CHAPTER 6

ANALYSIS OF INTERFACE ADHESION BY EQUILIBRIUM SWELLING STUDIES

6.1 Introduction
6.2 Experimental
6.3 Results and Discussion

6.3.1 Equilibrium swelling of isora/NR composites in organic solvents

6.3.1.1 Effect of curing temperature
6.3.1.2 Effect of fibre loading and bonding agent
6.3.1.3 Correlation with adhesion
6.3.1.4 Effect of chemical treatment
6.3.1.5 Dimensional changes of the composites

6.3.2 Swelling of isora/NR composites in fuels/oils used in automobiles

6.3.2.1 Effect of fibre loading and bonding agent
6.3.2.2 Effect of chemical treatment
6.3.2.3 Dimensional changes of the composites

6.4 References
6.5 Conclusions
Abstract

Equilibrium sorption studies have been conducted using organic solvents and commercial fuels like petrol, diesel and lubricating oil in order to understand the interfacial adhesion and performance of short isora fibre reinforced natural rubber composites under these environments. Effect of curing temperature, fibre loading and bonding agent on the equilibrium swelling of isora-natural rubber composites have also reported.

Part of the results of this chapter has been published in "Composites interfaces", Vol 13(4-6): 391; (2006) and a part has been published in "Bulletin of Materials Science", Vol. 29(1): 91; (2006)
6.1 INTRODUCTION

Swelling experiments of rubber composites are important for analyzing the service performance of these composites in such environments. Rubber articles come in contact with different liquids during service performance. This can happen either as a part of the service requirement as in the case of oil seals or by accidental splashing of oils and greases that occurs with automobile components. The contact of rubbers with organic solvents can be well explained by absorption and diffusion phenomena [1]. The amount of swelling at equilibrium was treated as a special case of Flory-Rehner theory. According to Flory-Rehner theory for swelling of a rubber polymer, at equilibrium

\[
\ln(1-V_t) + V_t + \frac{V_t^2}{V} + V_c \left( V_t^{1/3} - V_t/2 \right) / V_0 = 0
\]

where \( V_t \) is the volume fraction of rubber after swelling, \( \chi \) is the polymer-solvent interaction parameter, \( V_c \) is the number of moles of effective network chains in the initial or unswollen volume and \( V_0 \) and \( V_t \) are the molar volume of the solvent and polymer. An important difference between vulcanized and raw rubber is that the former possesses a structure, which cannot be broken down completely by any solvent. The material therefore swells and cannot be dispersed. The swelling behaviour of rubber vulcanizates is influenced by different factors such as the chemical nature, dimension and shape of the filler, compatibility of the solvent with the rubber and interfacial adhesion. The degree of cure in particulate filler reinforced vulcanizates by swelling method has been studied by Kraus [2]. The degree of restriction exerted by the reinforcing filler allows an equation of the form given by Kraus.

\[
\frac{V_{ro}/V_{rf}}{1-3c(1-V_{ro}^{1/3}) + V_{ro}^{-1}} = \frac{1}{(1-f)}
\]
Where \( V_{ro} \) is the volume fraction of rubber in the unfilled vulcanizates, \( V_{rf} \) is the volume fraction of rubber in the filled vulcanizates; \( f \) is the volume fraction of the filler, ‘\( c \)’ the constant characteristic of the filler which indicates the degree of adhesion. Several researchers have extensively studied the transport behaviour of various organic liquids in polymer composites [3-10]. Sorption experiments provide valuable information on the transport characteristics of polymer composites, i.e.; at what rate the liquid diffuses into the polymer matrix. The phenomenon of transport of liquids through rubbery polymers is controlled by the polymer structure, its cross link density, presence of fillers, penetrant size etc. Das has studied the adhesion between rubber and short glass and asbestos fibres using restricted swelling measurements [11]. Coran et al [12] have studied the solvent swelling of unidirectional rubber fibre composites. Maximum strength and reinforcement are achieved along the direction of fibre alignment. Swelling is a uniform restrictive force induced on the vulcanize samples and it will be anisotropic in well bonded and oriented fibre rubber composite. Because of the anisotropic nature of fibre rubber composites, the swelling is restricted in the direction of fibre alignment and consequently swelling becomes anisotropic. The improvement in reinforcement obtained by enhancing fibre matrix adhesion through the incorporation of a bonding system has been widely studied in the case of rubber vulcanizates [13]. Earlier researchers [14-15] have studied numerous techniques like H-block and strip adhesion; both dynamic and static conditions have been used to measure adhesion between fibre and rubber. While most of these techniques give a good relative indication of adhesion, the time dependent nature of the viscoelastic materials overshadows the real effect. Equilibrium swelling is another technique, which has been used to assess the fibre rubber adhesion. Fibres, if bonded effectively, are supposed to restrict the swelling of elastomers. Thus the procedure of restricted equilibrium swelling technique helps us to evaluate the resistivity of
Equilibrium swelling studies

