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Sorption and diffusion of aromatic hydrocarbons through filled natural rubber

G. Unnikrishnan and Sabu Thomas*
School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills PO, Kottayam, Kerala 686 560, India

and Siby Varghese
Rubber Research Institute of India, Kottayam, Kerala 686 009, India
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The sorption and diffusion of four aromatic hydrocarbons through vulcanized natural rubber filled with high-abrasion furnace black (HAF) and that filled with silica (Ultrasil VN3) at the same loading have been investigated in the temperature range of 28–70°C by conventional weight-gain experiments. The diffusion results have been analysed in terms of the Fickian diffusion equation. The transport behaviour in both types of samples was found to deviate from the regular Fickian trend, which has been explained in terms of the slow relaxation of rubber chains caused by the presence of fillers. The experimental diffusion data have been compared with the theoretical predictions. The variation of diffusion coefficient with concentration of the solvents has been discussed. From the sorption data, the enthalpy and entropy of sorption and the rubber–solvent interaction parameter have been computed. Copyright © 1996 Elsevier Science Ltd.

(Keywords: diffusion; sorption; filled natural rubber)

INTRODUCTION

The durability and mechanical properties of elastomeric networks are considerably improved by using carbon black as well as silica as filling components. The influence of these fillers on the transport characteristics of macromolecular membranes has been of intense interest to scientists for many years. Excellent reports on the effect of fillers on the diffusion and sorption processes exist[1–5]. In general, the presence of an active filler in a polymer matrix reduces the diffusion coefficient because the penetrant molecules have a more tortuous path to negotiate. The effect of interaction between the filler particles and the polymer also is of considerable importance. Kwei and Kumins[6] found that the sorption of chloroform by an epoxy resin was lowered by about 70% when 5% filler was incorporated. Boonstra and Dannenberg[7] presented the equilibrium swelling data of natural rubber and a number of synthetic rubbers in a variety of solvents. They used different types of fillers too. It was observed by them that fillers like carbon black caused a reduction in swelling of the membranes, which is commensurate with the volume loading of the filler. However, the effect was not specific for a particular solvent or elastomer. The non-carbon-black fillers caused a reduction in rubber swelling, which did not depend on the filler loading. Stickney and Mueller[8] studied the kinetics of swelling of carbon-black-filled styrene–butadiene rubber vulcanizates in the presence of isooctane. It was found that, for rubber vulcanizates, diffusivity increased with the concentration of the penetrant. Lawandy and Helaly[9] investigated the diffusion of chloroform in neoprene rubber vulcanizates consisting of different carbon black types and loadings. In this work, they found a decrease in penetration rate with the increase of particle size and a decrease in penetration rate at a higher degree of equilibrium volume swelling. These results were attributed to the wrinkles formed at the surface of the rubber at high equilibrium swelling. Horkay *et al.*[10] studied the effect of silica particles on the elastic and osmotic properties of chemically crosslinked polydimethylsiloxane networks swollen in toluene and compared with the corresponding unfilled gels. The elastic modulus of the filled samples was found to exceed considerably that of the unfilled samples, highlighting the reinforcing effect of silica particles, which behave like additional crosslinks. Though many outstanding works can also be cited from the literature, the influence of fillers on the transport properties through elastomeric membranes still needs additional information due to its industrial and technological importance.

The present work, which forms a part of our efforts to follow the transport behaviour of liquids through different filled elastomer matrices, describes the effect of a black filler (high-abrasion furnace black) and that of a non-black one (silica, Ultrasil VN3), both at the same loading, on the sorption and diffusion of four aromatic hydrocarbons through conventionally vulcanized natural rubber. Emphasis has been placed on following the transport mechanism, the temperature dependence of the transport process and the extent of rubber–solvent interaction.

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* To whom correspondence should be addressed

Table 1 Formulation of the mixes

		Mixes		
Ingredients	Function	Unfilled	Black-filled	Silica-filled
Natural rubber		100.0	100.0	100.0
Stearic acid	Activator system	1.5	1.5	1.5
Zinc oxide		5.0	5.0	5.0
HAF black	Filler		30.0	
Silica (Ultrasil VN3)	Filler		–	30.0
MOR*	Accelerator	0.6	0.6	0.6
Sulfur	Curing agent	2.0	2.0	2.0

* MOR = morpholine benzothiazyl sulfenamide

EXPERIMENTAL

The natural rubber (NR) used was of ISNR-5 grade supplied by the Rubber Research Institute of India, Kottayam. The fillers selected were carbon black (HAF N330; particle size 26–30 nm, surface area 70–90 $m^2 g^{-1}$) and silica (Ultrasil VN3; particle size 18 nm, surface area 210 $m^2 g^{-1}$). The solvents benzene, toluene, *p*-xylene and mesitylene used were distilled twice before use. All other chemicals were of laboratory reagent grade.

