S0032-3861(96)00457-0

Polymer Vol. 37 No. 26, pp. 5839–5848, 1996

0032-3861/96/$15.00 + 0.00

Molecular transport of aromatic hydrocarbons through crosslinked styrene-butadiene rubber membranes

Soney C. George and Sabu Thomas*
School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills P.O., Kottayam-686 560, Kerala, India

and K. N. Ninan
Propellant and Special Chemicals Group, Vikram Sarabhai Space Centre, Trivandrum-695 022, Kerala, India
(Received 13 April 1995; revised 25 January 1996)

Molecular transport of aromatic hydrocarbons through crosslinked SBR has been carried out in the temperature range 25–65°C. SBR has been vulcanized by four different vulcanizing techniques viz., conventional, efficient, dicumyl peroxide and a mixture consisting of sulfur and peroxide. SBR vulcanized with EV system showed highest solvent uptake tendency and that vulcanized with peroxide showed the lowest. The influence of penetrant size on sorption behaviour of SBR has been examined. The thermodynamic constants such as standard entropy, standard enthalpy and first-order kinetic rate constant have been evaluated. A correlation between theoretical and experimental sorption results was evaluated. The polymer–solvent interaction parameter (χ) was also computed from the diffusion data. Copyright © 1996 Elsevier Science Ltd.

(Keywords: diffusion; sorption; transport)

INTRODUCTION

Towards the end of the twentieth century, great attention has been focused on the field of diffusion, sorption and permeation because these basic phenomena play a vital role in several important areas of engineering and industry. The dimensional stability and integrity of the polymeric materials in presence of aggressive liquids are very important as far as their wide variety of applications such as separation process, controlled release of drugs and pesticides, food packaging, encapsulation of electronic circuits, etc.[1] are concerned. Extensive research has taken place in the field of diffusion and permeation of gases, vapours and liquids through polymers[2–5]. Several reports are available on rubber–solvent interactions[6–10]. These studies are extremely important in the continuing improvement of gaskets, hoses and protective apparel. Harogoppad *et al.*[11,12] investigated the sorption and diffusion behaviour of organic liquids through a series of polymer membranes (neoprene, styrene butadiene rubber, ethylene propylene diene rubber, natural rubber, etc.) and found that the mechanism of diffusion follows a Fickian trend. Transport of organic esters into fluoropolymers was conducted by Aminabhavi and Munnolli[13], who examined the effects of fluorine contents of fluoropolymers on transport process. Recently, in our laboratory, Unnikrishnan and Thomas[14], and Mathew *et al.*[15] investigated the role of the nature of crosslinks, fillers, etc., on the sorption and diffusion of aromatic hydrocarbons and styrene monomer through crosslinked natural rubber. Permeation studies are also using molecular probes to discover polymer structure. Chiang and Setton[16] used the solvent sorption method to investigate the morphology of a styrene–butadiene–styrene-block copolymer. Importance of permeation studies persist because a detailed experimental analysis is needed for designing economically viable barrier materials and membranes.

Styrene–butadiene rubber (SBR) is a general purpose synthetic rubber which has many applications. The high loading capacity, good flex resistance, crack initiation resistance and abrasion resistance of SBR make it useful in several engineering and industrial areas. Crosslinked SBR does not dissolve but swells in most solvents.

The present work focuses mainly on the effects of vulcanizing systems on the molecular transport of aromatic hydrocarbons through SBR membranes. The influence of penetrant size and temperature on transport behaviour has also been examined. From the swelling data, rubber–solvent interaction parameter, entropy and enthalpy of sorption and kinetic rate constants have been estimated. The experimental sorption data have been compared with the theoretical predictions.

---

* To whom correspondence should be addressed

Table 1 Compounding recipe (parts per hundred parts of rubber by weight)

Ingredients	EV	Mixed	CV	DCP
Styrene–butadiene rubber	100.0	100.0	100.0	100.0
Stearic acid	2.0	2.0	2.0	–
Zinc oxide	5.0	5.0	5.0	–
N-Cyclohexyl-2-benzothiazyl sulfenamide	2.0	1.0	1.0	–
Dicumyl peroxide	–	2.0	–	4
Sulfur	0.5	1.5	2.2	–

Table 2 Cure characteristics of the mixes EV, mixed, CV and DCP at 150°C

Cure properties	EV	Mixed	CV	DCP
Minimum torque (dN.m)	6.90	7.50	8.75	11.00
Maximum torque (dN.m)	20.90	33.50	56.00	97.30
Cure time (min) at 20 dN.m	43.00	13.35	17.50	3.00
Optimum cure time (min)	40.00	22.35	27.25	33.75

