Effects of Carbon black and Silica Fillers on Liquid Transport through SBR / EVA Blends

Summary

The transport characteristics of SBR/EVA blends loaded with black filler (ISAF) have been compared with those of a white filler (silica, Ultrasil VN3) loaded blends. The penetrants used are petrol, kerosene and diesel. The blends have been vulcanized by DCP. The silica incorporated blends have been found to sorb higher amount of the fuels compared to the ISAF filled systems. However, the difference between the equilibrium sorption values of carbon black and silica loaded blends have been found to be decreased with increase in EVA content of the matrix. For pure EVA, silica loading gives better solvent resistance than carbon black filling. The cure characteristics, swelling coefficient, diffusion coefficient and crosslink density have been computed to complement the experimental results.
Chapter 7  Effects of Carbon black and Silica Fillers on Liquid Transport through SBR/EVA Blend

7.1 Introduction
Reinforcing fillers such as silica and carbon black have a significant influence upon the properties of an elastomer, often increasing its mechanical durability and elastic properties, and modifying the sorption and permeability of diffusants through it. [1]. Excellent reports on the interaction of carbon black and silica filler reinforced polymer blends with solvents exist in literature. For example, Ismail et al.[2] studied the effect of filler loading on the cure time (t90) and swelling behaviour of standard Malaysian rubber/epoxide natural rubber (SMR L/ENR 25) and standard Malaysian rubber/styrene butadiene rubber (SMR L/SBR) blends, using carbon black (N 330), silica (Vulcasil C) and calcium carbonate. They found that for SMR L/ENR 25 blends, the t90 decreased with increase in carbon black loading, whereas the silica loaded systems showed an increasing trend. The calcium carbonate filled blends also exhibited a decreasing trend for the t90 with increase in filler loading. The percentage swelling in toluene and ASTM oil No. 3 decreased for both the blends (SMR L/ENR 25 and SMR L/SBR) with increase in filler loading; calcium carbonate system giving the highest swelling value, followed by silica and carbon black filled blends. Sirisinha et al.[3] investigated the phase morphology and oil resistance of 20/80 NR/NBR blends filled with different black fillers viz. N220, N330 and N660 and with non-black reinforcing fillers viz. precipitated and silane treated silica. The results revealed that the addition of filler, either carbon black or silica, to the blends caused a decrease in the dispersed phase (NR) size. It was also
found that silica filled blends showed lower resistance to oil than the carbon black loaded ones. The effect of silica filler on a foam of EPDM/water-swellable rubber (WSR) has been investigated by Sun et al. [4]. The silica filler has been found to accelerate the rate of swelling of the foam in water. The reinforcing ability and the increased solvent resistance by different fillers, for various polymeric systems, have been studied by several other researchers also [5-8].

The present work compares the effects of two fillers viz. intermediate super abrasion furnace (ISAF) and silica (SiO₂), of same loading, on the sorption and diffusion properties of SBR/EVA blends, vulcanized by DCP. The swelling coefficient, diffusion coefficient and crosslink density have been calculated to support the experimental observations.

7.2 Results and Discussion

7.2.1 Effect of ISAF Black on the Transport Behaviour of Pure SBR and EVA

Figure 7.1 shows the sorption behaviour of pure SBR, pure EVA, 30 phr ISAF loaded SBR and 30 phr of ISAF loaded EVA. The penetrant used was petrol. It has been found that the EVA matrix exhibits higher equilibrium sorption compared to the SBR matrix, unlike the behaviour in the other organic solvents such as aliphatic, chlorinated and aromatic hydrocarbons, as discussed in the previous chapters. 3, 4 and 5. Petrol, with a higher iso-octane content, unlike the individual straight chain hydrocarbons, can cause a plasticization effect on EVA. Due to plasticization the crystallites can undergo defolding to generate more free volume. This accounts for
the higher penetrant transport through EVA matrix. A similar trend has been shown by diesel and kerosene. On loading with ISAF black filler, $Q_o$ values of SBR and EVA matrices have been reduced significantly. This can be accounted in terms of the reinforcement of the filler particles within SBR and EVA matrices. However, the percentage reduction has been found to be higher for SBR/ISAF systems.