The NR samples were vulcanized by conventional vulcanization technique using accelerated sulfur. The formulation of the mixes used is given in *Table 1*. The mixing was done in a two-roll mixing mill (friction ratio 1 : 1.4) at 30°C. The vulcanization behaviour of the samples was studied by a Monsanto rheometer R100. In order to study the effect of cure time on the sorption process, the two types of samples, viz. carbon-black-filled NR and silica-filled NR, were cured for different cure times, i.e. t_{70}, t_{80} and t_{90}, where t_{70}, t_{80} and t_{90} represent the time at which a sample has been cured to 70, 80 and 90% of the maximum rheometric torque respectively. The curing was done on a hydraulic press at 160°C and under a pressure of 25 tonnes.

For diffusion experiments, NR samples reinforced with carbon black or loaded with silica particles were cut into uniform-size circular pieces (diameter = 1.9 cm) using a steel die. The thickness of the samples was measured at several points using a micrometer. Dry weights of the cut samples were taken before immersion into different liquids in air-tight test bottles. After immersion of the samples in the respective liquids, the bottles were placed in a thermostatically controlled oven. The samples were removed from the test bottles at periodic intervals, the wet surfaces dried between filter papers and the samples weighed immediately. They were then placed back into test bottles. The process was continued until equilibrium swelling was achieved. The experiments were conducted at 28, 50 and 70°C. A possible source of error in this method arises during the weighing operation where the sample has to be removed from the bottle. However, since the weighing was done within 30–40 s, the error can be neglected[11].

The results of sorption experiments are expressed as moles of liquid Q_t sorbed by 100 g of NR sample *versus* square root of time. Each value presented in this paper represents an average obtained from at least three experiments.

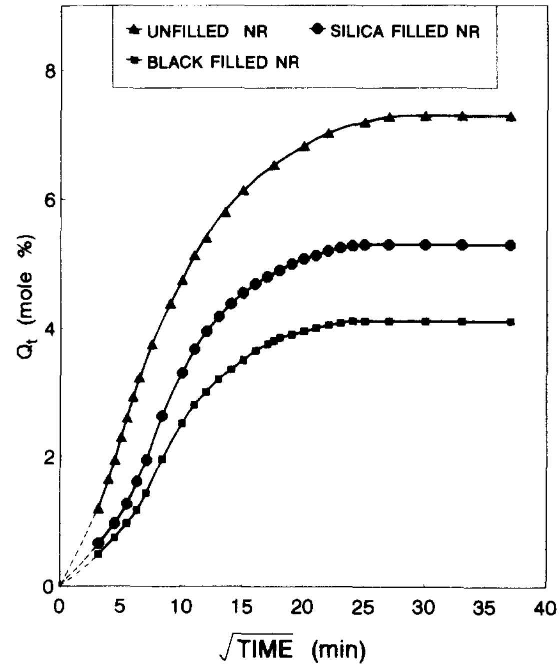

Figure 1 Mole per cent benzene uptake for unfilled, black-filled and silica-filled NR, cured to t_{90}, at 28°C

RESULTS AND DISCUSSION

The sorption curves of gum (unfilled), silica-filled and carbon-black-filled samples are given in *Figure 1*. The samples were cured to t_{90}. It can be seen from the figure that the loading of NR samples with carbon black as well as silica reduces Q_t values. Moreover, the carbon-black-incorporated samples take up a lesser amount of benzene compared to the silica-filled one. The same trend is shown in other solvents such as toluene, *p*-xylene and mesitylene too. The lower Q_t values exhibited by black-incorporated NR compared to the silica-filled one is attributed to the different surface chemistry of these fillers. The carbon black surface is almost non-polar while the surface of silica is polar due to the covering layer of polar silanol groups. Hence it is reasonable to argue that the non-polar carbon black will form stronger contacts with the likewise non-polar rubber than will the silica. On the other hand, the silica particles will prefer each other as interaction partners, especially as solubility forces are strengthened by specific hydrogen bonding. In other words, the carbon black vulcanizates are predominantly characterized by filler–polymer interaction,

Table 2 Values of degree of crosslinking $\nu \times 10^5$ ($\mathrm{mol\,cm^{-3}}$)