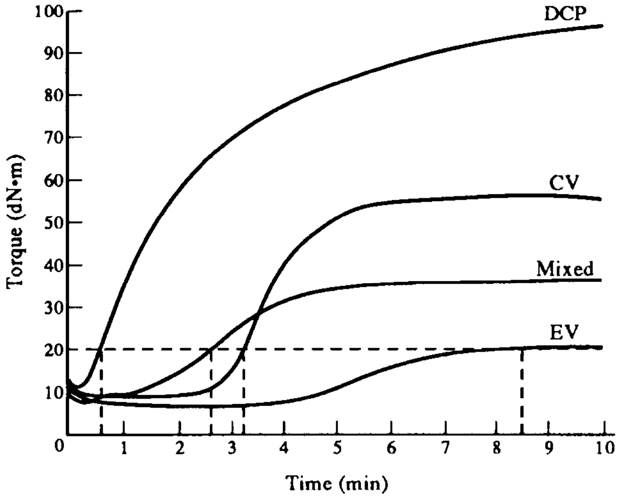

Figure 1 Rheographs of the mixes

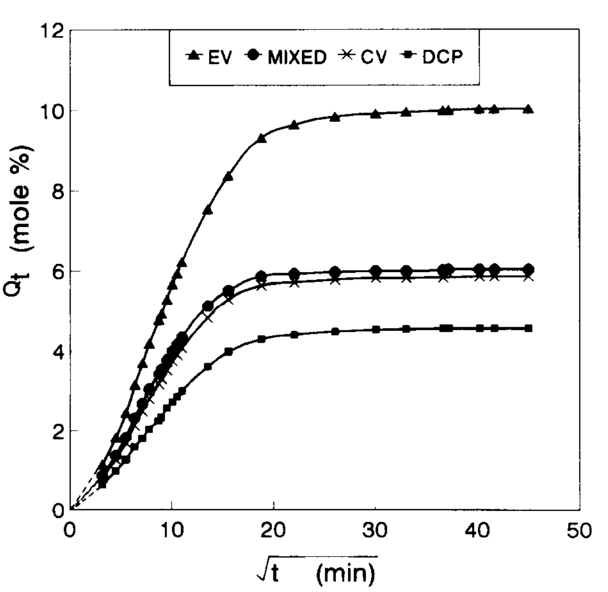

Figure 2 Mole per cent benzene uptake of SBR with different crosslinking systems at 25°C. (The samples were cured to a torque at 20 dN.m)

EXPERIMENTAL

Materials

SBR used was synaprene (1502) with 25% styrene content supplied by Synthetic and Chemicals Ltd., Bareilly, U.P., India. The solvents used were benzene, toluene, *p*-xylene and mesitylene (Merck India Ltd., Bombay, India) with 99% initial purity. All these solvents were distilled three times before use. All other rubber ingredients used were of laboratory reagent grade, supplied by Bayer India Ltd., Bombay, India.

Preparation of the samples

SBR was vulcanized by different crosslinking techniques: conventional, efficient, dicumyl peroxide and a mixture of sulfur and peroxide. 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 cure characteristics of the samples were studied in a Monsanto rheometer R-100. The rheographs of the mixes and the cure characteristics are given in *Figure 1* and *Table 2*, respectively. In order to study the effect of nature of crosslinks, all these samples were cured under a common rheometric torque 20 dN.m and it was assumed that under the same rheometric torque all these samples possess nearly the same crosslinking density. The samples were also vulcanized at optimum cure time. Under optimum cure time all samples are cured to 90% of the maximum torque. The curing was carried out in a hydraulic press at 150°C under a pressure of 25 tonnes.

Diffusion experiments

The SBR samples were cut circularly (diameter 1.96 cm), by means of a sharp steel die, from dried vulcanized sheets. The thickness of the membrane was measured at several points using a micrometer screw gauge having an accuracy of 0.001 cm and average value was taken. The cut samples were soaked in solvents in test bottles kept at constant temperature in a thermostatically controlled oven. The samples were removed from the bottles at intervals and weighed. They were then replaced in the test bottles. This process was continued until equilibrium swelling was attained. The weighings were accurate up to 0.001 g. Removal of the samples from the test bottles for weighing may generate error, but this error is found to be negligible since the samples are back in the test bottles within 30 s.

The results of diffusion experiments were expressed as moles of solvent uptake by 100 g of crosslinked SBR sample (Q_t mol%).

$$\text{i.e., } Q_t \text{ mol\%} = \frac{\dfrac{\text{Mass of solvent sorbed}}{\text{Molar mass of solvent}}}{\text{Mass of polymer}} \times 100 \qquad (1)$$

RESULTS AND DISCUSSION

Effect of the nature of crosslinks

The diffusion curves of crosslinked SBR, using different vulcanizing systems under a common torque are shown in *Figure 2*. The solvent used was benzene. In this figure, all the sorption curves are similar in nature. Initial portions are slightly sigmoidal in shape but later level off. The sigmoidal shape is associated with the time

