BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 26, pp. 4935–4942, 1995

0032-3861/95/$10.00 + 0.00

Transport of styrene monomer through natural rubber

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(Received 14 November 1994; revised 20 February 1995)

The diffusion and transport of inhibitor-free styrene through crosslinked natural rubber (NR) have been studied at various temperatures. NR has been vulcanized by conventional, efficient, peroxide and mixed vulcanization techniques. The dependence of diffusion coefficient on the crosslinking system has been studied for all the systems. The influence of temperature on the sorption and the activation energies of sorption have been calculated. The interaction parameter, permeability, sorption coefficient and molecular weight between crosslinks have been evaluated using the diffusion data. The effect of degree of crosslinking on the sorption characteristics of styrene through NR has also been investigated for the different crosslinking systems. The peroxide system showed lowest uptake and the conventional system showed highest uptake.

(Keywords: crosslinked natural rubber; diffusion; sorption)

INTRODUCTION

The diffusion properties of different liquids in polymers have been studied extensively by several authors[1–6]. Often the diffusion of liquids through rubbery polymers can be described by Fick's law of diffusion. However, there are instances where deviation from Fick's law has been observed. The transport phenomena of various solvents and monomers through polymers have also been investigated. The sorption properties of rubbery polymers are controlled by polymer structure, crosslink density, type of crosslinking, temperature, etc. In the study on swelling characteristics of natural rubber (NR) in aromatic hydrocarbon liquids, Harogoppad *et al.*[7] investigated the dependence of transport phenomena on polymer structure. The effect of crosslink density on diffusion has been observed by Poh *et al.*[8]. The dependents of swelling and absorption of given samples on temperature have also been investigated[9–11]. Harogoppad *et al.* made use of the temperature dependence of the transport coefficients to estimate the activation parameters from the Arrhenius plots[1].

The swelling and sorption behaviours of NR in various liquids are of great interest, as NR is a well known polymer having extensive use in everyday life. The swelling of natural rubber samples in the presence of monomers like styrene, methyl methacrylate, acrylonitrile, butyl acrylate, etc., is of great research interest, since it constitutes the preliminary step in the preparation of interpenetrating polymer networks (IPN)[12–14]. To prepare a rubber-based IPN, the swelling characteristics of the rubber in monomers are to be studied in detail. A clear and accurate knowledge about the swelling rate of the polymer in the monomers helps in controlling the composition, morphology and properties of the resulting IPN. However, no detailed investigation has been made so far on the kinetics of diffusion and sorption of styrene through natural rubber crosslinked by different curing systems such as conventional (CV), efficient (EV), peroxide (DCP) and mixed systems.

In this paper the swelling of NR in styrene monomer has been studied in the temperature range of 25–45°C. This will be the primary step for the development of IPN based on NR and polystyrene (PS) having various morphological features and property profiles. The NR was vulcanized by different techniques, viz. conventional, efficient, peroxide and mixed vulcanization systems. The influence of different vulcanizing systems on diffusion properties is analysed. For each crosslinking system, samples were vulcanized at different cure times so as to attain samples of different crosslink densities. The effect of crosslink density on sorption has been investigated. Finally the temperature dependence of diffusion and rubber–solvent interaction parameter χ are determined.

EXPERIMENTAL

Materials

The natural rubber (NR) used was of ISNR-5 grade and was supplied by Rubber Research Institute of India (RRII). The styrene monomer is made free of inhibitor by washing with 0.1% NaOH and dried using sodium sulfate before use for diffusion experiments. The chemicals used in the various vulcanizing systems are of laboratory reagent grade.

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Sample preparation

The formulations for different mixes are given in *Table 1*. The mixing was done in a two-roll mixing mill, as per ASTM procedure. The rheographs are taken for each mix to obtain the cure times (*Figure 1*). The mixes are cured at different time intervals: t_{100}, t_{90}, t_{80}. From the rheograph, the time corresponding to the maximum torque was taken as t_{100}. The optimum cure time, t_{90}, refers to the time for obtaining 90% of the maximum torque, i.e. 90% of t_{100}. The time corresponding to 80% of maximum torque was taken as t_{80}. The cure characteristics of the samples are given in *Table 2*.

Immersion/weight-gain experiments

For the swelling experiments, circular samples are cut from the different vulcanized sheets using a sharp steel die (diameter = 1.9 cm). The thickness of the sample was measured by means of a screw gauge. The samples are weighed on an electronic balance and then kept immersed in inhibitor-free styrene monomer in test bottles. The samples are taken out of the liquid at specific time intervals, the monomer adhering to the surface rubbed off, and the samples weighed and replaced in the test bottles. This process was continued till equilibrium is reached (i.e. after about 50 h). The time for each weighing was kept to a minimum (at most 40 s) to make the error due to the escape of solvent from the sample negligible. The values obtained are found to be perfectly reproducible. When conducting the experiments at temperatures higher than room temperature, the samples were kept to a thermostatically controlled air oven.

