Diffusion and transport of aromatic hydrocarbons through natural rubber

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The swelling of crosslinked natural rubber in aromatic hydrocarbons was investigated. Natural rubber was vulcanized by four vulcanizing systems, viz. conventional, efficient, dicumyl peroxide, and a mixture consisting of sulfur and dicumyl peroxide. The peroxide-crosslinked system showed the lowest solvent uptake. The effect of different fillers on the swelling nature of crosslinked natural rubber was studied using carbon black and silica fillers. The silica-filled sample took up higher amounts of solvents than carbon-filled sample. The dependence of the diffusion coefficient on crosslinking system, filler, temperature, etc., was also studied. The solvent–polymer interaction parameter was calculated from the diffusion data.

(Keywords: solvent diffusion; natural rubber; vulcanizing systems)

INTRODUCTION

The transport behaviour of organic liquids in polymers has been studied extensively for many years and reviewed by several authors[1–6]. Solvent diffusion in rubbery polymers can generally be described by Fick's laws of diffusion. Glassy polymers, however, because of their time-dependent response, exhibit non-Fickian or anomalous diffusion kinetics[7]. It is well known that the phenomenon of transport through rubbery polymers is controlled by polymer structure, its crosslink density, mode of crosslinking, presence of fillers, penetrant size, temperature, etc. Recently, the swelling characteristics of natural rubber and a number of other polymer membranes in the presence of aromatic hydrocarbon liquids were investigated by Harogoppad *et al.*[8]. In that work, they tried to investigate the dependence of the transport phenomenon on polymer structure. The effect of crosslink density on diffusion has been observed by many researchers. Representative results have been reported by Barrer and coworkers[9,10] for a series of normal and branched alkanes through crosslinked rubbers. For low levels of crosslinking, a linear relationship between the decrease in the diffusion coefficient and crosslink density was found. At high levels of crosslinking, the rate of decrease levels off. The swelling and absorption behaviours of bulk- and solution-crosslinked natural rubber networks were examined by Poh *et al.*[11]. They found that the solution-crosslinked networks swell/absorb more than the corresponding bulk-crosslinked networks having the same crosslink density. A large number of studies have been reported in the literature about the effect of fillers on the sorption behaviour of elastomers[12–14]. Generally, it is observed that the presence of an active filler reduces the extent of equilibrium swelling compared to the corresponding gum sample. The influence of penetrant size on diffusion was described by different workers[15,16], and it is found that the equilibrium sorption of the sorbents decreases linearly with increasing penetrant molecular size. It is also found that temperature activates the phenomenon of diffusion according to the Arrhenius equation[17].

Natural rubber (NR) is a well known polymer that has been widely used in a variety of industrial and engineering areas. The stability of NR in the presence of solvents is extremely important for its successful application. The aim of the present work is to investigate the effect of type of crosslinking system on the phenomenon of diffusion of aromatic hydrocarbons through NR. It also aims to study the effect of different types of filler on the swelling behaviour of NR. The temperature dependence of the diffusion coefficient and the rubber–solvent interaction in terms of the interaction parameter χ have also been presented.

EXPERIMENTAL

The natural rubber (NR) used was of ISNR-5 grade. The solvents benzene, toluene, *p*-xylene and mesitylene were of reagent grade and were distilled twice before use. The carbon black used was HAF (30 nm) and the silica was Hi-Sil (40 nm). All other chemicals were of laboratory reagent grade.

NR was vulcanized by four vulcanizing systems, viz. dicumyl peroxide (DCP), conventional (CV), efficient (EV), and a mixture of sulfur and dicumyl peroxide (mixed system). The formulation used is given in *Table 1*. To study the effect of vulcanizing system on the phenomenon of diffusion, the samples were cured in such a way that

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Table 1 Formulation of the mixes

	Mixes					
Ingredients	A	B	C	D	E	F
Natural rubber	100	100	100	100	100	100
Stearic acid	–	1.5	1.5	1.5	1.5	1.5
Zinc oxide	–	5	5	5	5	5
HAF black	–	–	–		30	–
Silica (Hi-Sil)	–	–	–	–	–	30
MOR[a]	–	0.6	–	0.6	0.6	0.6
TMTD[b]	–	–	1	–	–	–
CBS[c]	–	–	1.5	–	–	–
Dicumyl peroxide	4	–	–	1.5	–	–
Sulfur	–	2	0.6	1.5	2	2

[a] Morpholinebenzothiazyl sulfenamide
[b] Tetramethylthiuram disulfide
[c] *N*-Cyclohexyl-2-benzothiazyl sulfenamide