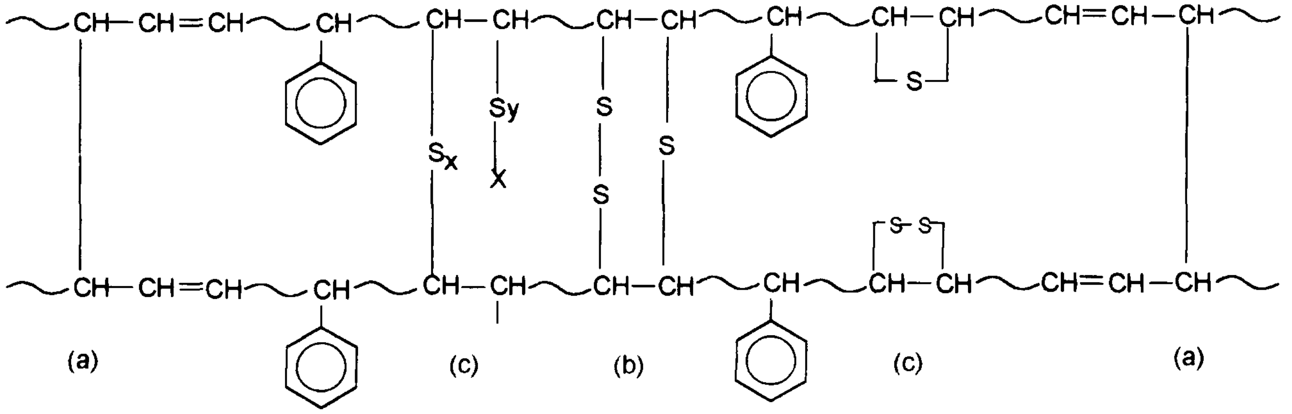

Figure 3 The general structural features of vulcanizate network (all systems included)

Table 3 Volume fraction (V_r) of swollen SBR (SBR samples cured to rheometric torque of 20 dN.m)

Solvent	EV	Mixed	CV	DCP
Benzene	0.103	0.160	0.164	0.201
Toluene	0.103	0.157	0.163	0.199
p-Xylene	0.101	0.158	0.161	0.190
Mesitylene	0.106	0.153	0.166	0.296

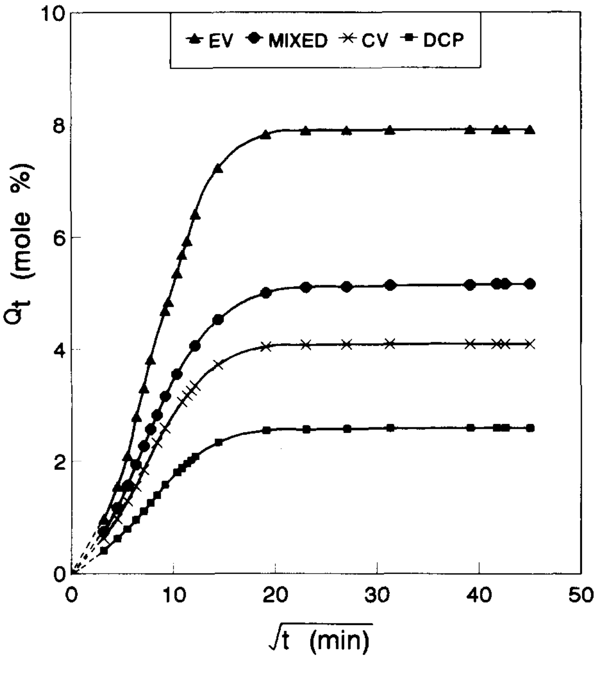

Figure 4 Mol% toluene uptake of SBR with different crosslinking systems cured up to t_{90}

taken by the polymer chains to respond to the swelling stress and rearrange themselves to accommodate the penetrant molecules[17]. Initially, the swelling rate is too high because of the large concentration gradient and the polymer sample is under intense solvent stress. As the concentration gradient decreases the swelling rate decreases and at the equilibrium swelling the concentration difference is almost nil. Similar sorption behaviour was exhibited in toluene, *p*-xylene and mesitylene. It is evident that SBR crosslinked with efficient system shows the highest amount of solvent uptake (Q_t mol%) whereas that vulcanized with peroxide exhibits the lowest amount of solvent uptake. SBR crosslinked with mixed and conventional systems take intermediate positions. The Q_t mol% values decrease in the order EV > mixed > CV > DCP.

The difference in the solvent uptake value for SBR vulcanized with different vulcanizing systems might be due to the formation of different types of bonds between rubber chains during vulcanization. *Figure 3* depicts the general structural features of vulcanizate networks[18]. The peroxide-vulcanized samples contain C-C linkages (a), the efficiently vulcanized samples contain mostly mono and disulfidic crosslinks (b), conventional vulcanized samples have mainly polysulfidic linkages in addition to pendant sulfides and cyclic sulfides (c), and samples vulcanized using mixed system have polysulfidic, monosulfide, disulfidic crosslinks in addition to C–C linkages (a, b and c). Network structure was characterized by Porter[19]. As expected, peroxide vulcanized samples show the lowest amount of solvent uptake among all samples since they contain mostly rigid crosslinks which are resistant to permeant mobility. Contrary to our expectation, efficiently vulcanized sample showed the highest amount of solvent uptake, even though it contains mostly monosulfidic and disulfidic linkages; SBR vulcanized with conventional system showed the lowest solvent uptake even though it possesses highly flexible polysulfidic linkages. SBR vulcanized with mixed system showed the uptake value second to efficient system. Based on the flexibility of the crosslinks, one would expect a high solvent uptake for the CV system. However, the observed anomaly could be explained on the basis of volume fraction of solvent swollen rubber (V_r) and can be determined by using the relation[20]

$$V_r = \left[1 + \frac{P_p}{P_s}\left[\frac{M_\infty}{M_0}\right] - \frac{P_p}{P_s}\right]^{-1} \tag{2}$$

where M_∞ is the mass of solvent taken up at equilibrium and M_0 is the initial mass of polymer sample. P_p and P_s represent the densities of polymer and solvent respectively.