![Bar Chart](image.jpg)

**Figure 7.1 Effect of ISAF black on pure SBR and EVA**

### 7.2.2 Effect of Silica on the Transport Behaviour of Pure SBR and EVA

Figure 7.2 shows the effect of silica on the sorption behaviour of pure SBR and EVA matrices. A sharp increase in the equilibrium sorption uptake has been observed when the SBR matrix was loaded with silica. However, the filled EVA matrix shows a reduction in the solvent uptake. The polar nature of the silica particles accounts for the difference in the sorption behaviour exhibited by the silica filled matrices. The surface of silica is polar due to siloxane and silanol groups as
shown in Figure 7.3. Since the reinforcement of the polar silica with the non-polar SBR matrix is poor, a higher $Q_e$ value has been observed compared to the unfilled sample. The polar silica particles can form aggregates of different sizes (filler-filler interaction) which may get distributed in a non-polar matrix non-uniformly. The filled EVA samples, however, has been found to exhibit a lower $Q_e$ value due to the better reinforcement of polar silica particles into the polar matrix.

![Equilibrium solvent uptake](image1)

**Figure 7.2** Effect of silica on the sorption behaviour of pure SBR and EVA

![Surface chemistry of silica](image2)

**Figure 7.3** Surface chemistry of silica
7.2.3 Effect of Fillers on Cure Properties of SBR/EVA Blends

SBR/EVA blends were incorporated with varying amounts of silica and ISAF black to study the cure characteristics. Figure 7.4 shows the optimum cure time \( t_{90} \) of 40/60 SBR/EVA blends containing 10, 20 and 30 phr of silica and ISAF black. The \( t_{90} \) value of the blend decreases upon filler incorporation, for both the silica and ISAF black filled systems. The \( t_{90} \) has been found to be higher for ISAF filled matrix than the silica filled one.

![Figure 7.4 Optimum cure time \( t_{90} \) of 40/60 SBR/EVA with 10, 20 and 30 phr of silica and ISAF black](image)

7.2.4 Effect of Fillers on the Transport Properties of SBR/EVA Blends

Figure 7.5 shows the sorption curves of unfilled 40/60 SBR/EVA blend and blends reinforced with 30 phr of ISAF and silica. It has been found that the loading of the matrices with carbon black and silica reduces the \( Q_t \) values. The carbon black
samples take lesser amount of solvent compared to the silica filled samples. The lower $Q_t$ value exhibited by the black incorporated blend, compared to the white filler system, can be attributed to the heterogeneity of the blends.

The difference in the equilibrium solvent uptake exhibited by ISAF black and silica filled blends can be justified from the surface morphology as shown in Figures 7.6 (a) and (b). It has been found that ISAF filled blend is more uniform than the silica filled one. This accounts for the observed solvent uptake behaviour of the blends reinforced with the two fillers.

![Sorption curves of 40/60/SBR/EVA and 40/60/30 SBR/EVA loaded with 30 phr of silica and ISAF black, in petrol](image.png)
Figure 7.6  SEM of (a) 40/60/30 SBR/EVA/ISAF black (b) 40/60/30 SBR/EVA/silica

7.2.5 Effect of Blend Ratio

Figure 7.7 shows the mole percent uptake of kerosene by the different SBR/EVA blends, reinforced with 30 phr of ISAF and silica. It has been found that the silica filled blends sorb higher amount of solvent than black loaded systems for all blend ratios. However, the difference between the $Q_\infty$ values of carbon black loaded system and those of silica filled blends, decrease with increase in EVA content in the blends. This can be attributed to the high interaction between silica particles and EVA. The polar groups of silica can interact with the polar groups of EVA to reduce the free volume.
Figure 7.7  Mole % uptake of kerosene by SBR/EVA blends reinforced with ISAF and silica

7.2.6 Swelling Coefficient

In order to assess the extent of the swelling behaviour of the blends reinforced with ISAF and silica, the swelling coefficients were calculated by the following equation [10]:

$$\alpha = \frac{w_2 - w_1}{w_1} \times \rho_s^{-1}$$ .......................... 7.1

where $w_1$ and $w_2$ are the weights of the samples before swelling and at equilibrium swelling and $\rho_s$ is the density of the solvent. Table 7.1 shows the swelling coefficient values of different filled blends in petrol and kerosene. The ISAF filled blends show lower swelling coefficient values, particularly when the SBR content in the blends is higher. However, the values gradually increase with increase in EVA content. The silica filled samples exhibit a reverse trend for the swelling coefficient values.
Table 7.1 Values of swelling coefficient