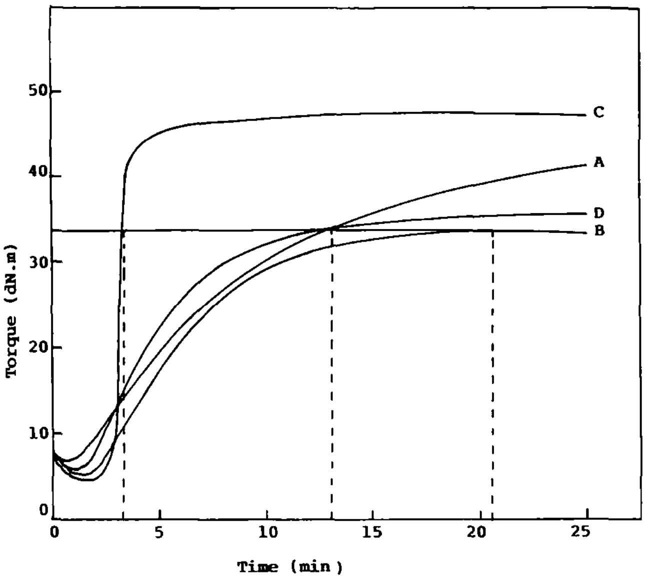


Figure 1 Rheographs of the mixes A, B, C and D

all of them develop the same rheometric torque, 33.8 dN m (*Figure 1*). The cure characteristics of the samples are given in *Table 2*. Since torque is proportional to crosslink density, it is assumed that all the samples have nearly the same crosslink density. However, this assumption is not always true in the absolute sense when we compare samples with different crosslinking systems[18]. Hence we have also used samples cured up to their optimum cure time (t_{90}) for these studies. The influence of different fillers on the diffusion process was followed by curing the filled NR samples to their respective optimum cure time.

For sorption experiments, circular samples were punched out from the vulcanized sheets using a sharp steel die (diameter = 1.9 cm). The thickness of the samples was measured using a micrometer. The samples were then immersed in liquids taken in test bottles, kept at constant temperature, in an air oven. The samples were removed from the bottles at periodic intervals and weighed. They were then placed back into the test bottles. The process was continued until equilibrium swelling was achieved. There is a possible source of error in this method, namely that the sample has to be removed from the solvent for weighing. However, if the sample is placed back into the bottle within 40 s, the error due to the escape of solvent from the sample can be neglected.

The results of sorption experiments were obtained by plotting the mole uptake Q_t of the liquid by 100 g of the polymer against square root of time.

RESULTS AND DISCUSSION

Figures 2 and *3* show the diffusion curves of NR crosslinked with four vulcanizing systems, viz. DCP (mix A of *Table 1*), CV (mix B), EV (mix C) and the mixed system (mix D). The solvents used were benzene and toluene. The experiments were conducted at 28°C. From these figures it is clear that NR crosslinked with the CV system absorbs the highest amount of liquid, whereas that crosslinked using the DCP system takes up the lowest

Table 2 Cure characteristics of the mixes A, B, C and D

Cure properties	A	B	C	D
Minimum torque (dN m)	7.0	5.0	4.5	5.6
Maximum torque (dN m)	44.8	33.8	47.4	36.0
Cure time (min) at 33.8 dN m	13.0	20.5	3.5	13.0
Scorch time (min)	1.8	2.4	2.5	2.0
Optimum cure time (min)	22.0	11.0	3.5	10.0