Table 3 shows the values of volume fraction of swollen rubber. The lowest value among them is for efficiently vulcanized samples. The next higher value is for SBR vulcanized with mixed system. The remaining positions are taken up by conventional- and peroxide-vulcanized

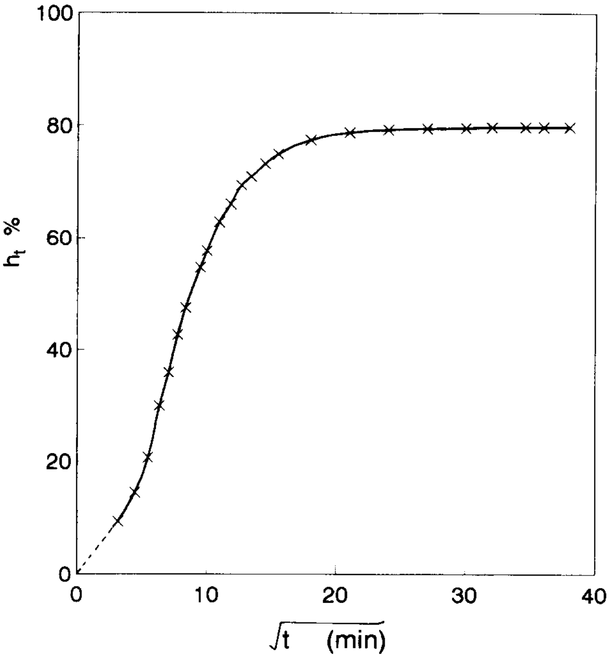

Figure 5 Per cent increase in thickness of optimum cured CV sample in benzene

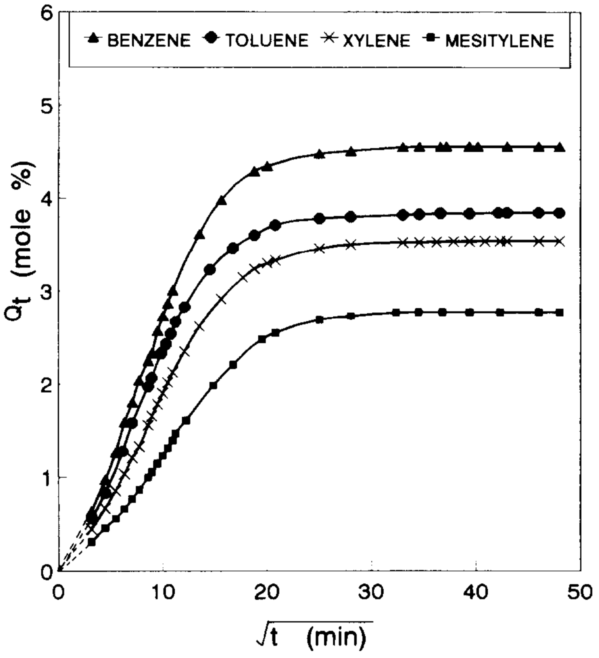

Figure 6 Mole per cent solvent uptake of peroxide system at 25°C

samples. Thus, the volume fraction of swollen rubber decreases in the order DCP > CV > mixed > EV. Because the volume fraction of swollen rubber is proportional to crosslink density, it can be concluded that as the volume fraction values decrease the crosslink density also decreases. Therefore, the solvent uptake behaviour follows the order DCP < CV < mixed < EV. In this context, it is important to mention that same extent of crosslinking cannot be achieved by curing the sample to the same rheometric torque.

In order to verify the solvent uptake of SBR vulcanized to t_{90} (90% of the maximum torque), the optimum cured (t_{90}) samples were also subjected to diffusion experiments. *Figure 4* represents the sorption curves of crosslinked SBR in toluene. It is interesting to note that in optimum cured samples the same trend was also followed and the solvent uptake values decrease in the order EV > mixed > CV > DCP.

Sorption analyses were also carried out by measuring the thickness instead of weights at periodic intervals[20]. By plotting per cent increase in thickness (h_t%) against square root of time one can get a similar diffusion pattern as in the previous case (this is illustrated in *Figure 5*).