Table 1 Formulations for the mixes

Ingredient (phr)[a]	CV	EV	DCP[b]	Mixed
NR	100	100	100	100
Stearic acid	1.5	1.5		
Zinc oxide	5	5		
MOR[c]	0.6			0.6
TMTD[d]		1		
CBS[e]		1.5		
DCP			4	1.5
Sulfur	2	0.6		1.5

[a] Parts per hundred rubber by weight
[b] Dicumyl peroxide
[c] Morpholinebenzothiazyl sulfenamide
[d] Tetramethylthiuram disulfide
[e] *N*-Cyclohexyl-2-benzothiazyl sulfenamide

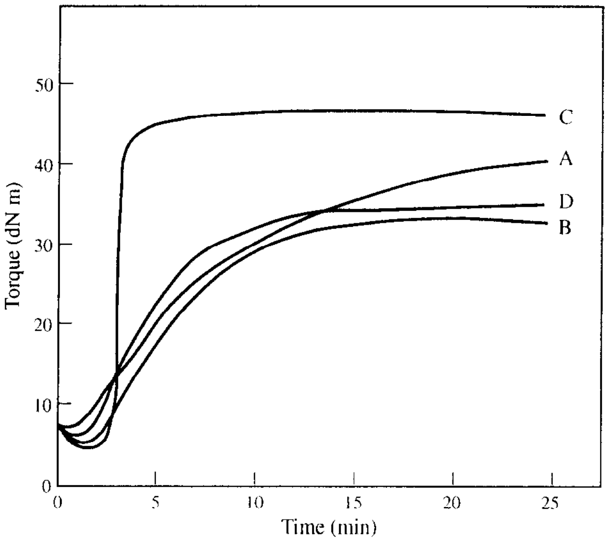

Figure 1 Rheographs of the mixes: A, DCP; B, mixed; C, EV; D, CV

Table 2 Cure characteristics of the mixes

Cure characteristics	CV	EV	DCP	Mixed
Minimum torque (dN m)	5.6	4.5	7	5
Maximum torque (dN m)	36	47.4	44.8	33.8
Scorch time (min)	2.0	2.5	1.8	2.4
Optimum cure time (min)	9	5	25	10

The mole per cent uptake, Q_t, for the monomer by 100 g of the polymer was plotted against the square root of time and the results are analysed[15]. The Q_t value is defined by:

$$Q_t = \frac{M_e(\mathrm{m})/M_r(\mathrm{m})}{M_i(\mathrm{s})} \times 100 \qquad (1)$$

where $M_e(\mathrm{m})$ is the mass of monomer at equilibrium, $M_r(\mathrm{m})$ is the relative molecular mass of the monomer, and $M_i(\mathrm{s})$ is the initial mass of the sample. When equilibrium was reached, Q_t was taken as Q_∞, i.e. mole uptake at infinite time.

RESULTS AND DISCUSSION

To obtain conclusions from the diffusion experiments, the sorption curves were analysed. The Q_∞ values are given in *Table 3*. *Figures 2*, *3* and *4* show the diffusion curves of NR crosslinked by the four vulcanized systems having optimum cure (t_{90}) at three different temperatures, 25, 35 and 45°C. The figures show clearly that monomer uptake is higher in the case of conventional and mixed systems and lowest in the peroxide system. The efficient vulcanizing system takes an intermediate position. The difference in the Q_∞ values for the various systems is partly due to the different types of crosslinking present in them. The structure of networks formed during vulcanization is shown in *Figure 5*. The polysulfidic linkages in conventional vulcanization impart high chain flexibility. In the mixed system both polysulfidic and C–C linkages are present. But as DCP is a slow curing reagent and as the cure time for the mixed system was 10 min, which is not enough to effect complete peroxide curing (the vulcanization time for the NR/DCP system is 25 min (*Table 2*)), the linkages

Table 3 Values of Q_∞ for different samples

Temp. (°C)	Cure time	CV	EV	DCP	Mixed
25	t_{100}	6.0935	4.4989	3.3623	6.029
	t_{90}	5.4790	4.2800	3.3819	5.597
	t_{80}	5.5497	4.2273	3.4033	5.5786
35	t_{100}	6.016	4.4096	3.4128	6.196
	t_{90}	5.5679	4.342	3.5076	5.6443
	t_{80}	5.4518	4.2082	3.5794	5.897
45	t_{100}	6.5039	4.7559	3.4619	6.050
	t_{90}	6.1026	4.4039	3.5076	5.752
	t_{80}	6.076	4.5086	3.5784	5.850

formed may be predominantly polysulfidic. As a result the monomer molecules are more readily accommodated between the rubber chains in the case of conventional as well as mixed systems. The efficiently vulcanized samples with mono- and disulfidic linkages are comparatively less flexible and monomer uptake is lower in this case. In the case of DCP-cured system, less-flexible C–C linkages are present and hence lowest Q_∞ values are observed. The diffusion curves for undercured and overcured samples for the four systems were also analysed. In all cases and at different temperatures the same trend was observed