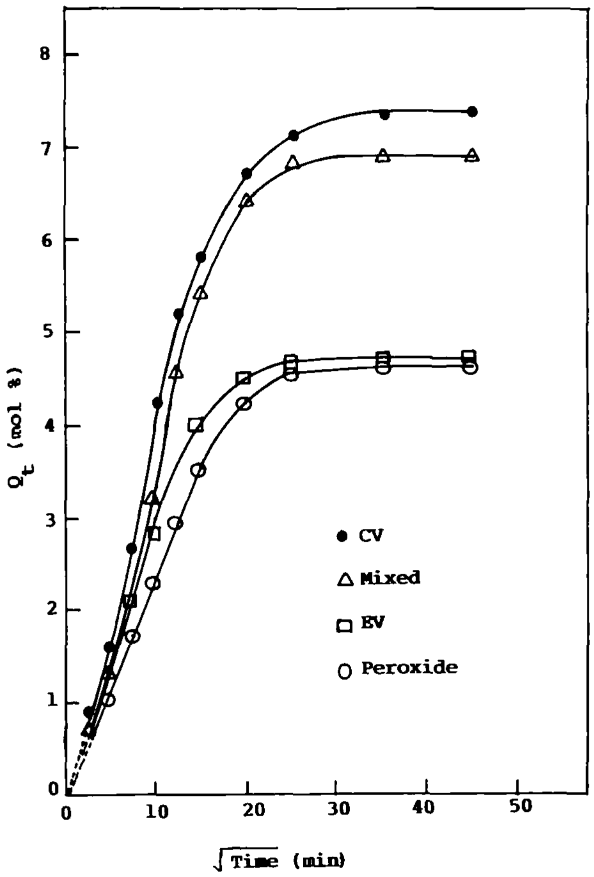


Figure 2 Mole per cent benzene uptake of natural rubber with different crosslinking systems at 28°C (the samples were cured to a torque of 33.8 dN m)

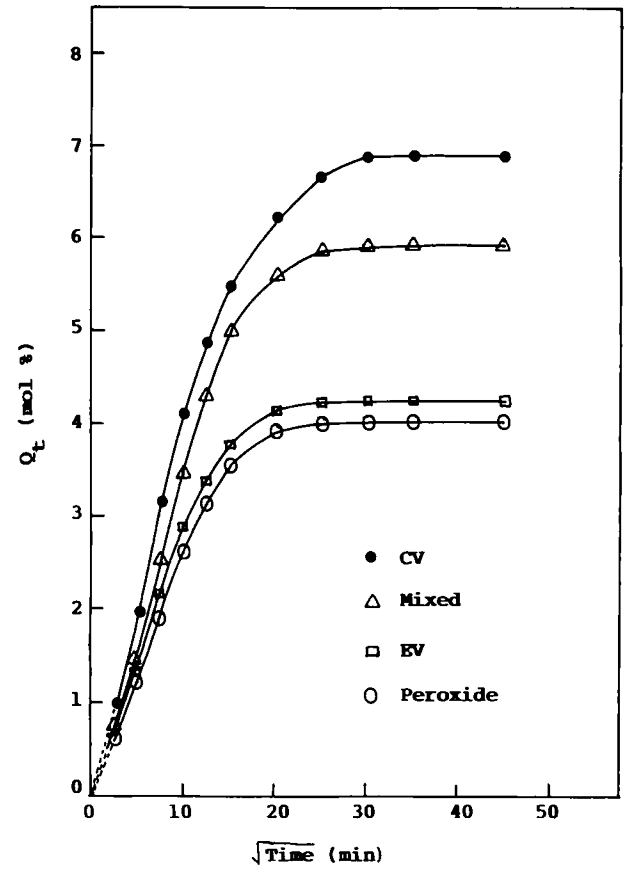


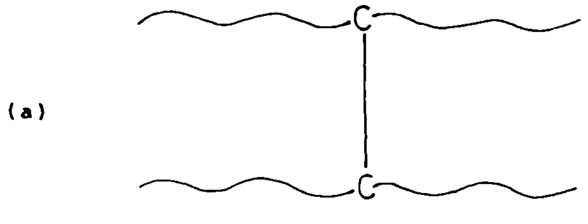
Figure 3 Mole per cent toluene uptake of natural rubber with different crosslinking systems at 28°C (the samples were cured to a torque of 33.8 dN m)

amount. The samples crosslinked by mixed and EV systems take intermediate positions. The difference in the maximum Q_t values of NR with different crosslinking systems may be due to the different types of crosslinks present in them. The structure of the networks formed during vulcanization is depicted in *Figure 4*. The polysulfidic linkages in the CV system impart high chain flexibility to the network. This helps to accommodate more solvent between rubber chains. NR vulcanized with the mixed system also has polysulfidic linkages along with C–C linkages. Hence this system stands second to the CV system in showing the maximum mole per cent uptake value. The EV system contains mainly mono- or disulfidic linkages, which do not make the chains so flexible as do polysulfidic linkages. Therefore, this system shows lower Q_t value compared to CV and mixed systems. The DCP system, having only stable C–C bonds, shows the lowest Q_t values. For the other two aromatic hydrocarbons, namely *p*-xylene and mesitylene, the sorption curves are not presented graphically so as to minimize the number of figures; but the same trend was observed also with them.