	Carbon black			Silica		
Solvent	t_{70}	t_{80}	t_{90}	t_{70}	t_{80}	t_{90}
Benzene	4.80	5.01	5.12	3.49	3.74	3.85
Toluene	5.24	5.45	5.57	3.60	3.83	3.96
p-Xylene	5.37	5.62	5.71	3.85	3.97	4.05
Mesitylene	5.74	5.87	5.95	4.02	4.09	4.17

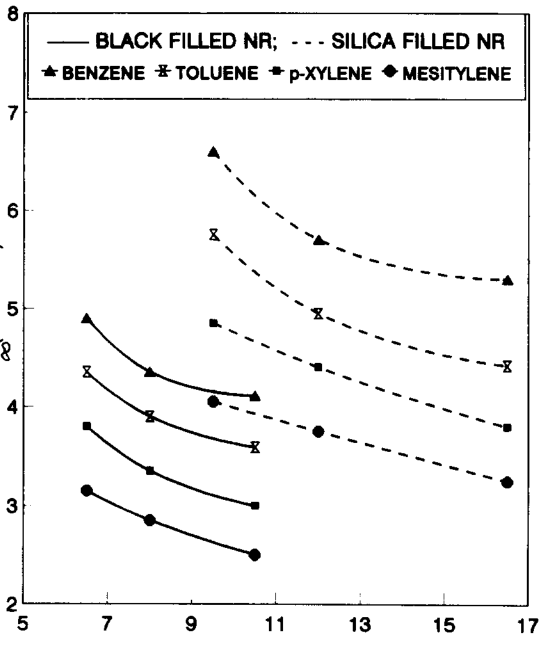

Figure 2 Dependence of maximum equilibrium sorption value (Q_∞) on cure time at 28°C

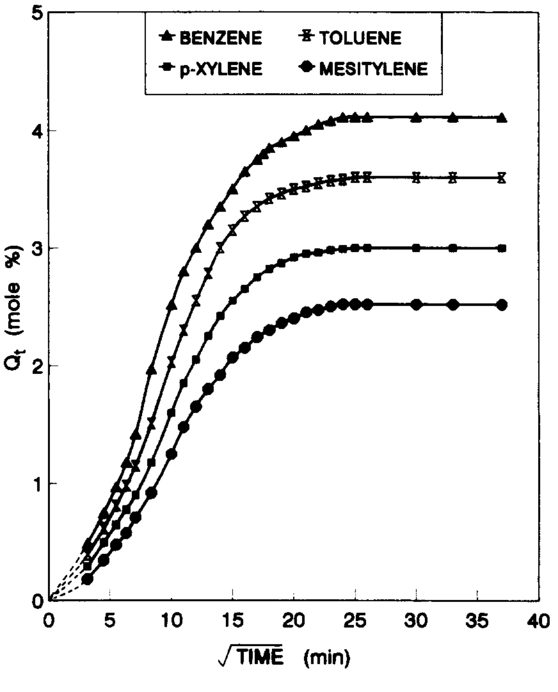

Figure 3 Mole per cent solvent uptake for black-filled NR, cured to t_{90}, at 28°C

while in silica compounds filler–filler interaction is predominant. Owing to the strong filler–polymer interaction the bound rubber[12] content is quite high in carbon-black-loaded rubber. This effectively restricts the mobility of individual polymer chains and thus causes the rubber to exhibit low sorption behaviour. In addition, the accelerator in the rubber mix can be deactivated by the polar surface of silica, leading to ineffective curing of the samples. This results in lower crosslink density of silica-filled samples, which can cause low resistance of the samples towards solvents.

For further confirmation, we have estimated the molar mass, M_c, between crosslinks of NR samples using the Flory–Rehner theory[13]:

$$M_c = \frac{-\rho_p V(\phi)^{1/3}}{\ln(1-\phi)+\phi+\chi\phi^2} \tag{1}$$

where ρ_p is the density of rubber, V is the molar volume of solvent, and ϕ and χ are the volume fraction of rubber in the solvent-swollen sample and the rubber–solvent interaction parameter respectively, obtained as described later. The values of the degree of crosslinking (ν) determined[14] as $1/2M_c$ for different samples are given in *Table 2*. It is evident from the table that the degree of crosslinking is lower for all the silica-filled samples compared to the corresponding HAF-filled ones. This clearly supports our observation of the higher solvent uptake tendency of silica-loaded samples. One surprising point to be noted here is that the values of degree of crosslinking change with the variation of solvents. However, while considering the significance of crosslink density, it is necessary to distinguish between the apparent concentration of physical crosslinks (X_{phys}) and the concentration of chemically discrete crosslinks (X_{chem}) that result directly from vulcanization. Langley[15] has shown that the physical effects and chemical effects are simply additive, and thus $X_{\mathrm{phys}} = X_{\mathrm{chem}} + X_{\mathrm{init}}$, where X_{init} is the initial crosslink density due to entanglements, constraints or other effects not due to chemical changes. This view is supported by Coran and coworkers[16]. Since the rubber chain entanglements can be different in different solvents, the M_c values obtained from Flory–Rehner theory, when applied to a series of rubber–solvent systems, can be regarded as physical crosslink entanglements rather than chemical crosslinks. In other words, the changes in the rubber chain entanglement density in different solvents can probably be the reason for the variation of M_c and ν values with change of solvent. Such variations in M_c values for phase-segrated polyurethane membranes with some halogen-containing solvents have been obtained earlier by Schneider *et al.*[17]. Aminabhavi and coworkers[18] also made similar observations for different polymer–solvent systems.

The influence of cure time on the sorption behaviour of carbon-black- and silica-filled samples is shown in *Figure 2*. For both type of samples, the maximum value of Q_t decreases with increasing cure time. This can be attributed to the increase in the number of effective crosslinks introduced between the rubber chains by the curing agent with increase in cure time. In *Figure 3* the sorption curves of carbon-black-filled NR samples cured to t_{90} in benzene, toluene, *p*-xylene and mesitylene are presented. There is a systematic trend in the sorption

Table 3 Analysis of sorption results of NR–solvent systems

	n						$k \times 10^2$ (min^{-n})					
	Carbon black			Silica			Carbon black			Silica		
Solvent	t_{70}	t_{80}	t_{90}	t_{70}	t_{80}	t_{90}	t_{70}	t_{80}	t_{90}	t_{70}	t_{80}	t_{90}
Benzene	0.68	0.69	0.73	0.64	0.66	0.69	3.10	3.06	3.01	3.23	3.12	3.08
Toluene	0.66	0.67	0.72	0.63	0.64	0.67	3.00	2.98	2.86	3.13	3.08	3.06
p-Xylene	0.65	0.65	0.71	0.61	0.63	0.66	2.61	2.60	2.52	2.88	2.76	2.65
Mesitylene	0.63	0.64	0.69	0.60	0.61	0.63	2.59	2.49	2.38	2.62	2.57	2.46

Table 4 Diffusion coefficients and permeation coefficients of NR–solvent systems

	$D \times 10^7$ (cm^2 s^{-1})						$p \times 10^6$ (cm^2 s^{-1})					
	Carbon black			Silica			Carbon black			Silica		
Solvent	t_{70}	t_{80}	t_{90}	t_{70}	t_{80}	t_{90}	t_{70}	t_{80}	t_{90}	t_{70}	t_{80}	t_{90}
Benzene	7.53	6.97	6.20	8.78	8.62	8.57	2.88	2.36	1.99	4.52	3.83	3.54
Toluene	6.82	6.51	5.64	7.90	7.11	6.98	2.59	2.03	1.80	4.05	3.14	2.88
p-Xylene	5.86	5.12	4.89	6.09	5.46	5.35	2.22	1.73	1.56	3.12	2.41	2.13
Mesitylene	4.97	4.61	4.01	5.14	4.94	4.33	1.87	1.55	1.20	2.50	2.16	1.69

behaviour of the four aromatic hydrocarbons, i.e. with an increase in molecular weight of the penetrant there is a decrease in Q_t values. The same trend is shown by silica-filled samples also in all the solvents.

In order to understand the mechanism of transport through the NR samples, the sorption data have been fitted to the equation[19]:

$$\log(Q_t/Q_\infty) = \log k + n \log t \tag{2}$$

where Q_t and Q_∞ are the mole per cent increase in sorption at time t and at equilibrium respectively; and k is a constant that depends on the structural characteristics of the rubber and gives information about the interaction between rubber and the solvents. For a polymer with slab geometry, a value of $n = 0.5$ indicates the Fickian mode of transport, while $n = 1$ shows case II (relaxation-controlled) transport. Values of n between 0.5 and 1 suggest anomalous transport behaviour. The values of n and k, obtained by least-squares estimations, for our systems are given in *Table 3*. The n values suggest that the transport mechanism in both carbon-black and silica-filled samples deviates from the normal Fickian mode and hence can be classified as anomalous. Deviations from the Fickian sorption are associated with the time taken by the rubber segments to respond to the swelling stress and rearrange themselves to accommodate the solvent molecules. The reinforcement with filler particles imparts a high degree of restriction to the rearrangement of rubber chains and also to the flexibility of polysulfidic crosslinks introduced between rubber chains during conventional vulcanization[11]. Thus the observed anomalous diffusion involves the counteractions between the ability of the rubber segments to rearrange in the presence of solvents and restriction imparted to this by the reinforced filler particles. The deviation has been found to be pronounced in the case of black-loaded samples compared to the corresponding silica-filled ones. It is also observed that there is a regular trend in the values of k, i.e. with an increase in molecular weight of the solvent there is a decrease in the value of k. Moreover, the k values are found to be decreasing with increase in cure time. This indicates the decrease in rubber–solvent interaction with increasing molecular size of penetrant and cure time of rubber. These observations parallel the decrease in the values of sorption equilibrium.

The kinetic parameter, the diffusion coefficient or diffusivity D, for the different NR–penetrant systems was calculated using the equation[20]:

$$D = \pi(h\Theta/4Q_\infty)^2 \tag{3}$$

where h is the initial sample thickness, Θ is the slope of the linear portion of the sorption curves before attainment of 50% equilibrium and Q_∞ has the same meaning as in equation (2). The values of D for different systems are given in *Table 4*. It is clear from the table that the D values are higher for silica-filled samples in given penetrant compared to the corresponding black-loaded ones. Again, it is seen that the D values decrease with increase in cure time, for both black-filled and silica-loaded rubber. In addition, the D values are found to decrease with increase in the molecular weight of the penetrants for a given sample.

The D values determined using equation (3) are incorporated into the following equation to generate theoretical sorption curves[21,22]:

$$\frac{Q_t}{Q_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-D(2n+1)^2\pi^2 t}{h^2}\right) \tag{4}$$

where Q_t, Q_∞, t and h have the same meanings as before. This equation describes the Fickian mode of transport. The experimental sorption curves for carbon-black- and silica-loaded samples cured to t_{90} in *p*-xylene are compared with the theoretical curves in *Figures 4a* and *4b*. The overall agreement between the experimental and theoretical plots is not so good, which also suggests the deviation of the transport mechanism from the normal Fickian mode in both samples.

In order to see the dependence of diffusion coefficient values on the concentration of the solvents, the slight sigmoidal sorption rate curves were analysed by the

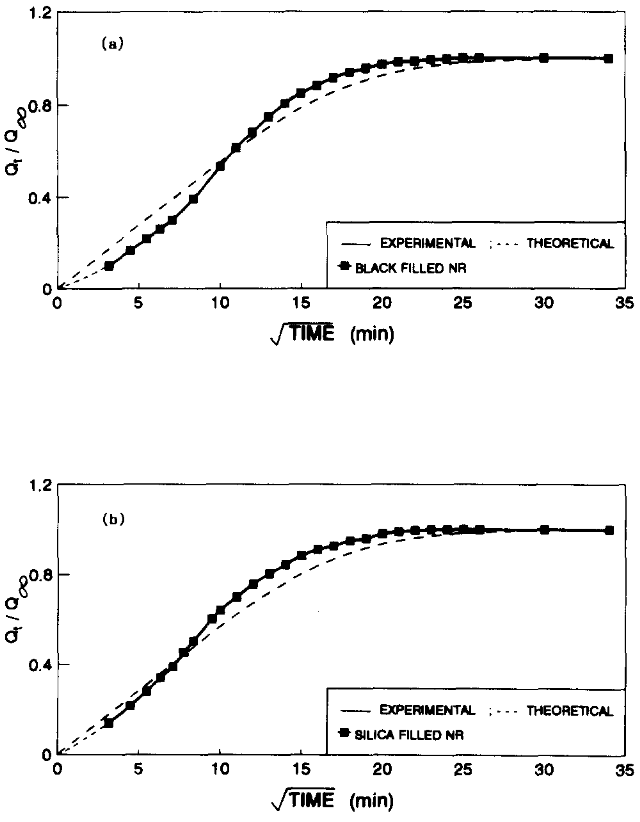

Figure 4 Comparison between experimental and theoretical sorption curves for NR, cured to t_{90}, in *p*-xylene: (a) black; (b) silica