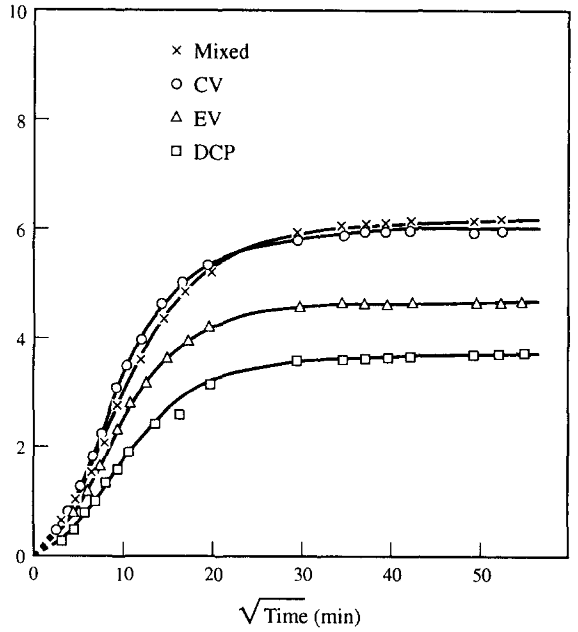

Figure 2 Sorption curve showing the mole per cent uptake of optimum cured CV, EV, mixed and peroxide samples at 25°C

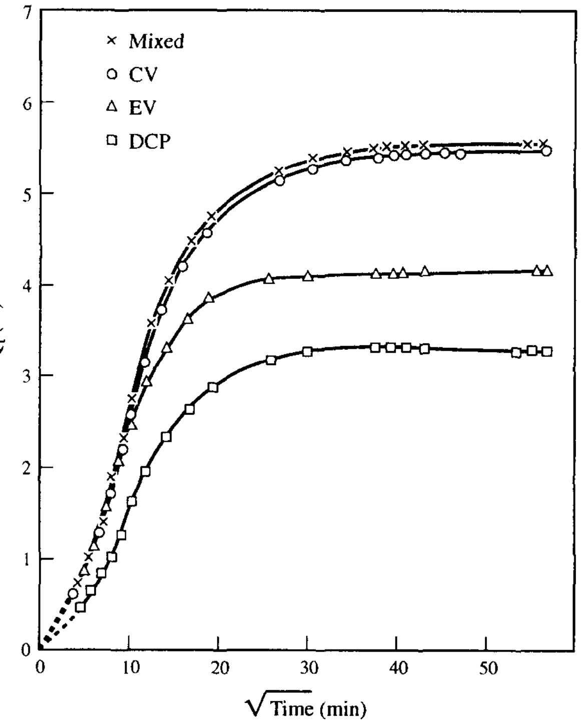

Figure 3 Sorption curve showing the mole per cent uptake of optimum cured CV, EV, mixed and peroxide samples at 35°C

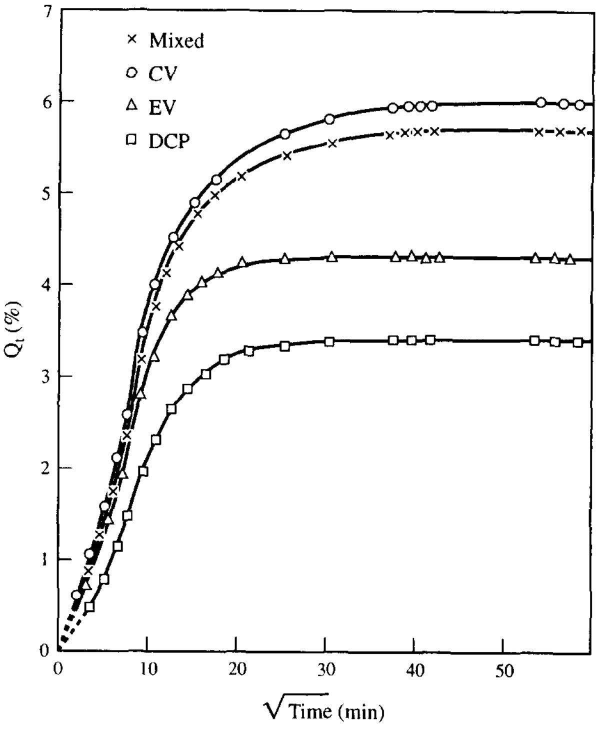

Figure 4 Sorption curve showing the mole per cent uptake of optimum cured CV, EV, mixed and peroxide samples at 45°C

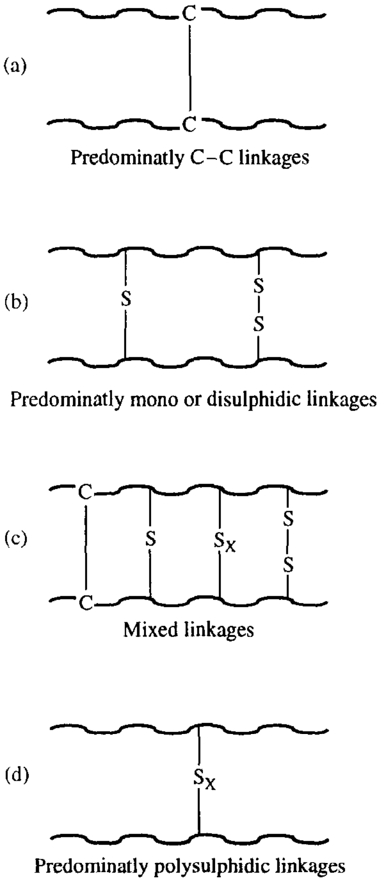

Figure 5 Schematic representation of the crosslinks formed during curing: (a) peroxide, (b) efficient, (c) mixed and (d) conventional vulcanization