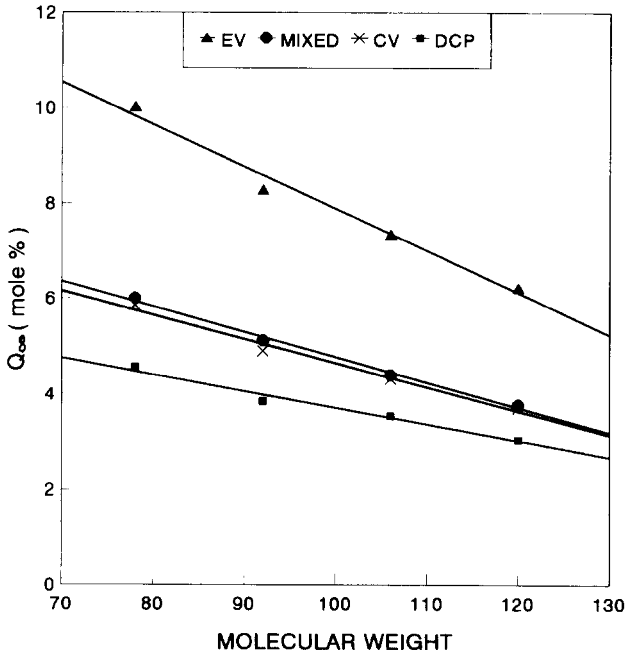

Figure 7 The variation of maximum mol% solvent uptake with molecular weight of the solvent

Effect of penetrant size

There is a systematic trend in the sorption behaviour of liquids of different molecular size. With an increasing size of the solvent molecules, there is a decrease in the value of Q_t mol% (*Figure 6*) in all the systems. Among the solvents used in this work, benzene shows the maximum value of Q_t mol% and mesitylene the minimum. Toluene and *p*-xylene have intermediate positions. The decrease in Q_t mol% uptake with increase in penetrant size might be due to the greater activation energy needed for activation of the diffusion process. This is clearly manifested in the plot of Q_∞ against molecular weight of solvent (*Figure 7*). It can be seen that the Q_∞ values decrease with the increase of molecular weight of the penetrant molecule.

Mechanism of transport

The results of the sorption experiments were analysed by using the empirical relation[11,21,22]

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

where Q_t is the mol% sorption at time t and Q_∞ is the mol% sorption at equilibrium; k depends upon structural features of polymer in addition to its interaction with the solvent; n indicates the mechanism of sorption.

Table 4 Analysis of sorption data of aromatic hydrocarbons and SBR membrane at different temperatures (SBR samples cured to a rheometric torque of 20 dN.m)

Solvent	Temperature (°C)	*n*				$k \times 10^2$ ($g g^{-1} min^{-n}$)			
		EV	Mixed	CV	DCP	EV	Mixed	CV	DCP
Benzene	25	0.72	0.73	0.70	0.64	2.14	2.66	2.70	3.18
	50	0.74	0.73	0.73	0.67	2.20	2.88	2.69	3.18
	65	0.77	0.75	0.71	0.65	2.04	2.69	3.10	3.41
Toluene	25	0.72	0.70	0.67	0.63	2.29	2.94	3.01	2.37
	50	0.73	0.69	0.65	0.61	2.40	3.35	3.86	3.88
	65	0.75	0.72	0.68	0.72	2.34	2.98	3.35	3.09
p-Xylene	25	0.72	0.69	0.68	0.63	1.87	2.67	2.45	2.90
	50	0.67	0.67	0.64	0.59	2.48	2.98	3.30	3.69
	65	0.74	0.69	0.73	0.65	2.01	3.18	2.51	3.18
Mesitylene	25	0.73	0.70	0.69	0.65	1.48	1.94	1.92	2.22
	50	0.73	0.70	0.70	0.63	1.91	2.40	2.54	3.00
	65	0.76	0.73	0.72	0.69	1.71	2.26	2.52	2.37

Table 5 Values of $D \times 10^7$ at different temperatures $cm^2 s^{-1}$ (SBR samples cured to a rheometric torque of 20 dN.m)

Solvent	Temperature (°C)	EV	Mixed	CV	DCP
Benzene	25	5	8	7	9
	50	6	11	6	12
	65	7	12	10	12
Toluene	25	5	7	7	9
	50	6	9	9	11
	65	8	9	9	20
p-Xylene	25	4	6	6	8
	50	6	6	6	7
	65	6	9	9	11
Mesitylene	25	3	4	4	6
	50	5	7	7	7
	65	5	7	9	9

If $n = 0.5$, the mechanism of sorption is termed as Fickian, and this occurs when the rate of diffusion of permeant molecules is much less than the polymer segment mobility. If $n = 1$, the mechanism of sorption is non-Fickian. This arises when the rate of diffusion of permeant molecules is much greater than polymer segmental mobility. If *n* lies between 0.5 and 1, then mechanism of sorption follows an anomalous trend. Here, the permeant mobility and polymer segment relaxation rates are similar. By regression analysis, the values of *n* and *k* are obtained as slope and intercept, respectively and are placed in *Table 4*. The correlation coefficient values are found to be 0.999. The values of *n* range from 0.61 to 0.77 and it implies that the mechanism of sorption follows an anomalous trend. The *n* values of peroxide vulcanized samples are more close to 0.5 and hence possess a tendency to show the Fickian behaviour. Conversely, *n* values of other samples are greater than 0.64 and hence they exhibit anomalous behaviour. Here, the polymer relaxation and rate of diffusion are comparable. The anomalous behaviour exhibited might be due to the leaching out of additives from the sulfur vulcanized rubber compound. This was, in fact, evident from the coloration of the solvents and the change in refractive index of the solvent. Similar reports are also available in the literature[23].

