0.54</td>
<td>4.31</td>
<td>4.60</td>
<td>5.12</td>
<td>4.82</td>
<td>5.01</td>
<td>5.36</td>
</tr>
<tr>
<td>k x 10²</td>
<td>4.31</td>
<td>4.60</td>
<td>5.12</td>
<td>4.82</td>
<td>5.01</td>
<td>5.36</td>
<td>4.21</td>
<td>4.76</td>
<td>5.09</td>
<td>4.82</td>
<td>5.01</td>
<td>5.36</td>
</tr>
<tr>
<td></td>
<td>3.11</td>
<td>3.48</td>
<td>3.96</td>
<td>3.84</td>
<td>3.81</td>
<td>4.46</td>
<td>3.07</td>
<td>3.43</td>
<td>3.82</td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td>2.64</td>
<td>2.94</td>
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<td></td>
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</table>
The kinetic parameter, diffusion coefficient \( D \) for the different systems under investigation was determined by using Equation IV.1. In order to introduce the swelling correction, the computed values of \( D \) were modified by considering the volume fraction \( \phi \) of rubber in the swollen samples using Equation IV.2. The modified diffusion coefficient values, known as intrinsic diffusion coefficient, are given in Table V.2. The \( D^* \) values increase regularly from DCP to CV system in a given penetrant. It is also seen that these values decrease with increase in the polarity of the penetrant. These observations parallel the equilibrium sorption values.

<table>
<thead>
<tr>
<th>System</th>
<th>Penetrant</th>
<th>( \text{CH}_2\text{Cl}_2 )</th>
<th>( \text{CHCl}_3 )</th>
<th>( \text{CCl}_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCP</td>
<td>4.01</td>
<td>5.11</td>
<td>5.51</td>
<td></td>
</tr>
<tr>
<td>EV</td>
<td>4.58</td>
<td>5.63</td>
<td>6.06</td>
<td></td>
</tr>
<tr>
<td>Mixed</td>
<td>5.17</td>
<td>6.86</td>
<td>7.41</td>
<td></td>
</tr>
<tr>
<td>CV</td>
<td>6.81</td>
<td>8.34</td>
<td>9.60</td>
<td></td>
</tr>
</tbody>
</table>

The temperature susceptibility of NR samples in \( \text{CCl}_4 \) was investigated by conducting the sorption experiments at 45 and 60°C. However, in the case of other solvents, the influence of temperature could not be studied due to their low boiling points. Figure V.5 shows the increase in the rate and equilibrium sorption of CV sample, in \( \text{CCl}_4 \), with temperature.
Figure V.5. Temperature dependence of mole per cent CCl₄ uptake of CV system.
The mechanical properties of swollen networks have been the object of numerous investigations for the past several years. Dogadkin et al. [4] examined the effect of swelling, as a result of liquid sorption and diffusion, on the strength of vulcanizates. They showed that swelling decreases the strength of rubber in different ways depending on the type of rubber, type of liquid and the nature of interaction between rubber and liquid. Rennar and Oppermann [5] studied the swelling behaviour and mechanical properties of endlinked poly(dimethyl siloxane) (PDMS) networks and randomly crosslinked polyisoprene networks. They concluded that the measurements of the small-strain modulus and the determination of the equilibrium degrees of swelling of PDMS and polyisoprene networks both demonstrate the importance of permanent entanglements or other topological interactions giving rise to an enhancement of network density.

One of the most informative mechanical experiments for any polymeric material is the determination of its stress-strain curves in tension. From the stress-strain curves it is possible to determine the differences in the deformation characteristics of rubber samples under an applied load. These curves vary depending upon the nature and distribution of crosslinks in the rubber network. Figure V.6 shows the stress-strain curves of NR crosslinked by the four techniques, viz., DCP, CV, EV and Mixed. These curves are typical of crosslinked elastomers. The marching trend of the curves in Figure V.6 is associated with the strain induced crystallisation behaviour of NR [6]. From the figure it follows that for a particular strain, the value of stress is maximum for the sample crosslinked by DCP. The same trend is observed at all strain values. It is also clear from the figure that the slope of the initial portion of the curves is maximum for DCP sample indicating its higher modulus. This is definitely associated with the higher degree of crosslinking of DCP samples. The modulus is found to decrease in the order DCP > EV > Mixed > CV. This is in good agreement with the equilibrium sorption values of the rubber samples in different solvents.
Figure V.6. Stress-strain curves of NR samples before swelling.
Figure V.7 shows the stress-strain curves of NR samples after reaching equilibrium saturation in CCl₄. The modulus is found to decrease very significantly under swollen conditions for all the samples; the reduction being predominant for CV sample. The strain at break is found to be reduced to about \( \frac{1}{4} \)th of the deformation of the corresponding unswollen samples. A comparison of Figures V.6 and V.7 gives a very interesting observation that the marching trend of the rubber samples, in the unswollen stage, disappears after they attain equilibrium saturation in a solvent. This can be explained by the absence of strain-induced crystallisation in the solvent saturated rubber samples. The random distribution of solvent molecules in the swollen specimens effectively opposes the alignment of rubber segments under the applied load thereby preventing strain-induced crystallisation.

Figure V.8 shows the stress-strain behaviour of CV samples after reaching equilibrium in CH₂Cl₂, CHCl₃ and CCl₄. The stress values are found to be higher for the sample swollen in CH₂Cl₂, for all strain values. The mechanical properties of swollen specimens are governed by different types of relaxation mechanisms which involve the intramolecular motions of segments and the molecular motions involving conformation changes in chain entanglements. The physical entanglements of the rubber chains contribute significantly to the deformation characteristics of the networks in addition to the contribution of chemically discrete crosslinks. Since the physical entanglements vary depending on the interaction of the rubber segments with the solvents, it is reasonable to think that the stress-strain behaviour of the same rubber sample in different solvents will be different. Of the three solvents in this work, CCl₄ exhibits higher rubber-solvent interaction as can be seen from the equilibrium sorption values. Therefore, the rubber sample exposed to CCl₄ has only minimum contribution of physical crosslinks (due to lesser entanglements) to the total crosslink density. In otherwords, the minimum modulus and tensile strength of NR sample swollen in CCl₄ compared to other rubber-solvent systems is associated with the lower degree of physical entanglements in it.
Figure V.7. Stress-strain curves of NR samples after reaching equilibrium in CCl₄.
Figure V.8. Stress-strain curves of CV sample in different solvents.
Figure V.9 shows the variation of tensile strength of different NR samples as a function of the exposure time in the solvent CCl₄, for the first 24 h. It is seen that the tensile strength values of all the samples decrease regularly as the time of exposure to liquid medium increases. This is in quantitative agreement with the expectation that increase in liquid imbibition weakens the attractive forces between the macromolecular chains of NR. It is interesting to see that almost half of the total reduction in tensile strength of all the samples occurs during the first 6 h of exposure to the solvent medium. The rate of decrease declines with increase in exposure time.

Figure V.10 represents the stress-strain curves of NR samples after a sorption-desorption cycle. Evidently, the curves follow the behaviour of those of the unswollen samples (Figure V.6). However, the stress values are found to be a little lower for all strain values compared to the curves of unswollen samples. This reduction may probably be due to the removal of ENM during a cycle of sorption and desorption.
Figure V.9. Variation of tensile strength of NR samples with exposure time in CCl₄.
Figure V.10. Stress-strain curves of NR samples after a sorption-desorption cycle.
References


3. Lewis, P. M. *NR Tech.* 1986, 17(4), 57.