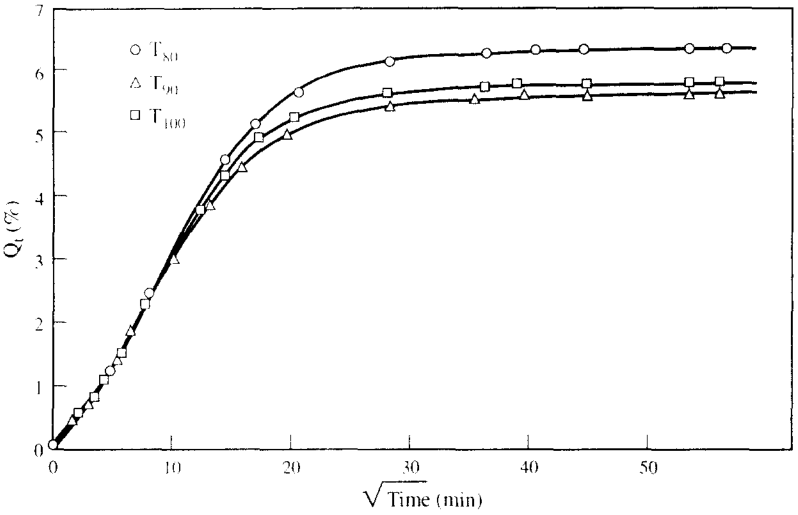

Figure 6 Sorption curve showing the mole per cent uptake of conventional vulcanized samples with different cure times

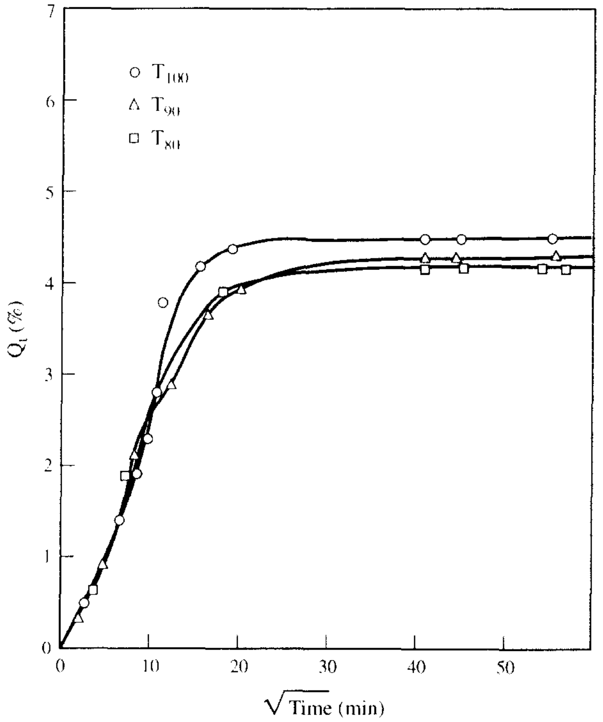

Figure 7 Sorption curve showing the mole per cent uptake of efficient vulcanized samples with different cure times

(CV, mixed > EV > peroxide). The other major factor that contributes to the difference in the monomer uptake is the crosslink density, which is discussed later on in this paper.

Samples cured at different cure times (t_{100}, t_{90}, t_{80}) for the same vulcanizing system at the same temperature show different Q_∞ values, which may be explained by the degree of crosslinking. The diffusion curves for CV samples with different cure times (t_{100}, t_{90}, t_{80}) at room temperature were analysed (*Figure 6*). The t_{100} and t_{80} samples show greater uptake than the optimum cured (t_{90}) samples. The same is the case with efficient, peroxide and mixed systems (*Figures 7, 8* and *9*). The t_{100} samples are overcured and hence some of the crosslinks formed may undergo rupture. This facilitates higher monomer uptake. On the other hand, for t_{80} samples, the system is undercured and therefore the crosslinks may not be fully formed. Here also monomer uptake is made easy. In the t_{90} samples the crosslinks are optimum and complete for the best balance of properties. Therefore the monomer uptake is minimum in this case. We have also analysed the behaviour at different temperatures. The trend was exactly the same. Therefore, the same explanation holds good for all samples at different temperatures.