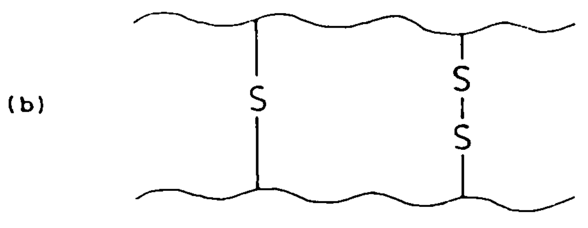
In order to see whether the above trend is shown under other conditions also, we have conducted sorption experiments using samples cured at their optimum cure time (t_{90}). In *Figure 5*, the sorption behaviours of DCP, EV, mixed and CV systems cured up to t_{90} are compared. It is seen that here also the CV system shows the maximum mole per cent uptake. We have also studied the effect of cure time on the phenomenon of diffusion. *Figure 6* shows the effect of cure time on the diffusion process of toluene into the EV system. The rate and maximum mole per cent uptake decrease with increase in the cure time. This is in accordance with our expectation that the rate of diffusion decreases with increase in the crosslink density.

The diffusion curves of different filler-incorporated samples are shown in *Figure 7*. Both the systems were cured by conventional vulcanization (formulation of mixes E and F in *Table 1*) up to t_{90}. Though the loadings of carbon black and silica are the same (30 phr), the carbon-black-incorporated samples absorb a lesser amount of toluene compared to the silica-filled samples. In the case of carbon-filled samples, rubber forms bound rubber[19] with carbon black, which effectively binds the individual polymeric chains. Moreover, since the surface of silica is polar, it can deactivate the accelerator, which leads to the ineffective curing of the sample. Hence the silica-filled sample shows an increased solvent uptake compared to the carbon-filled sample. The volume fraction of rubber in these samples was calculated using the equation:

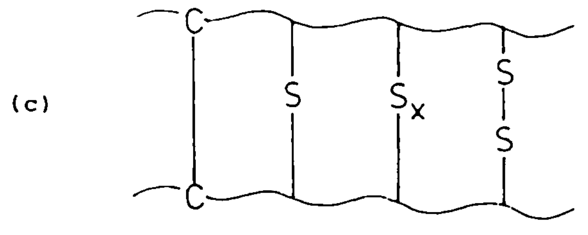
$$\phi=\frac{(d-fw)\rho_r^{-1}}{(d-fw)\rho_r^{-1}+A_0\rho_s^{-1}} \qquad (1)$$



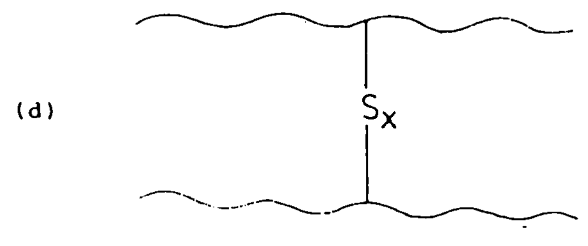
Predominantly C-C linkages



Predominantly mono or disulfidic linkages



Mixed linkages



Predominantly polysulfidic linkages

Figure 4 Structure of the networks formed during vulcanization: (a) peroxide system; (b) EV system; (c) mixed system; (d) CV system

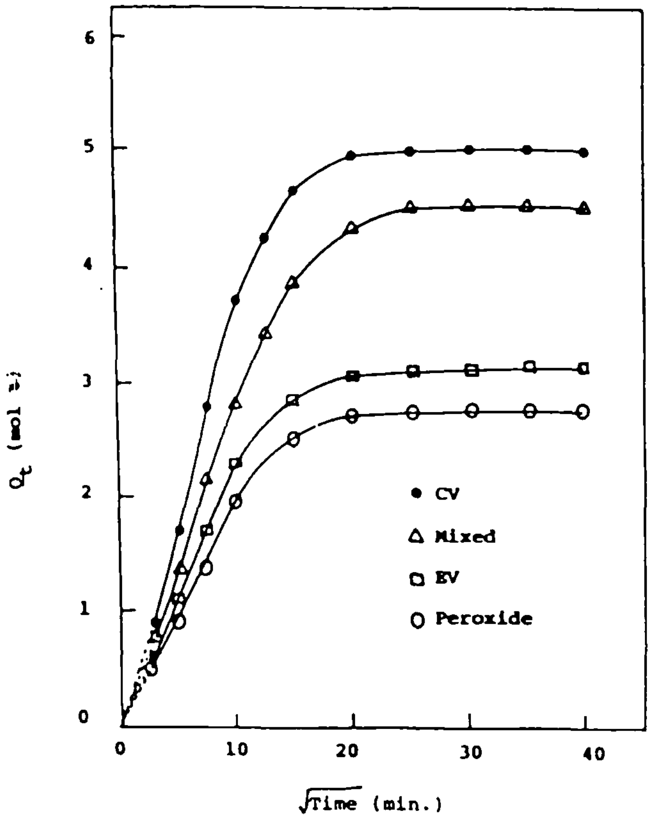


Figure 5 Mole per cent mesitylene uptake of natural rubber, with different crosslinking systems, cured up to t_{90}

where d is the weight after drying out the sample, w is the weight of the swollen sample, A_0 is the weight of the absorbed solvent, f is the fraction of insoluble components, and ρ_r and ρ_s are the densities of rubber and solvent, respectively. In this work the volume fraction of rubber in the carbon-filled sample was found to be 0.2186, while that of the silica-filled sample was 0.1714. Therefore, the lower uptake value of carbon-filled sample is associated with its high crosslink density (high value of ϕ).