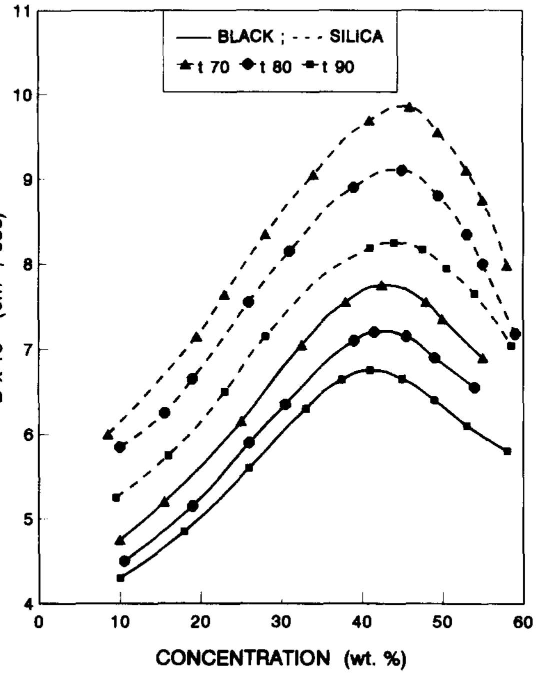

Figure 5 Diffusion coefficient *versus* concentration for black-filled and silica-filled NR, with different cure time, in toluene at 28°C

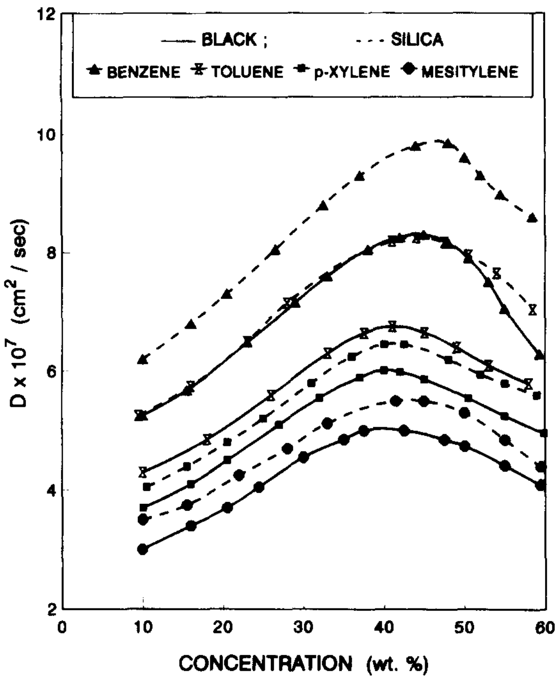

Figure 6 Diffusion coefficient *versus* concentration for black-filled and silica-filled NR, cured to t_{90}, in various solvents at 28°C

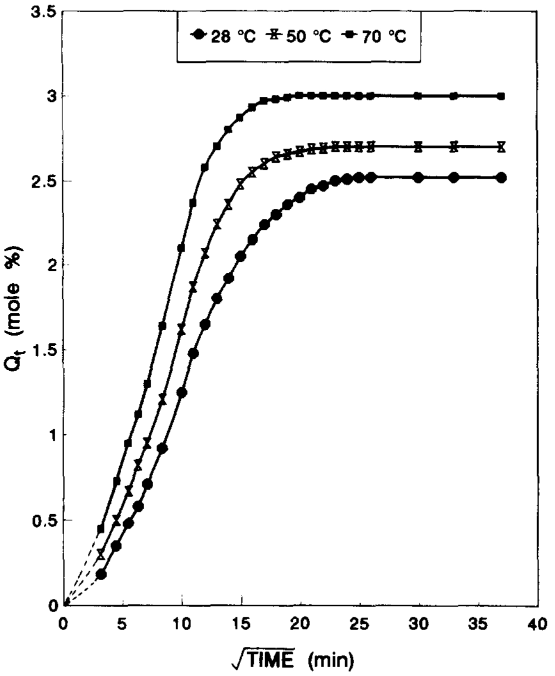

Figure 7 Temperature dependence of mole per cent sorption for black-filled NR, cured to t_{90}, in mesitylene

Joshi–Astarita model[23] where the model parameters were varied incrementally over a prescribed range and the fit to the experimental data was subjected to a least-squares test to select the best set of values. The D values resulting from equation (3), ignoring the initial slight curvature for both carbon-black- and silica-loaded samples, in different solvents are presented in *Figures 5* and *6*. The D values go through maxima with concentration, and the results from this analysis are found to be only slightly higher than those obtained from equation (3).

The transport process of small molecules through rubbery polymers involves a solution–diffusion mechanism and hence the permeability or permeation coefficient P is the product of diffusivity D and solubility S (i.e. $P = DS$). The S values are taken as grams of liquid sorbed per gram of rubber. The values of P computed for different NR–penetrant systems are also given in *Table 4*. The permeability values also are found to follow the same trend as that of diffusivity.