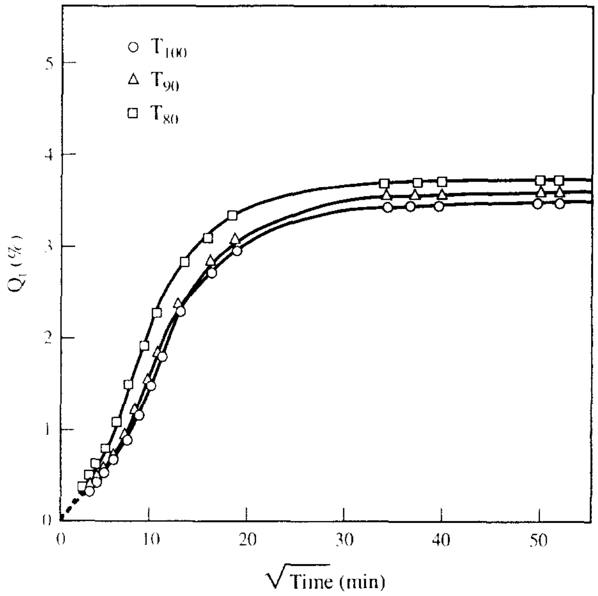

Figure 8 Sorption curve showing the mole per cent uptake of peroxide vulcanized samples with different cure times

The volume fraction of rubber, ϕ, in the solvent-swollen samples was calculated using[16] :

$$\phi = \frac{w_1/\rho_1}{w_1/\rho_1 + w_2/\rho_2} \qquad (2)$$

where w_1 is the weight of the rubber sample, ρ_1 the density of natural rubber, w_2 the weight of styrene monomer in the swollen sample, and ρ_2 the density of the monomer. The high value of ϕ is an indication of high crosslinking density. The values are given in *Table 4*. The ϕ values of DCP-cured samples were found to be higher, showing high crosslink density and hence low monomer uptake. The ϕ values are lowest for CV and mixed samples, which show high monomer uptake. For EV system the value comes in between those of CV and DCP systems, which shows the intermediate swelling characteristics. At high temperature (35 and 45°C) and for different degrees of curing, the same pattern was followed.

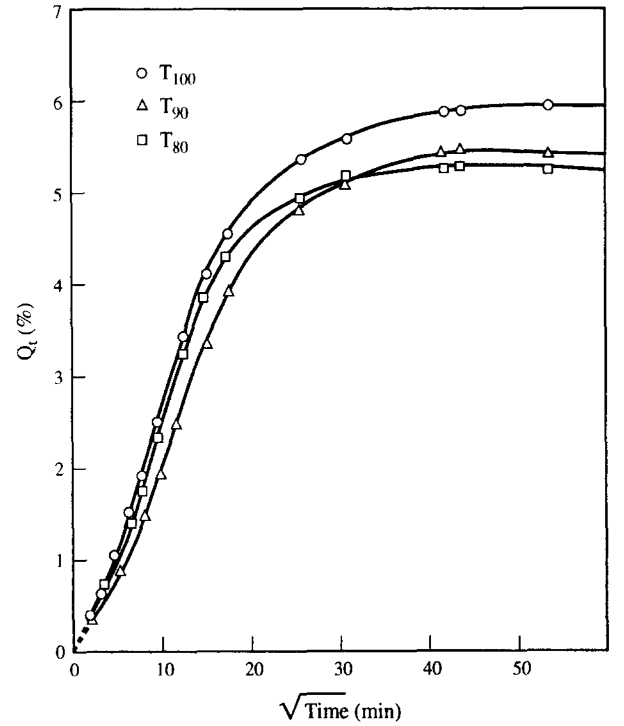

Figure 9 Sorption curve showing the mole per cent uptake of mixed vulcanized samples with different cure times

Table 4 Values of ϕ for different samples

Temp. (°C)	Cure time	CV	EV	DCP	Mixed
25	t_{100}	0.1286	0.1666	0.2113	0.1295
	t_{90}	0.1411	0.1823	0.2101	0.1384
	t_{80}	0.1394	0.1745	0.2090	0.1401
35	t_{100}	0.1299	0.1693	0.2085	0.1267
	t_{90}	0.1415	0.1715	0.2116	0.1373
	t_{80}	0.1412	0.1712	0.2022	0.1322
45	t_{100}	0.1212	0.1588	0.2056	0.1264
	t_{90}	0.1284	0.1596	0.2007	0.1355
	t_{80}	0.1289	0.1663	0.2067	0.1334

The values of swelling coefficient (α) were calculated using[17]:

$$\alpha = \frac{M_s}{M_0} \times \frac{1}{\rho_0} \tag{3}$$

where M_s is the mass of solvent (mass of swollen sample − original mass of polymer sample), ρ_0 the solvent density and M_0 the mass of the polymer sample. The swelling coefficient α is a measure of the volume of solvent in unit mass of the polymer. The values are given in *Table 5*. The swelling coefficient is in the order DCP < EV < CV, mixed. The swelling coefficient is found to increase with temperature.

To understand the mechanism of sorption, the values obtained were fitted to the equation[10]:

$$\log (Q_t/Q_\infty) = \log k + n \log t \tag{4}$$

where Q_t is the mole per cent increase in uptake at time t, Q_∞ the mole per cent increase in uptake at equilibrium, t the time and k a constant characteristic of the polymer, which indicates the interaction between polymer and solvent. The values of n and k were determined by linear regression analysis. In all cases the correlation coefficients were found to be 0.99.