composites towards commonly available solvents like toluene, n-hexane etc. The resistance is strongly influenced by the strength of the fibre matrix adhesion. The solvent effects, especially when coupled with changing temperature affect a wide variety of mechanical and thermophysical properties.

The diffusion of solvents and relaxation process in a rubber sample above its $T_g$ are governed by the segmental mobility of the chains, which in turn are considered to be affected by the total free volume and its distribution within the elastomer matrix [16]. Aminabhavi et al have studied the sorption and transport of organic solvents by polymer membrane [17]. This chapter presents the restricted equilibrium swelling of isora natural rubber composites with respect to the effects of curing temperature, fibre loading, chemical modification of fibre surface and bonding agent. The equilibrium swelling is studied in relation to the interfacial adhesion also.

6.2 EXPERIMENTAL

The formulation of the mixes used in this investigation is given in Table 6.1. The procedure for the swelling data analysis and their vulcanization characteristics are reported in Chapters 2 and 4 respectively.

Circular specimens of diameter 20 mm. were punched out from the vulcanized sheets. Thicknesses and diameters of the specimens were measured by means of a screw gauge and vernier calipers respectively. Specimens of known weight were immersed in the solvents (toluene and hexane) and automobile fuels and oils in diffusion test bottles and kept at room temperature. Samples were removed from the bottles at periodic intervals and the wet surfaces were quickly dried using tissue paper and the weights of the specimen after swelling were determined at regular intervals until no further increase in solvent uptake was detected. Thickness and diameter of the specimen after equilibrium swelling were also measured.
Table 6.1 Compound Formulation [phr]

<table>
<thead>
<tr>
<th>Ingrédients</th>
<th>$X_{10}$</th>
<th>$X_{20}$</th>
<th>$X_{30}$</th>
<th>$X_{40}$</th>
<th>$X_{10b}$</th>
<th>$X_{20b}$</th>
<th>$X_{30b}$</th>
<th>$X_{40b}$</th>
<th>$Y_{30}$</th>
<th>$Y_{30b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF resin</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.5</td>
<td>5.0</td>
<td>7.5</td>
<td>10</td>
<td>-</td>
<td>7.5</td>
</tr>
<tr>
<td>Silica</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>2.0</td>
<td>3.0</td>
<td>4.0</td>
<td>-</td>
<td>3.0</td>
</tr>
<tr>
<td>Hexa</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.6</td>
<td>3.2</td>
<td>4.8</td>
<td>6.4</td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td>Fibre</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Fibre [U]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Fibre [T]</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Basic recipe: NR-100, ZnO-5.0, Stearic acid-2.0, TDQ-1.0, S2.5 low temp curing system [ZDC-1.0,Xantahate- 0.75] For conventional system [CBS- 0.6,TMTD- 0.1]. [Conventionally cured composites are represented by $X$, eg; $X_{30b}$-30 phr loading with bonding agent cured by conventional systems] U-untreated, T- alkali treated

6.3 RESULTS AND DISCUSSION

6.3.1 Equilibrium swelling of isora/NR composites in organic solvents

6.3.1.1 Effect of curing temperature

Figures 6.1(a) and (b) show the variation of the mol% uptake in toluene and hexane with curing temperature of the composites. In both solvents the uptake of solvent is lowest for the composite vulcanized at 100°C. The same trend is observed in the case of composites containing treated fibres and treated fibres with bonding agent.