There is a systematic trend in the sorption behaviour of liquids of different molecular size. With an increase in the molecular size of the solvent molecules, there is a decrease in the value of Q_t (*Figure 8*) in all the systems. Benzene shows the maximum value of Q_t and mesitylene the minimum, among the solvents used in this work. Toluene and *p*-xylene take intermediate positions. The effect of molecular weight of the solvent on the maximum mole per cent uptake is illustrated in *Figure 9*. It is seen that the values of Q_∞ decrease linearly with increase in the molecular weight of the solvent in all the systems. The values of swelling coefficient (α) were calculated using the equation:

$$\alpha=\frac{M_\infty-M_0}{M_0}\times\frac{1}{\rho_s} \qquad (2)$$

where M_∞ is the mass of the swollen rubber sample (i.e. equilibrium saturation), M_0 is the original mass of the polymer membrane and ρ_s is the solvent density. The values of swelling coefficient are given in *Table 3*. The swelling coefficient values decrease in the order CV > mixed > EV > DCP. It can also be seen that these

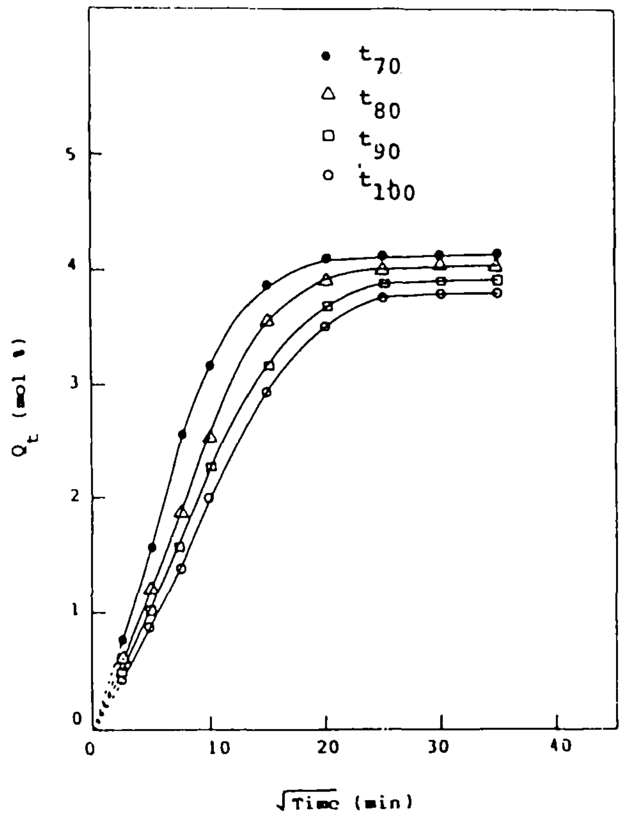


Figure 6 Mole per cent toluene uptake of EV system at different cure times

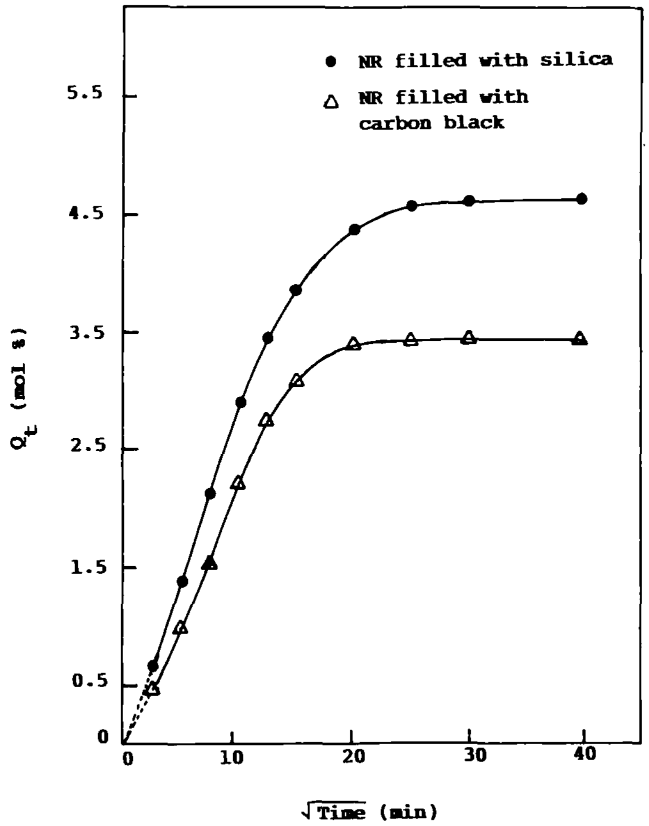


Figure 7 Mole per cent toluene uptake of natural rubber with different fillers, at 28°C