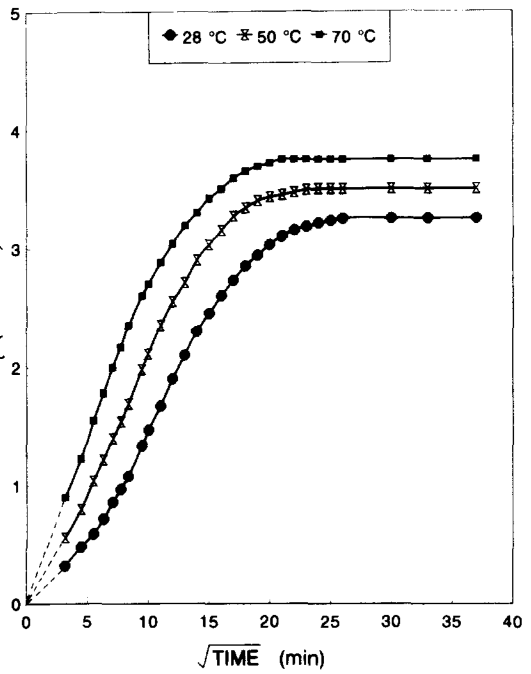

Figure 8 Temperature dependence of mole per cent sorption for silica-filled NR, cured to t_{90}, in mesitylene

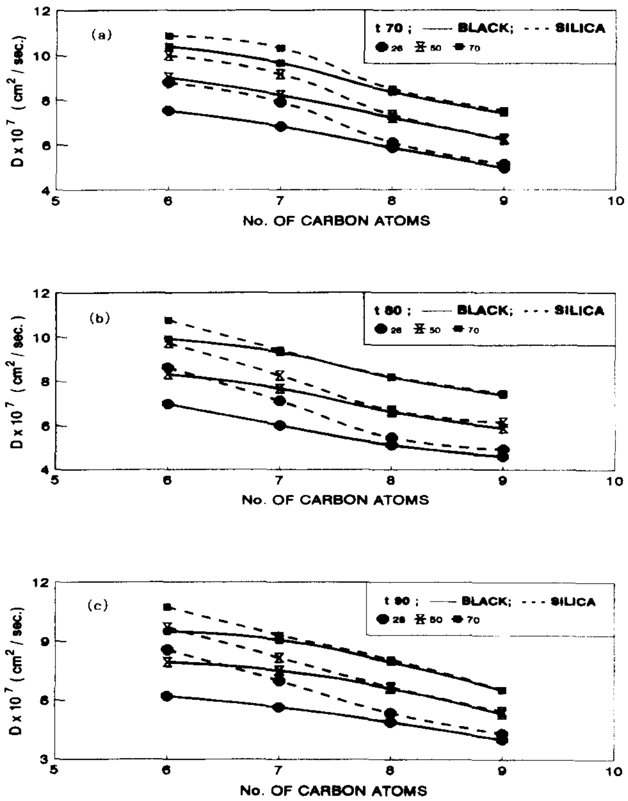

Figure 9 Dependence of diffusion coefficient on number of carbon atoms of aromatic hydrocarbons for NR cured to (a) t_{70}, (b) t_{80} and (c) t_{90} at 28, 50 and 70°C

The influence of temperature on black-filled and silica-filled NR can be followed from *Figures 7* and *8* respectively. The solvent used was mesitylene. It can be seen from the figures that temperature considerably activates the diffusion process in both cases. The change in the diffusivity values with temperature for both carbon-black- and silica-loaded samples in different solvents can be followed from *Figures 9a*, *9b* and *9c*, where the *D* values are plotted as a function of number of carbon atoms of the solvents at different temperatures and cure time.

Table 5 Values of interaction parameter

Solvent	Carbon black t_{70}	Carbon black t_{80}	Carbon black t_{90}	Silica t_{70}	Silica t_{80}	Silica t_{90}
Benzene	0.54	0.56	0.59	0.46	0.47	0.49
Toluene	0.48	0.50	0.53	0.41	0.43	0.46
p-Xylene	0.38	0.42	0.44	0.33	0.34	0.37
Mesitylene	0.37	0.40	0.43	0.28	0.31	0.33