The value of n is equal to 0.5 for a Fickian diffusion mechanism. When the value falls between 0.5 and 1, the diffusion is anomalous. In this system, i.e. for NR and styrene, a slight deviation from the Fickian mode of diffusion is shown at all temperatures (*Table 5*). The values of k for different systems were also determined from equation (4) (*Table 5*). From the swelling data the diffusion coefficient D was calculated using[6]:

$$D = \pi (h\theta/4Q_\infty)^2 \tag{5}$$

where θ is the slope of the linear portion of the sorption curves and h is the initial thickness of the sample. The values of diffusion coefficients are given in *Table 6*. The peroxide system shows highest D value, as it has the lowest Q_∞ values. The CV and mixed systems have lowest diffusion coefficients. Also, it is noticeable that, in each system, the value of D increases with temperature. The increase of diffusion with temperature invariably points out the activation of the diffusion process at higher temperature.

Table 5 Values of swelling coefficient, n and k at different temperatures

Temp. (°C)	Cure time	Swelling coefficient				n				$k \times 10^n$ (g/g min^2)			
		CV	EV	DCP	Mixed	CV	EV	DCP	Mixed	CV	EV	DCP	Mixed
25	t_{100}	6.771	5.123	3.855	6.913	0.6161	0.6192	0.6310	0.6627	3.05	3.19	2.66	2.12
	t_{90}	6.279	4.921	3.878	6.4186	0.5727	0.6344	0.5994	0.6300	3.83	3.15	2.96	2.62
	t_{80}	6.302	4.826	3.9029	6.3265	0.6334	0.6375	0.6537	0.5888	2.73	3.29	3.05	3.24
35	t_{100}	6.899	5.051	3.912	7.105	0.5452	0.5906	0.5564	0.5489	4.62	5.05	3.96	4.33
	t_{90}	6.252	4.979	3.8396	6.472	0.5628	0.5986	0.6456	0.6810	3.86	4.13	3.18	2.36
	t_{80}	6.2668	4.825	4.0119	6.763	0.6638	0.6509	0.6732	0.6418	2.76	3.33	3.34	3.05
45	t_{100}	7.467	8.456	3.981	7.1239	0.6075	0.5102	0.5840	0.5510	3.50	6.22	6.53	4.90
	t_{90}	6.996	5.4318	4.022	6.580	0.6246	0.6035	0.6574	0.5798	3.35	4.50	3.06	4.21
	t_{80}	6.966	5.169	4.1032	6.7109	0.6142	0.5938	0.5627	0.5673	3.40	4.76	5.93	4.75

The permeability of a small monomer molecule into a polymer membrane depends on the diffusivity as well as the solubility or sorption of the monomer in the membrane. Therefore, the sorption coefficient has been calculated using[15]:

$$S = \frac{M_\infty}{M_p} \tag{6}$$

where M_∞ is the mass of the solvent taken up at equilibrium swelling and M_p is the mass of the polymer sample. The values of S are given in *Table 6*. The sorption coefficient is found to be maximum for CV and mixed and minimum for DCP. The EV system has intermediate values. The maximum sorption coefficient of CV and mixed systems indicates that the monomer molecules are easily absorbed and accommodated in these network systems. The DCP system shows the lowest capability to accommodate the monomer molecules.

The permeabilities of natural rubber to liquid molecules can be expressed mathematically by the equation[16]:

$$P = DS \tag{7}$$

where P is the permeability coefficient. The permeability coefficients estimated are given in *Table 6*. It is noticed that the peroxide system has the highest value, highlighting the high permeability of the peroxide system.

The diffusion coefficient characterizes the ability of the monomer molecule to move among the polymer segments. The sorption coefficient is related to the equilibrium sorption of the penetrant. A large value of S shows a tendency for the monomer to dissolve into the polymer. The permeability coefficient implies the net effect of sorption and diffusion.

On analysing *Table 6* we can see that the DCP system shows the highest values of diffusion coefficient and permeation coefficient, while CV and mixed systems show the lowest values. As the values of the sorption coefficient are low compared to the diffusion coefficient, it can be concluded that the permeability is controlled significantly by the process of diffusion. By analysing the effect of temperatures, it can be seen that diffusion and permeation are activated by temperature (*Table 6*). But the effect of temperature on sorption does not show a regular trend (*Table 6*).

The swelling data have been used to calculate the monomer–polymer interaction parameter, χ and the molecular weight between crosslinks, M_c. In this approach, first, the polymer–solvent interaction parameter has been estimated by the equation[18]:

$$\chi = 0.34 + V_r(\delta_A - \delta_B)^2/RT \tag{8}$$

where V_r is the molar volume of solvent, R the gas constant, T the temperature, and ρ_A and ρ_B the solubility parameters of polymer and monomer, respectively. The values for the NR/styrene system at 25, 35 and 45°C are 0.801, 0.786 and 0.773, respectively. It is found that the interaction parameter changes inversely with rise in temperature. This suggests a high polymer–solvent interaction at high temperature.

The molecular weight between crosslinks has been calculated from the equation[10]:

$$M_c = -\frac{\rho_p V \phi^{1/3}}{\ln(1-\phi) + \phi + \chi\phi^2} \tag{9}$$

where V is the molar volume of solvent and ρ_p is the density of the polymer. The degree of crosslinking is given by[19]:

$$\nu = 1/(2M_c) \tag{10}$$

The values of M_c and ν are given in *Table 7*. The values given in the table highlight the fact that the peroxide system has the highest crosslink density and CV and mixed systems with polysulfidic linkages have the lowest crosslink density. This again explains why the monomer uptake is highest in CV and mixed systems and lowest in the peroxide system.