A comparison of the mol% uptake of the solvent for the composites cured at 100°C and 150°C in toluene and n-hexane is given in Figure 6.2. It may be observed that in both solvents the uptake of solvent is high for the composites cured at high temperature (150°C). This shows that there is better fibre rubber adhesion when the composite is cured at 100°C and it is likely that at higher temperature (150°C) the
Equilibrium swelling studies

Figure 6.1 Variation of mol% uptake of solvents with curing temperature of the composites

(a) Toluene

(b) n-Hexane

Figure 6.2 Comparison of the mol% uptake of the solvents for the composites (30 phr) cured at 100°C and 150°C
fibre and rubber shows a tendency to degrade as evident from the results of our earlier studies [18].

6.3.1.2 Effect of fibre loading and bonding agent

Figures 6.3 (a) and (b) give the variation of mol% uptake of the solvents (toluene and n-hexane) with fibre loading for the composites cured at 100°C. For both the solvents it is clear that as fibre loading increases, equilibrium solvent intake decreases. This is obviously due to the increased hindrance exerted by the fibres at higher loadings. It is also observed that for the composites containing bonding agent there is a sharp decrease in the uptake of solvents. A highly bonded system would exhibit high resistance to swelling compared to the nonbonded systems.

![Graphs showing variation of mol% uptake with fibre loading for toluene and n-hexane](image)

(a) Toluene  
(b) n-Hexane

Figure 6.3 Effect of fibre loading and bonding agent on equilibrium sorption of NR/isora composites cured at 100°C

6.3.1.3 Correlation with adhesion.

Table 6.2 gives the change in volume fraction of the rubber due to swelling (\(V_t\)) for
vulcanizates containing different loadings of fibre for both systems. It is evident that the composites containing bonding agent have substantially lower ($V_c$) values than those without bonding agent. It was reported that the adhesion between rubber and fibres could be evaluated by restricted equilibrium swelling measurements. With the increase in extent of adhesion between rubber and fibre, the factor $V_c$ decreases [11]. A high resistance to swelling indicates superior bonding.

Table 6.2 Change in the volume fraction of rubber due to swelling for the composites cured at 100°C and 150°C

<table>
<thead>
<tr>
<th>Composites</th>
<th>Ratio of the change in volume fraction of rubber due to swelling [$V_c$]</th>
<th>Toluene</th>
<th>n-Hexane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Curing temp</td>
<td>100°C</td>
<td>150°C</td>
</tr>
<tr>
<td>GUM</td>
<td></td>
<td>0.94</td>
<td>1.09</td>
</tr>
<tr>
<td>X10</td>
<td></td>
<td>0.89</td>
<td>0.93</td>
</tr>
<tr>
<td>X20</td>
<td></td>
<td>0.83</td>
<td>0.87</td>
</tr>
<tr>
<td>X30</td>
<td></td>
<td>0.79</td>
<td>0.83</td>
</tr>
<tr>
<td>X40</td>
<td></td>
<td>0.76</td>
<td>0.80</td>
</tr>
<tr>
<td>X50</td>
<td></td>
<td>0.85</td>
<td>0.89</td>
</tr>
<tr>
<td>X50b</td>
<td></td>
<td>0.73</td>
<td>0.85</td>
</tr>
<tr>
<td>X30b</td>
<td></td>
<td>0.65</td>
<td>0.73</td>
</tr>
<tr>
<td>X40b</td>
<td></td>
<td>0.55</td>
<td>0.70</td>
</tr>
<tr>
<td>Y30</td>
<td></td>
<td>0.69</td>
<td>0.76</td>
</tr>
<tr>
<td>Y30b</td>
<td></td>
<td>0.55</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Figures 6.4 (a) and (b) give the sorption curves obtained by plotting $Q_t$ (the mol% uptake of the solvent) versus square root of time in toluene for a 30 phr loaded fibre.
composite cured at 100°C and 150°C respectively. The uptake of the solvent is less in the case of composite cured at 100°C, which shows the better interfacial bonding for low temperature cured samples.