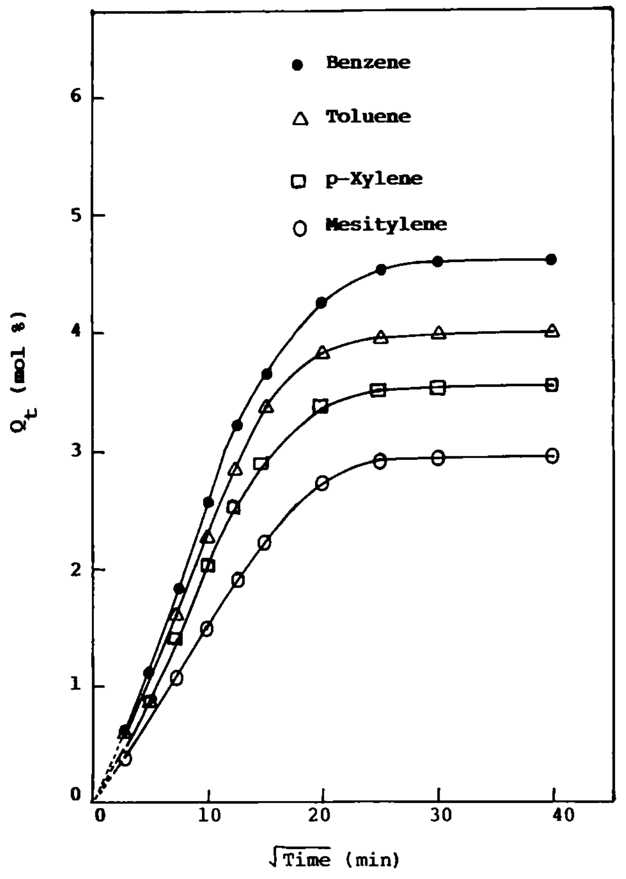


Figure 8 Mole per cent solvent uptake of peroxide system at 28°C

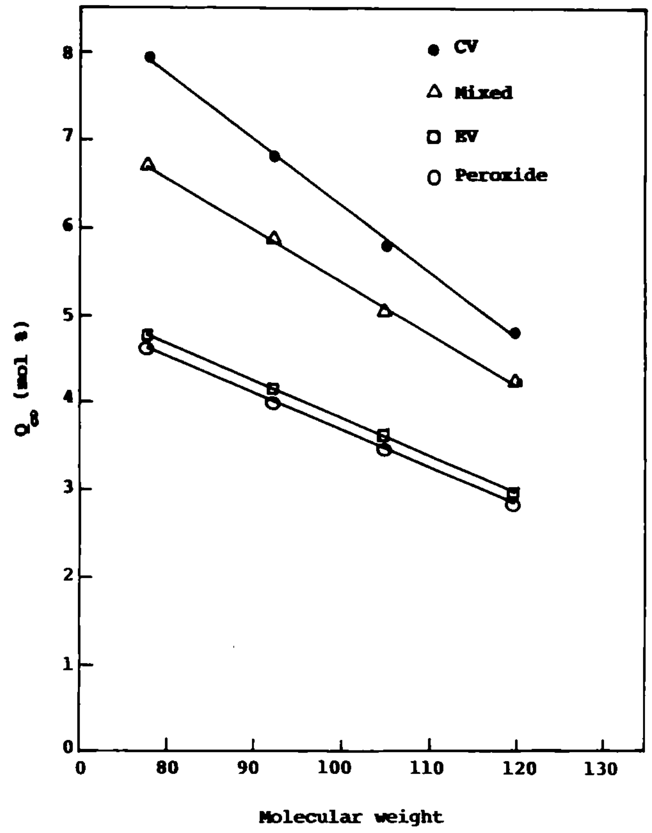


Figure 9 Dependence of maximum mole per cent solvent uptake on molecular weight of the solvent

values decrease with increase in the molecular weight of the penetrant.