We have calculated the polymer–solvent interaction parameter χ from the variation of volume fraction of rubber in the swollen samples with temperature using the equation[22]:

$$\chi = \frac{(\mathrm{d}\phi/\mathrm{d}T)[\phi/(1-\phi) + N\ln(1-\phi) + N\phi]}{2\phi(\mathrm{d}\phi/\mathrm{d}T) - \phi^2 N(\mathrm{d}\phi/\mathrm{d}T) - \phi^2/T} \tag{5}$$

Here ϕ is the volume fraction of rubber in the swollen sample determined as:

$$\phi = \frac{(d - fw)\rho_\mathrm{p}^{-1}}{(d - fw)\rho_\mathrm{p}^{-1} A_0 \rho_\mathrm{s}^{-1}} \tag{6}$$

where *d* is the weight after drying the sample, *w* is the initial weight of the sample, A_0 is the weight of the absorbed solvent, *f* is the fraction of insoluble components, and ρ_p and ρ_s are the densities of rubber and solvent respectively. *N* for equation (5) is calculated from ϕ as:

$$N = \frac{\phi^{2/3}/3 - 2/3}{\phi^{1/3} - 2\phi/3} \tag{7}$$

Equation (5) was found to be quite satisfactory for determining the χ values of NR samples, cured to different cure times, in a given penetrant, while the usual other equations yield only one χ value for a given rubber–penetrant system irrespective of cure time. The calculated values of χ are given in *Table 5*. It is interesting to note that the χ values are lower for silica-filled samples compared to the corresponding carbon-filled samples in a given penetrant, suggesting higher rubber–solvent interaction in the former case.

From the amount of liquid sorbed by a given mass of rubber, the equilibrium sorption constant K_s has been determined as:

$$K_\mathrm{s} = \frac{\text{number of moles of penetrant sorbed}}{\text{unit mass of the polymer}}$$

Using the values of K_s, the enthalpy ΔH and entropy ΔS of sorption are determined using Van't Hoff's equation:

$$\log K_\mathrm{s} = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \tag{8}$$

The values of ΔH and ΔS are given in *Table 6*. The ΔH values, which are negative in all cases, increase regularly from t_{70} to t_{90} for both black- and silica-filled vulcanizates. The values also exhibit a regular increase from benzene to mesitylene for a given sample. These trends indicate a decreased exothermicity of the sorption

Table 6 Thermodynamic functions ΔH and ΔS

	$-\Delta H$ (kJ mol^{-1})						ΔS (J mol^{-1} K^{-1})					
	Carbon black			Silica			Carbon black			Silica		
Solvent	t_{70}	t_{80}	t_{90}	t_{70}	t_{80}	t_{90}	t_{70}	t_{80}	t_{90}	t_{70}	t_{80}	t_{90}
Benzene	1.21	1.08	0.96	1.91	1.73	1.56	24.01	22.80	21.55	29.12	26.98	24.87
Toluene	1.05	0.93	0.82	1.69	1.54	1.38	21.98	20.73	19.24	26.29	24.74	22.45
p-Xylene	0.81	0.72	0.63	1.48	1.38	1.24	19.04	17.81	16.91	23.89	21.98	20.87
Mesitylene	0.72	0.64	0.56	1.36	1.27	1.14	17.87	15.10	13.82	21.78	20.86	19.14

process with both increase in cure time of rubber and increase in molecular size of solvents. The ΔS values also show a regular trend, i.e. decrease from t_{70} to t_{90}, for both black-loaded and silica-filled samples in a given penetrant. The values also show a regular decrease from benzene to mesitylene for a given sample. These observations clearly indicate that the spontaneity of the sorption process varies inversely with both the cure time of the rubber and the molecular size of the penetrants.

CONCLUSION

In the present work, the transport of four aromatic hydrocarbons through natural rubber filled with carbon black (HAF) or with silica (Ultrasil VN3) at the same loading has been investigated. It was found that the black-incorporated samples sorb a lesser amount of aromatic solvents compared to the silica-filled ones. This has been explained in terms of the high bound rubber content and the crosslink density of black-filled vulcanizates due to high rubber–filler interaction. The mechanism of transport in both black- and silica-loaded natural rubber was found to follow an anomalous trend as indicated by the deviations from the theoretical curves describing Fickian transport. The transport coefficients have been observed to vary inversely with both the cure time of the rubber and the penetrant molecular size. The calculated thermodynamic functions indicated higher rubber–solvent interaction in silica-filled samples than the black-loaded ones, and supported the observation of decrease in equilibrium sorption values with both cure time of rubber and molecular size of penetrants. Since a deep knowledge of the behaviour of natural rubber in aggressive liquid environments is highly essential for its successful applications, the parameters estimated in this work are of practical importance.

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