![Equilibrium sorption curves of the vulcanizates in toluene at 25°C](image)

(a) Cured at 100°C  
(b) Cured at 150°C

Figure 6.4  Equilibrium sorption curves of the vulcanizates in toluene at 25°C

At the same fibre loading, the amount of solvent sorbed by a composite at equilibrium is less for the composite containing bonding agent compared to that without bonding agent. Another interesting observation is that the initial rates of diffusion is fast for the composite without bonding agent which is more pronounced in the case of composite cured at 150°C. This is because of the fact that in unbonded fibre rubber composites the solvent can penetrate into the polymer along the thickness direction and also through the weak interfaces parallel and perpendicular to the fibre orientation. The initial driving force for swelling is higher in unbonded composites as a result of large
number of voids at the interface. But in the case of composites with bonding agent the interface is strong and the liquid can penetrate into the polymer only through the space between the fibre ends. As a result, the diffusion rate is slow in composites with good bonding. The same observations have also been reported in the case of sisal rubber composites [4]. The uptake of aliphatic solvent is less than that of aromatic solvent. Normal hexane, which is puckered in nature, avails greater surface area than toluene, which is planar. Hence it is difficult for hexane to penetrate into the composite than toluene with the result that the solvent uptake is less for hexane.

6.3.1.4 Effect of chemical treatment
The effect of chemical treatment of fibre on equilibrium swelling of the composites is given in figures 6.2 and 6.4. It is observed that in composites containing treated fibres, the solvent uptake is reduced further, which is due to the enhanced interfacial bonding between the fibre and rubber. This prevents the transport of solvent to some extent through the interface. The effect of chemical treatment on the fibre surface is evident from SEM studies explained in Chapter 3. The fibrillar nature as well as the porosity of the fibre is revealed in the fibre topography. On alkali treatment due to the dissolution of impurities and waxy materials from the surface, the pores become more significant and fibres become thinner than the untreated fibre. This renders roughness to the fibre thereby enhancing the mechanical interlocking at the interface. Thus it is clear that equilibrium liquid uptake can provide information regarding the efficiency of interfacial bonding. On comparing the equilibrium uptake of composites containing treated and untreated isora fibres it can be seen that the former composites are better than the latter in resisting the uptake of both solvents as evident from the figures 6.2 and 6.4

6.3.1.5 Dimensional changes of the composites
The percentage increase in thickness at equilibrium swelling in toluene is shown in Figures 6.5 (a) and (b) for the composites cured at 100°C and 150°C respectively.
It is observed that the change in thickness is higher for the composite containing bonding agent and it increases with fibre loading. In a well-bonded, oriented fibre rubber composite, the swelling is anisotropic. It will swell to a greater extent in the direction perpendicular to the fibre orientation. This is because the oriented fibres will prevent the penetration of the liquid in the direction perpendicular to the flat surfaces of the specimen. Hence the solvent can diffuse into the polymer only through a direction parallel to fibre orientation. Thus swelling was considered to be constrained in one direction and as a result the thickness of the specimen increased considerably. The percentage increase in thickness was found to be higher for the composite cured at higher temperature (150°C) as evident from the figure 6.5. This also accounts for the better reinforcement of the composite cured at lower temperature.

The optical photographs of the unswollen and swollen samples of varying fibre
loadings cured at 100°C in hexane are shown in Figure 6.6

![Image of Optical photographs of the samples cured at 100°C before and after swelling in n-hexane at 25°C](image)

**Figure 6.6** Optical photographs of the samples cured at 100°C before and after swelling in n-hexane at 25°C

From the figure it is clear that as fibre loading increases, the diameter of the swollen samples decreases. At the same fibre loading [30phr] the diameter of the bonded composite is lower than that of the unbonded composite as evident from the figure 6.6. From this it is clear that in highly bonded composites swelling occurs predominantly in the thickness direction. Thus the restricted equilibrium swelling can be used to measure the extent of interfacial bonding between the fibre and rubber.