<table>
<thead>
<tr>
<th>SBR/EVA</th>
<th>ISAF (30 phr)</th>
<th>Silica (30 phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Petrol</td>
<td>Kerosene</td>
</tr>
<tr>
<td>100/0</td>
<td>0.3805</td>
<td>0.0555</td>
</tr>
<tr>
<td>80/20</td>
<td>0.5651</td>
<td>0.0845</td>
</tr>
<tr>
<td>60/40</td>
<td>0.6845</td>
<td>0.1453</td>
</tr>
<tr>
<td>40/60</td>
<td>0.7746</td>
<td>0.2308</td>
</tr>
<tr>
<td>20/80</td>
<td>0.9212</td>
<td>0.3327</td>
</tr>
<tr>
<td>0/100</td>
<td>1.0832</td>
<td>0.4829</td>
</tr>
</tbody>
</table>

7.2.7 Effect of Penetrants

Figure 7.9 shows the sorption curves of 80/20/30 SBR/EVA/silica blends in different solvents viz. petrol, kerosene and diesel. It is clear from the figure that petrol has higher interaction with the matrix compared to the other two penetrants used. The equilibrium solvent uptake is in the order: petrol > kerosene > diesel.

Figure 7.9  Sorption curves of 80/20/30 SBR/EVA/silica blends in petrol, kerosene and diesel at 26 °C
Figure 7.10 presents a comparison of the equilibrium solvent uptake of 80/20 SBR/EVA blends loaded with the same amounts of ISAF black and silica. It follows from the figure that the $Q_\infty$ values decrease with increase in molecular weight of the solvents used.

![Comparison of equilibrium solvent uptake of 80/20 SBR/EVA blends loaded with 30 phr of ISAF black and silica](image)

**Figure 7.10** Comparison of equilibrium solvent uptake of 80/20 SBR/EVA blends loaded with 30 phr of ISAF black and silica

### 7.2.8 Comparison of Crosslink Density

Figure 7.11 shows the comparison of crosslink density of SBR/EVA blends filled with silica and ISAF black fillers, computed as per Equation 5.2. It has been found that the crosslink density is inversely proportional to the solvent uptake value, which is in agreement with the $Q_\infty$ values.
7.2.9 Diffusivity and Permeability

Diffusion of a solvent through a polymer matrix expands the system and thus weakens the molecular interaction between the neighbouring polymer chains. Hence the polymer chains between the crosslinks move freely and the molecular mobility of the network is enhanced by the diffusion of the molecules. The movement of the penetrants through the matrix is significantly controlled by the presence of fillers. The intrinsic diffusion coefficient values for the different blend composition filled with 30 phr of silica, calculated by Equation 3.3, are compiled in Table.7.2. It has been found that $D^*$ values regularly decrease with increase in EVA content in the blends for a given solvent. These values also decrease with increase in the molecular weight of the probe molecules.
Table 7.2 Diffusion coefficient values at 26 °C

<table>
<thead>
<tr>
<th>Sample/silica</th>
<th>$D^* \times 10^6$ (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Petrol</td>
</tr>
<tr>
<td>100/0/30</td>
<td>3.50</td>
</tr>
<tr>
<td>80/20/30</td>
<td>1.75</td>
</tr>
<tr>
<td>60/40/30</td>
<td>1.04</td>
</tr>
<tr>
<td>40/60/30</td>
<td>0.92</td>
</tr>
<tr>
<td>20/80/30</td>
<td>0.62</td>
</tr>
<tr>
<td>0/100/30</td>
<td>0.59</td>
</tr>
</tbody>
</table>

Figure 7.12 shows the variation of $D^*$ and $P$ values of SBR/EVA loaded with 30 phr of silica, with the weight % of EVA in the blends. It has been found that the diffusion coefficient values show a gradual decrease with increase in the EVA content in the blends. This is due to the high tortuosity exhibited by the crystallites of EVA to the penetration of solvent molecules, and also due to the better reinforcement of silica in the blends with higher EVA content. The difference in $D^*$ and $P$ values exhibited by SBR rich blends has been found to be higher than those in the EVA rich blends. This trend can be due to the inversion of EVA from the dispersed to the continuous phase, which leads to a slower diffusion process.
Figure 7.12 Variation of $D^*$ and $P$ values with weight % of EVA in kerosene at 26 °C

7.3 Conclusion

SBR/EVA blends with intermediate superabrasion furnace (ISAF) and those with the same loading of silica (SiO$_2$) have been prepared and their transport characteristics have been compared. It was found that the ISAF filled samples sorbed lower amount of solvents compared to the silica filled ones except for pure EVA which showed better solvent resistance when loaded with silica. This trend has been attributed to the uniform distribution of the polar silica filler within the polar EVA phase. The difference between the equilibrium sorption values of black and white filler loaded blends decreased with increase in EVA content in the matrix. The swelling coefficient, diffusion coefficient, permeation coefficient, and crosslink density were calculated to support the experimental observations.
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References