In order to understand the mechanism of sorption, the sorption data obtained were fitted to the following equation[17,20,21]:

$$\log(Q_t/Q_\infty) = \log k + n \log t \qquad (3)$$

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 characteristic of the polymer. It also shows the interaction of the polymer with solvent molecules. The value of n normally lies between 0.5 and 1. If n is close to 0.5, the mechanism of diffusion is regular Fickian, where diffusion coefficients are functions of concentration only. When $n=1$, the mechanism is non-Fickian. The values of n and k are calculated by least-squares analysis and are given in *Table 3*. The obtained values of n suggest an almost Fickian diffusion mechanism in all our systems. From the data of swelling experiments, the diffusion coefficient D was calculated using the equation[22]:

$$D = \pi\left(\frac{h\theta}{4Q_\infty}\right)^2 \qquad (4)$$

where Q_∞ has the same meaning as before, θ is the slope of the linear portion of the sorption curves before attainment of 50% equilibrium and h is the initial sample thickness. The calculated values of D for the solvents in different crosslinking systems are given in *Table 4*. It can be seen from the table that the DCP system, with the lowest Q_t value, shows the highest value of D and the CV system, with the highest Q_t value, shows the lowest D value.

The temperature dependence of diffusion in the systems under study has been followed by conducting experiments at 50 and 70°C in addition to those at 28°C. *Figure 10* shows the influence of temperature on the CV system in toluene. It has been observed that the Q_t value increases with rise in temperature. The same trend is shown by the other systems also. The increase in the values of the diffusion coefficient with rise in temperature is given in *Table 5*. These values clearly support the fact that temperature activates the diffusion process.

The decrease in the value of the diffusion coefficient with increase in the number of carbon atoms of the solvent is shown in *Figure 11*. This also is in agreement with our expectation that high-molecular-weight solvents diffuse at a lower rate than low-molecular-weight ones.

The rubber–solvent interaction parameter χ has been calculated using the equation[17]:

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

where ϕ is the volume fraction of rubber in the solvent-swollen sample and N is calculated from ϕ using the equation:

$$N = \frac{\phi^{2/3}/3 - 2/3}{\phi^{1/3} - 2\phi/3} \qquad (6)$$

The values of χ for NR–toluene systems are given in *Table 5*. There is a gradual decrease in the value of χ from DCP system to CV system, suggesting the highest rubber–solvent interaction in the latter case.

From the maximum mole per cent uptake of the solvent, expressed as sorption constant K_s, the values of

Table 3 Analysis of sorption data of NR + aromatic hydrocarbons (NR samples cured to a torque of 33.8 dN m)

	Swelling coefficient				n at 28°C				$k \times 10^2$ ($g\,g^{-1}\,min^{-n}$) at 28°C			
Solvent	DCP	EV	Mixed	CV	DCP	EV	Mixed	CV	DCP	EV	Mixed	CV
Benzene	4.41	4.68	6.82	7.61	0.64	0.61	0.62	0.60	3.9	3.8	3.0	2.8
Toluene	4.33	4.52	6.34	7.46	0.63	0.64	0.63	0.64	3.7	3.7	3.0	2.7
p-Xylene	4.27	4.34	6.19	7.14	0.62	0.56	0.58	0.63	3.3	3.1	3.0	2.5
Mesitylene	4.06	4.07	5.87	6.78	0.62	0.60	0.61	0.64	2.9	2.9	2.8	2.1

Table 4 Values of $D \times 10^7$ at 28°C ($cm^2\,s^{-1}$) (NR samples cured to a torque of 33.8 dN m)

System	Benzene	Toluene	*p*-Xylene	Mesitylene
DCP	11.4	10.4	8.9	4.1
EV	9.2	8.6	6.7	3.0
Mixed	6.1	5.6	5.2	2.2
CV	5.1	4.3	4.0	2.1