The temperature dependence of transport coefficients (P, D and S) can be used for calculating the energy of activation for the processes of diffusion and permeation, from the Arrhenius relationship[15]:

$$X = X_0 \exp(-E_X/RT) \tag{11}$$

where X is P, D or S and X_0 represents P_0, D_0 or S_0, which are constants; E_X is the activation energy, R the universal gas constant and T the absolute temperature.

The Arrhenius plots of log D and log P *versus* $1/T$ are shown in *Figures 10* and *11*, respectively. From the slopes of the curves, E_P and E_D can be calculated by linear regression analysis. The correlation coefficients are very

Table 6 Values of diffusion coefficient, sorption coefficient and permeation coefficient at various temperatures for different curing systems

Temp. (°C)	Cure time	$D \times 10^7$ (cm^2 s^{-1})				S (g/g)				$P \times 10^7$ (cm^2 s^{-1})			
		CV	EV	DCP	Mixed	CV	EV	DCP	Mixed	CV	EV	DCP	Mixed
25	t_{100}	2.68	3.60	5.83	2.63	6.337	4.678	3.491	6.287	16.98	16.84	20.34	16.51
	t_{90}	3.05	2.98	5.50	3.45	5.694	4.512	3.5172	5.8216	17.35	13.43	19.28	20.07
	t_{80}	3.41	2.71	5.91	3.05	5.771	4.396	3.5394	5.7381	19.67	11.89	20.82	17.47
35	t_{100}	3.11	3.15	6.50	3.28	6.257	4.5816	3.584	6.446	19.43	14.42	23.27	21.12
	t_{90}	3.60	3.11	8.16	4.20	5.6705	4.5161	3.4827	5.870	20.41	14.02	28.39	24.05
	t_{80}	3.68	3.73	4.65	2.96	5.6840	4.376	3.6869	6.1341	20.90	16.30	17.11	18.14
45	t_{100}	3.26	4.53	6.85	4.26	6.773	6.2066	3.6108	6.461	22.07	28.08	24.72	27.51
	t_{90}	4.11	3.45	9.93	4.28	6.3457	4.9266	3.647	5.968	26.05	16.97	36.14	25.80
	t_{80}	3.81	3.86	5.80	3.37	6.3181	4.6888	3.7216	6.086	24.04	18.06	21.57	20.48

Table 7 Values of M_c and degree of crosslinking

System	Cure time	M_c 25°C	M_c 35°C	M_c 45°C	$\nu \times 10^{+5}$ 25°C	$\nu \times 10^{+5}$ 35°C	$\nu \times 10^{+5}$ 45°C
CV	t_{100}	13208.37	13840.5	15964.96	3.785	3.612	3.131
	t_{90}	11684.9	12212.9	15019.18	4.279	4.094	3.329
	t_{80}	11834.02	12378.2	14648.96	4.225	4.039	3.413
EV	t_{100}	9211.52	9553.67	11029.84	5.4279	5.233	4.533
	t_{90}	8154.95	9462.7	11014.5	6.131	5.283	4.539
	t_{80}	8628.68	9288.19	10430.01	5.794	5.383	4.793
DCP	t_{100}	6773	7421.3	8049.8	7.382	6.737	6.2113
	t_{90}	6833.6	7331.3	8330.6	7.316	6.82	6.0119
	t_{80}	6787.7	7633.38	8008.43	7.366	6.550	6.243
Mixed	t_{100}	12966.2	14235.7	15325.02	3.856	3.512	3.262
	t_{90}	11860.7	12681.02	13990.03	4.215	3.942	3.573
	t_{80}	11717.2	13350.7	14041.9	4.267	3.745	3.560