Except in toluene the values of *k*, as expected, are found to decrease with increasing penetrant size. For toluene, the values of *k* are higher in all the systems and hence it supports that toluene has good interaction with crosslinked SBR. The values of *n* and *k* at higher temperatures are given in *Table 4*. However, no systematic trend could be seen at higher temperatures.

Diffusivity, sorptivity and permeability

Diffusivity is a kinetic parameter which depends on the polymer segmental mobility. This was determined by using the relation[11,23,24]

$$D = \pi(h\theta/4Q_\infty)^2 \qquad (4)$$

where *D*, the diffusion coefficient; θ is the slope of the sorption curves before attainment of 50% equilibrium; *h* is the initial thickness of the polymer sample; and Q_∞ has the same meaning as in equation (2). The estimated values of diffusivity are given in *Table 5*. From the dependence of *D* on the number of carbon atoms of the penetrants, as shown in *Figure 8*, it is found that *D* varies inversely with increase in the number of carbon atoms. An inverse relationship was observed with *D* and molar volume. The efficiently vulcanized (EV) samples show the highest uptake and therefore the lowest D values. The peroxide-vulcanized samples show the highest *D* value. The *D* values vary in the order EV < CV < mixed < DCP. Sorption describes the initial penetration and dispersal of permeant molecules into the polymer matrix. Sorption coefficient is calculated from the equilibrium swelling using the relation[23]

$$S = M_\infty/M_0 \qquad (5)$$

M_∞ and M_0 have the same meaning as in equation (1).

Table 6 Values of sorption coefficients (S) and permeation coefficients ($P = DS$) (SBR samples cured to a rheometric torque of 20 dN.m)

Solvent	Temperature (°C)	S (g g^{-1})				$P(DS) \times 10^6$ cm^2 s^{-1}			
		EV	Mixed	CV	DCP	EV	Mixed	CV	DCP
Benzene	25	7.83	4.70	4.57	3.56	3.91	3.76	3.20	3.20
	50	7.57	4.57	4.47	3.43	4.54	5.03	2.68	4.12
	65	7.63	4.57	4.39	3.55	5.34	5.48	4.39	3.91
Toluene	25	7.63	4.71	4.51	3.54	3.82	3.30	3.16	3.18
	50	7.72	4.61	4.34	3.65	4.64	4.15	3.90	4.01
	65	7.33	4.52	4.29	3.30	5.87	4.07	3.86	6.59
p-Xylene	25	7.79	4.67	4.57	3.75	3.12	2.80	2.75	2.99
	50	7.23	4.58	4.36	3.35	4.34	2.75	2.62	2.34
	65	7.35	4.33	4.06	3.35	4.41	3.89	3.66	3.69
Mesitylene	25	7.48	4.53	4.44	3.65	2.24	1.81	1.77	2.19
	50	7.05	4.07	4.06	3.44	3.53	2.85	2.84	2.41
	65	6.86	4.01	3.92	3.24	3.42	2.81	3.53	2.92

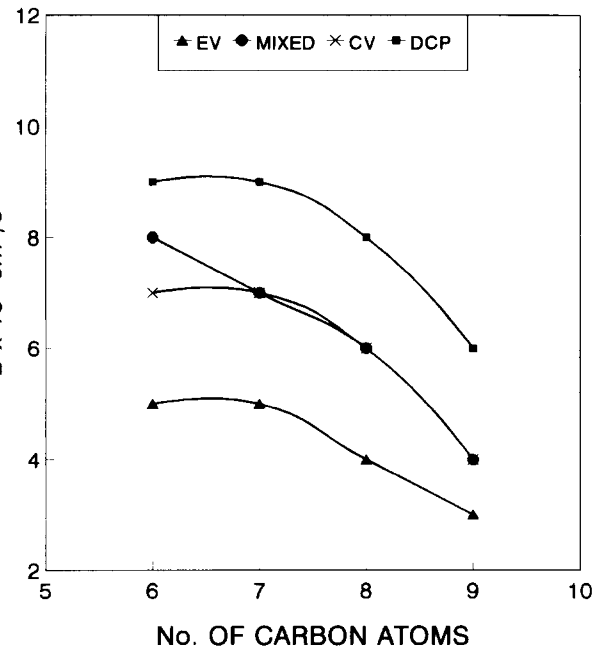

Figure 8 Dependence of diffusivity (D) on the number of carbon atoms of aromatic hydrocarbons