### 6.3.2 Swelling of isora/NR composites in oils used in automobiles

#### 6.3.2.1 Effect of fibre loading and bonding agent

Figures 6.7 (a) and (b) give the variation of % swelling index with fibre loading for the composites cured at low temperature (100°C) in fuels like petrol and diesel. It is clear that as fibre loading increases, equilibrium solvent uptake decreases. These observations are similar to those obtained in the case of organic solvents like toluene and hexane. Also for the composites containing bonding agent there is a sharp decrease in the uptake of solvents. Here also a highly bonded system would exhibit high resistance to swelling compared to the unbonded systems.
Figure 6.7 Variation of the % swelling index with fibre loading for the composites cured at 100°C in (a) petrol and (b) diesel.

Figure 6.8 Variation of the % swelling index with fibre loading for the composites cured at 100°C in lubricating oil at 27°C and 70°C.
The effect of fibre loading and bonding agent on the swelling index of the composites in lubricating oil at different temperatures is given in Figure 6.8. Here also as fibre loading increases the swelling in oil decreases. At room temperature the composites show greater resistance to swelling. As temperature increases the swelling in oil increased. At higher temperature the viscosity of the oil decreases, the molecules are free to move and can very well penetrate into the composite. The presence of bonding agent in the composites restricts the swelling considerably due to the strong interfacial adhesion. Maximum uptake of solvent was observed with petrol followed by diesel and then lubricating oil. The low molecular weight hydrocarbons present in petrol can easily penetrate into the material. As the molecular size increases as in diesel and lubricating oil, the uptake of oil decreases. This may be due to the larger size of solvent molecule that hinders the molecule from entering into the voids or solvent pockets present in the composite.

<table>
<thead>
<tr>
<th>Mixes</th>
<th>Petrol</th>
<th>Diesel</th>
<th>Lubricating oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gum</td>
<td>3.46</td>
<td>1.93</td>
<td>0.808</td>
</tr>
<tr>
<td>X_{10}</td>
<td>2.71</td>
<td>1.65</td>
<td>0.626</td>
</tr>
<tr>
<td>X_{10b}</td>
<td>2.57</td>
<td>1.28</td>
<td>0.561</td>
</tr>
<tr>
<td>X_{20}</td>
<td>2.58</td>
<td>1.35</td>
<td>0.540</td>
</tr>
<tr>
<td>X_{20b}</td>
<td>2.32</td>
<td>1.11</td>
<td>0.423</td>
</tr>
<tr>
<td>X_{30}</td>
<td>2.42</td>
<td>1.09</td>
<td>0.451</td>
</tr>
<tr>
<td>X_{30b}</td>
<td>2.31</td>
<td>1.02</td>
<td>0.387</td>
</tr>
<tr>
<td>X_{40}</td>
<td>2.41</td>
<td>0.96</td>
<td>0.41</td>
</tr>
<tr>
<td>X_{40b}</td>
<td>1.91</td>
<td>0.88</td>
<td>0.369</td>
</tr>
<tr>
<td>Y_{30}</td>
<td>2.12</td>
<td>1.01</td>
<td>0.411</td>
</tr>
<tr>
<td>Y_{30b}</td>
<td>1.95</td>
<td>0.90</td>
<td>0.379</td>
</tr>
</tbody>
</table>

Table 6.3 Swelling coefficient of the mixes in various oils
It was reported that the liquid uptake increases as the molecular size increases and reaches a maximum value and then decreases [19]. The swelling coefficient of the mixes in various oils is given in Table 6.3. It is clear that mixes with bonding agent have comparatively low values than the unbonded ones, which is due to the improved interfacial bonding between fibre and rubber.