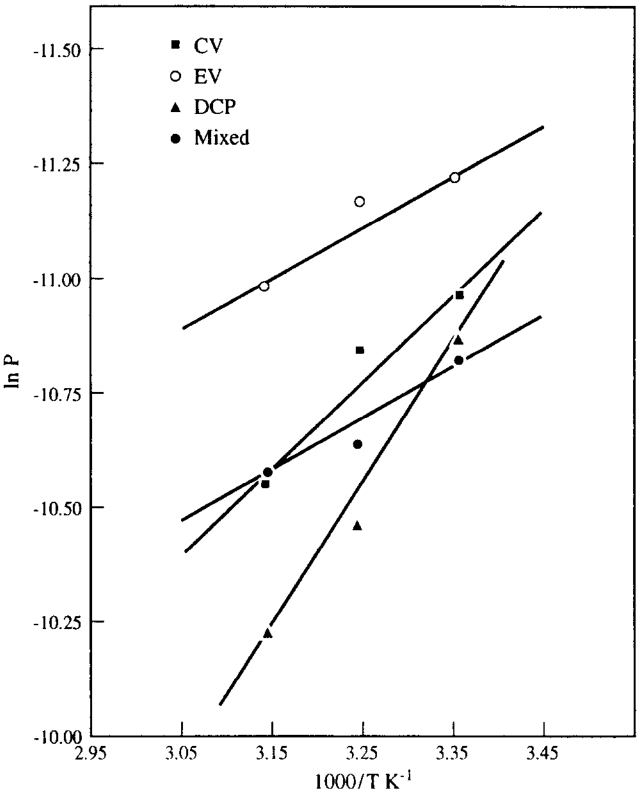

Figure 10 Arrhenius plots of ln P vs. $1/T$

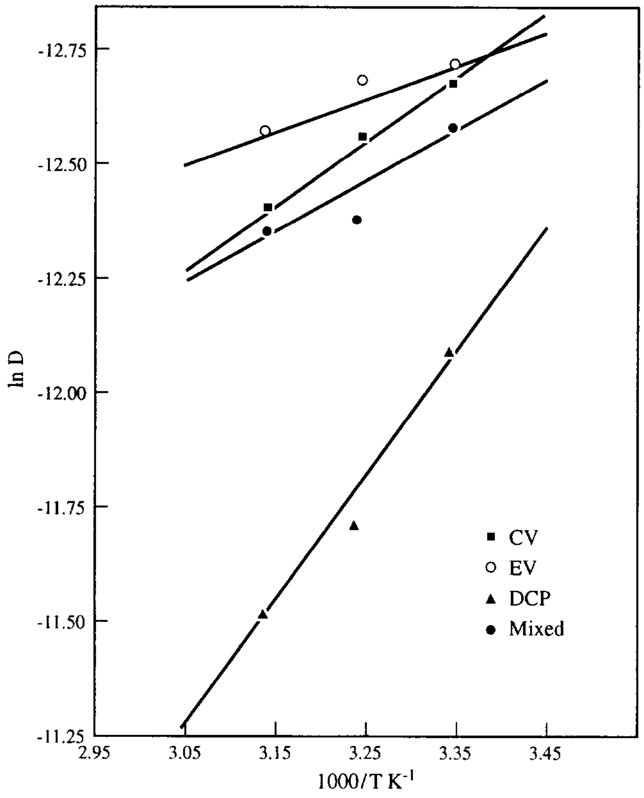

Figure 11 Arrhenius plots of ln D vs. $1/T$

close to 0.99. The activation energy of permeation E_P is found to be greater than the activation energy of diffusion E_D. The values of E_P and E_D are given in *Table 8*. The values given are for the t_{90} samples for CV, EV, DCP and mixed systems.

The heat of sorption ΔH_s is given by:

$$\Delta H_s = E_P - E_D \qquad (12)$$

The values of ΔH_s are also given in *Table 8*. The enthalpy and entropy of sorption have been calculated using the van't Hoff relation[20]:

$$\ln K_s = \Delta S/R - \Delta H_s/RT \qquad (13)$$

The values obtained by the linear regression method are given in *Table 9*. The values of ΔS and ΔH are positive.

Table 8 Values for activation energy

System	E_P (kJ mol^{-1})	E_D (kJ mol^{-1})	ΔH_s (J K^{-1} mol^{-1})
CV	15.970	11.76	4.21
EV	7.866	5.74	2.12
DCP	24.805	23.34	1.465
Mixed	9.958	8.564	1.394

From the values of ΔH and ΔS the free energy ΔG has been calculated as:

$$\Delta G = \Delta H - T\Delta S \qquad (14)$$

The ΔG values are given in *Table 9*. It is interesting to note that the ΔG values of all the systems are negative, showing spontaneous sorption.

Table 9 Thermodynamic functions ΔH, ΔS and ΔG

System	Cure time	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	$-\Delta G$ (kJ mol^{-1})
CV	t_{100}	2.529	33.7	7.513
	t_{90}	4.2089	28.48	4.278
	t_{80}	3.518	26.2	4.278
EV	t_{100}	2.5866	21.42	3.796
	t_{90}	1.1234	16.18	3.698
	t_{80}	2.5622	20.60	3.5766
DCP	t_{100}	1.1548	14.2	3.0708
	t_{90}	1.4436	15.35	3.1307
	t_{80}	1.991	17.25	3.1495
Mixed	t_{100}	1.1596	15.83	3.5577
	t_{90}	1.076	18.24	4.359
	t_{80}	1.9027	21.05	4.370

CONCLUSION

From this study on the diffusion of styrene monomer through natural rubber, it is clear that the crosslinking system has an important role in determining the diffusion coefficient. The uptake is in the order: peroxide < EV < CV, mixed. This has been explained based on the flexibility of the network and the crosslink density. The presence of rigid C–C linkages and high crosslink density of peroxide system account for the lowest monomer uptake in the peroxide-crosslinked system. On the other hand, the relatively flexible polysulfidic linkages present in the CV and mixed systems and their low crosslink density account for their high monomer uptake. As expected the EV system showed intermediate behaviour. Also, the extent of curing influences the diffusion characteristics. The uptake is lowest in t_{90} samples and it is high for both t_{100} and t_{80} samples. It is found that the temperature activates the diffusion process in all cases. The values of n are suggestive of a slight deviation from the Fickian mode of diffusion. The polymer–solvent interaction parameter χ was calculated and decreased with temperature. The free energy of sorption was found to be negative for all systems, suggesting spontaneous sorption.

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