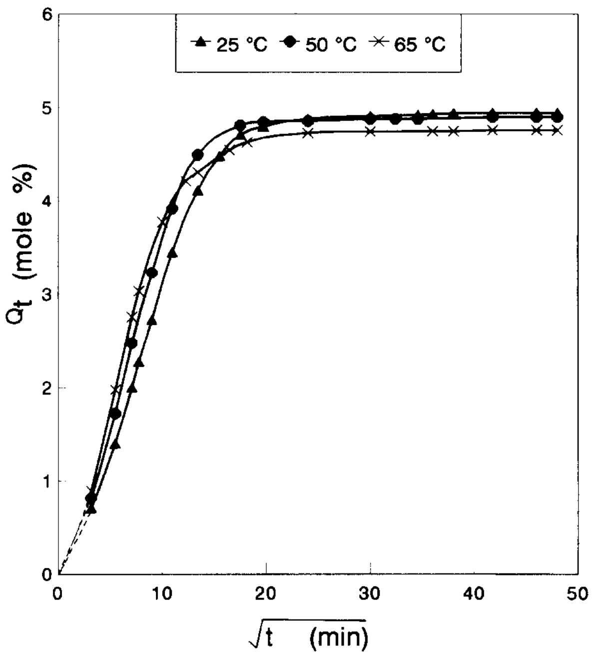

Figure 9 Temperature dependence of mol% uptake of CV system

Sorption coefficient is a thermodynamic parameter which depends on the strength of the interactions in the polymer/penetrant mixture. Permeation is a collective process of diffusion and sorption and hence the permeability of solvent molecules into polymer membrane depends upon both diffusivity and sorptivity. Hence the permeation coefficient[23,24] (P) can be defined as

$$P = D \cdot S \tag{6}$$

where D is the diffusion coefficient and S denotes sorption coefficient. *Table 6* shows the values of S and P. It is clear that sorption coefficient is a direct indicator of absorbed solvent molecules in crosslinked SBR. S is found to be maximum for the EV samples and minimum for peroxide-vulcanized samples in all the solvents. Thus, sorption coefficient, unlike diffusion coefficient shows a trend in all the solvents. The maximum sorption coefficient for the EV system reveals that the absorbed solvent molecules are better accommodated by the efficiently crosslinked sample than by the mixed and CV systems and samples vulcanized with peroxide show the least capacity to accommodate the solvent molecules.

The permeation coefficient values are also found to decrease with increasing penetrant size. The highest values are obtained for EV samples as in the earlier case.

Effect of temperature

Diffusion experiments were conducted at 50 and 65°C

Table 7 Thermodynamic parameters standard free energy ΔG^0 (kJ mol^{-1}) standard enthalpy ΔH^0 (kJ mol^{-1}) and standard entropy ΔS^0 (J mol^{-1} k^{-1}) (SBR samples cured to a rheometric torque of 20 dN.m)

Solvent	System	ΔG^0	$-\Delta H^0$	$-\Delta S^0$
Benzene	EV	5.71	0.61	21.21
	Mixed	6.26	1.12	27.12
	CV	7.03	0.84	26.47
	DCP	7.68	1.15	26.26
Toluene	EV	6.13	1.00	23.91
	Mixed	7.36	0.85	27.58
	CV	7.48	1.09	28.76
	DCP	8.04	1.15	30.89
p-Xylene	EV	6.93	−2.94	13.47
	Mixed	6.81	4.23	37.07
	CV	7.80	2.15	33.34
	DCP	8.31	2.50	36.26
Mesitylene	EV	6.88	1.83	29.25
	Mixed	8.09	3.18	37.79
	CV	8.19	1.97	34.11
	DCP	8.65	2.40	37.07

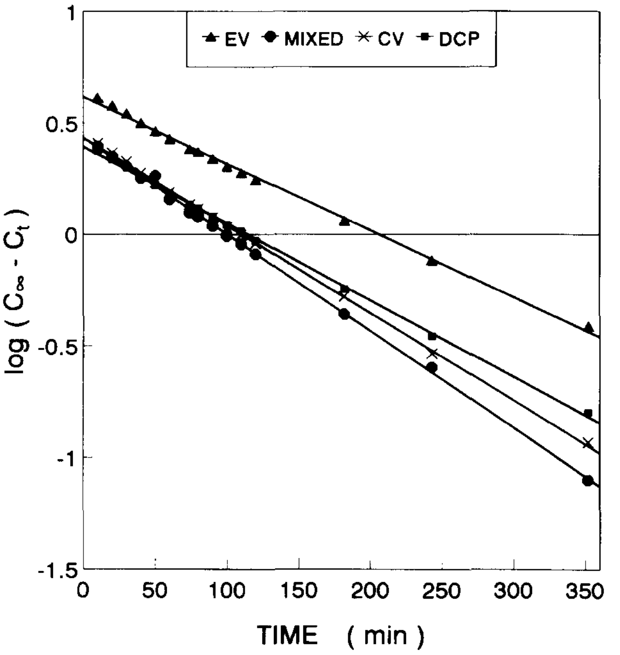

Figure 10 Plots of log $(C_\infty - C_t)$ *versus* time for vulcanized SBR in benzene

in addition to those at 25°C in order to study the effect of temperature on the diffusion phenomenon in SBR. As the temperature increases the rate of diffusion also increases. However, the maximum solvent uptake values (Q_∞) marginally decrease. This can be understood from *Figure 9*, where Q_t mol% is plotted as a function of time at various temperatures for CV system. All the other systems (DCP, mixed, EV) showed the same trend. In all cases, the slope of the linear portion in the sorption curve increases with temperature, indicating that the diffusion process is temperature activated. The shapes of the sorption curves is exactly same as those at 25°C for all the systems studied. This implies that the solvent sorption process occurs by the same mechanism as those at 25°C. The decrease in maximum uptake values with increasing temperature is attributed to the increasing rate of desorption. As equilibrium approaches, the rate of desorption overcomes the sorption process and hence the decrease in maximum solvent uptake with increasing temperature, even though there is increasing free volume and segmental mobility at high temperature. The high desorption at high temperature is partly associated with the leaching out of the additives.