6.3.2.2 Effect of chemical treatment

![Swelling Index Comparison](image)

**Figure 6.9** Comparison of the % swelling index for the composite containing untreated and alkali treated fibres in lubricating oil

The effect of chemical treatment of fibres on equilibrium swelling of the composites in various oils can also be evident from the figures 6.9 and 6.10. It is observed that in composites containing treated fibre, the solvent uptake is reduced further, which is due to the enhanced interfacial bonding between the fibre and rubber. This prevents the transport of solvent to some extent through the interface.
Equilibrium swelling studies

Figure 6.10 Comparison of the % swelling index for the composite containing untreated and alkali treated fibres in (a) petrol and (b) diesel

Thus it is clear that equilibrium liquid uptake can provide information regarding the efficiency of interfacial bonding. On comparing the solvent uptake of composites containing chemically modified fibres with that of untreated ones it can be seen that the former composites are better than the latter in resisting the uptake of solvents/oils as evident from the figures 6.9 and 6.10.

6.3.2.3 Dimensional changes of composites

The percentage increase in thickness at equilibrium swelling for the composites cured at 100°C in petrol and diesel are shown in figures 6.11(a) and (b). Here also as in the case of toluene the change in thickness is higher for the composite with bonding agent and it increases marginally with fibre loading.
Gum vulcanizates showed lower swelling in the thickness direction due to the sharp alignment of molecules in a particular direction during the milling and moulding operations. Anisotropic swelling becomes more pronounced when fibre is incorporated. At higher loadings the increase in thickness in both composites (bonded/unbonded) is comparable. The number of fibres in unit volume increases and penetrant molecule finds it more difficult to diffuse into the polymer and therefore entire swelling will take place in the thickness direction. At low fibre loadings, the penetrant can enter into the matrix both in the direction parallel and perpendicular to the fibre orientation. When bonding is poor, the matrix swells both in diameter and thickness directions. As a result, at low loading and also in the absence of bonding agent, the net swelling took place in the thickness direction is less. Although during
Equilibrium swelling studies

swelling dimensional changes are shown by both bonded and unbonded composites, the effect is more pronounced in the case of composite with bonding agent especially at low fibre loadings. In diesel the percentage increase in thickness is less compared to that of petrol. The penetration of large hydrocarbon molecules in diesel is difficult and hence increase in thickness is less.

Optical photographs of samples cured at 100°C for varying fibre loadings before and after swelling in petrol are shown in figure 6.12.

![Optical photographs of samples cured at 100°C for varying fibre loadings before and after swelling in petrol](image)

Figure 6.12 Optical photographs of the samples of varying fibre loadings before and after swelling in petrol

From the figure it is clear that as fibre loading increases the diameter of the swollen samples decreases. At the same fibre loading [30phr] the diameter of the bonded composite is lower than that of the unbonded composite as evident from figure 6.13. From this it is evident that in unbonded composites swelling occurs predominantly in the thickness direction.
Chapter 6

Figure 6.13 Optical photographs of the samples with and without bonding agent before and after swelling in petrol.

Figure 6.14 Optical photographs of the samples of varying fibre loadings after swelling in diesel.
In diesel, the diameter of the samples at equilibrium swelling is found to be less affected when compared to that swelling in petrol and shows a slight decrease with increase in volume loading of the fibre. At higher loading in the case of bonded composites, the swelling is restricted and take place mostly in the thickness direction as evident from figure 6.11(b). Thus the restricted equilibrium swelling can be used to measure the extent of interfacial bonding between the fibre and rubber.

6.4 CONCLUSIONS
Equilibrium swelling observed in isora fibre reinforced natural rubber is lower for the composite cured at 100°C compared to that cured at 150°C in solvents like toluene and hexane. The uptake of aromatic solvent is higher than aliphatic solvent for the composites. Maximum uptake was observed with petrol followed by diesel and then lubricating oil.

Increased fibre content resulted in reduced swelling. The % swelling index and swelling coefficient are substantially low for composites with bonding agent. Composites containing alkali treated fibre absorbed less solvent compared to those with untreated fibre indicating that alkali treatment improves the adhesion between fibre and rubber. At higher fibre loadings swelling predominantly took place in the thickness direction.
Chapter 6

6.5 REFERENCES