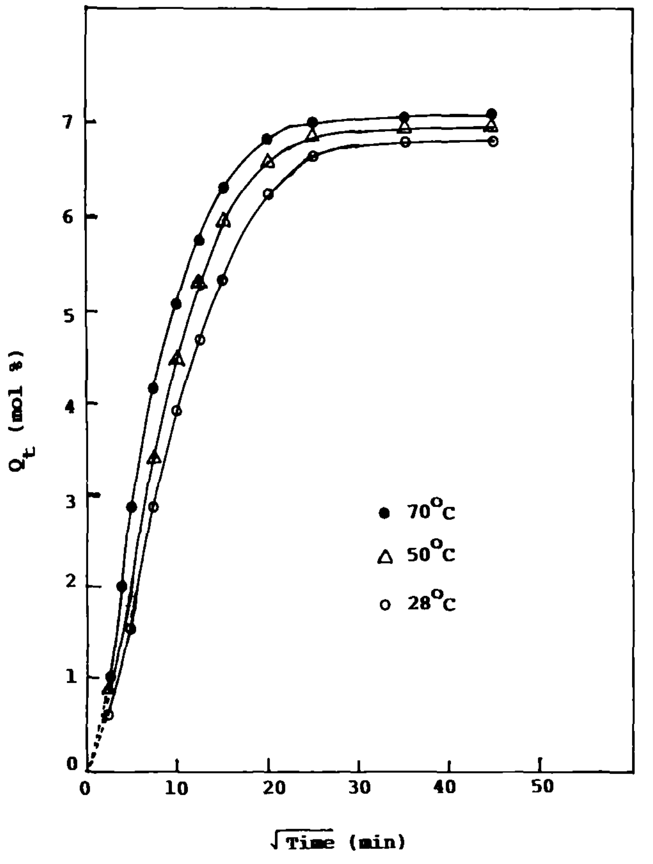


Figure 10 Temperature dependence of mole per cent toluene uptake of CV system

the enthalpy ΔH_s and entropy ΔS of sorption were calculated using Van't Hoff's relation:

$$\log K_s = \frac{\Delta S}{2.303R} - \frac{\Delta H_s}{2.303RT} \qquad (7)$$

The values of ΔH_s and ΔS are given in *Table 5*. The entropy-of-sorption data are negative in all cases, suggesting the retainment of liquid-state structure of solvent molecules even in the sorbed state[17].

Table 5 Values of diffusion coefficient at different temperatures and thermodynamic functions for NR + toluene (NR samples cured to a torque of 33.8 dN m)

	$D \times 10^7$ ($cm^2\,s^{-1}$)					
System	28°C	50°C	70°C	χ	ΔH_s ($kJ\,mol^{-1}$)	ΔS ($J\,mol^{-1}\,K^{-1}$)
DCP	10.4	11.1	12.9	0.30	0.7312	−14.04
EV	8.6	9.9	10.2	0.29	0.8581	−16.14
Mixed	5.6	6.8	7.8	0.28	0.6788	−17.00
CV	4.3	6.0	7.0	0.27	0.8791	−18.86

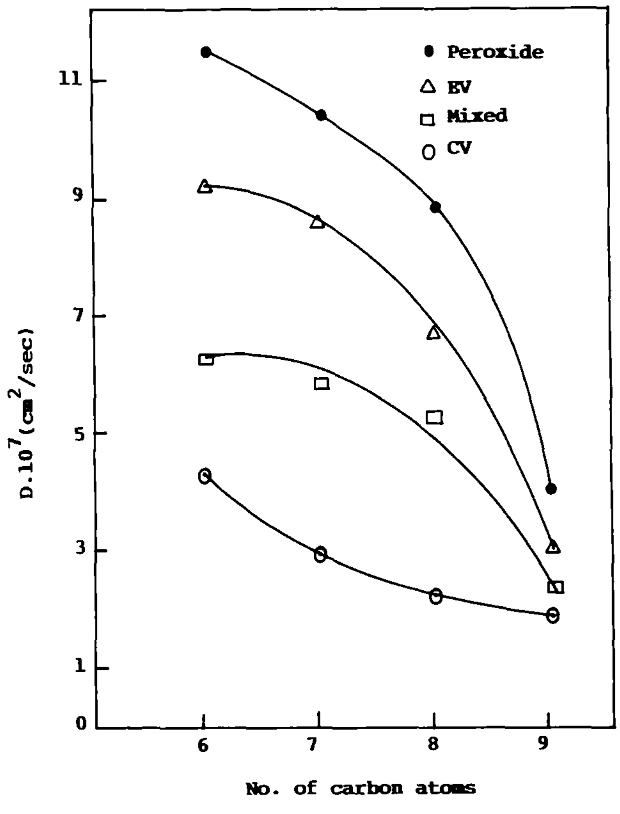


Figure 11 Dependence of diffusion coefficients D on the number of carbon atoms of the aromatic hydrocarbons

CONCLUSIONS

The crosslinking system in vulcanized NR plays an important role in the diffusion of solvents into the NR matrix. The maximum uptake values decrease in the order CV system > mixed system > EV system > DCP system, although all systems have nearly the same crosslink density. The carbon-black-filled NR samples take up a lower amount of solvent than silica-filled ones. In a given system, the maximum uptake value decreases with increase in molecular weight of the solvent. Temperature activates the phenomenon of diffusion in all the samples. The χ values for the different systems indicate maximum rubber–solvent interaction for the CV system.

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