There is an increase in the diffusion coefficient (D) values with increasing temperature as in *Table 5*. This is clear evidence for increasing the rate of sorption with increasing temperature. Sorption coefficient values are found to decrease with increasing temperature (*Table 6*). Permeation coefficients are not showing any systematic trend with increasing temperature (*Table 6*).

Thermodynamic and kinetic parameters

Swelling occurs during sorption of penetrant molecules into the pores of polymer matrix. Swelling is considered as a result of two thermodynamic phenomena. An increase of entropy of polymer–solvent matrix by the introduction of small molecules as diluent and a decrease of entropy of polymer by isotropic dilation. The former is actually the entropy of mixing between polymer and solvent molecules and acts as a driving force for swelling. Hence, the standard entropy (ΔS^0) and standard enthalpy (ΔH^0) for crosslinked SBR and solvents were determined by using the Van't Hoff relation[24]

$$\log K_s = \frac{\Delta S^0}{2.303\,R} - \frac{\Delta H^0}{2.303\,R}\frac{1}{T} \tag{7}$$

where K_s is the thermodynamic sorption constant[25]. From the slopes and intercept of the least-square fit of the linear plot of $\log K_s$ against $1/T$ one can obtain the values of ΔH^0 and ΔS^0.

The standard free energy (ΔG^0) of the process was determined from the values of ΔH^0 and ΔS^0 by using the relation

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{8}$$

The values of ΔG^0, ΔH^0 and ΔS^0 are given in *Table 7*.

The ΔS^0 values are negative, which implies the retainment of liquid state structure of solvents even in the sorbed state within the polymer. In all the cases, the lowest negative value of ΔS^0 is for efficiently vulcanized samples and as the penetrant size increases the $-\Delta S^0$ increases. This suggests that small molecules permeate through the membrane easily, while larger molecules could retain their liquid structure more effectively in the polymer matrix. Standard enthalpy (ΔH^0) values are also found to be negative. The sorption is therefore said to be an exothermic process.

The free energy values are positive and of small magnitude. In all the systems and in all the liquids the free energy values increase in the order EV < mixed < CV < DCP. Therefore, it can be concluded that the sorption process is more spontaneous in efficiently vulcanized samples and less feasible in peroxide-vulcanized samples. Standard free energy increases with increasing penetrant size for each system.

During diffusion and sorption of solvents through polymer membrane a structural rearrangement in the polymer matrix occurs and hence it might induce the kinetic behaviour. Kinetic behaviour depends mainly on the segmental mobility and availability of free volume within the polymer matrix. As a result, transport of liquids through the polymer membrane is considered as a rate-controlled kinetic process which can be studied by first-order kinetic rate equation[23,26].

$$\mathrm{d}c/\mathrm{d}t = k'(C_\infty - C_t) \qquad (9)$$

On integration, equation (9) yields

$$k't = 2.303 \log(C_\infty/C_\infty - C_t) \qquad (10)$$

where k' is the first-order rate constant (min^{-1}). C_t and C_∞ represent concentration at time t and at equilibrium. Plot of log $(C_\infty - C_t)$ against time is shown in *Figure 10*. From the slope of the plot, we can estimate the values of k and they are given in *Table 8*. The estimated error in the values of k' are found to be within ± 0.001. The kinetic rate constant is a measure of the speed with which a solvent molecule penetrates the medium. The values are found to range from $5.34 \times 10^{-3}\,\mathrm{min}^{-1}$ to $19.33 \times 10^{-3}\,\mathrm{min}^{-1}$ and most of the values come within close proximity, indicating the unique nature of molecular transport in crosslinked SBR. The efficiently vulcanized (EV) samples bear lowest rate constant values compared with all other samples. The rate constant values suggest that the transport of organic liquids through EV sample is a comparably slow process, even though it has the highest swelling at equilibrium. This fact is also supported from the low D values (*Table 5*) for EV samples. The rate constant values are found to decrease with increasing penetrant size. Moreover, in all the cases the rate constants tend to increase with increasing temperature and further support the fact that rate of diffusion is increased by increasing the temperature.

Table 8 Kinetic data for crosslinked SBR-solvent systems ($k' \times 10^3$, min^{-1}) (SBR samples cured to a rheometric torque of 20 dN.m)

		$k \times 10^3$, min^{-1}			
Solvent	Temperature (°C)	EV	Mixed	CV	DCP
Benzene	25	7.71	10.05	9.50	8.39
	50	8.73	12.63	11.22	10.16
	65	11.27	19.33	13.21	12.67
Toluene	25	7.42	10.03	9.08	8.12
	50	8.29	15.06	13.87	12.58
	65	12.53	12.11	15.76	8.96
p-Xylene	25	6.80	9.72	7.69	7.08
	50	6.66	8.50	8.23	5.80
	65	8.43	13.10	12.27	8.78
Mesitylene	25	5.54	6.54	6.09	5.34
	50	7.07	8.82	9.68	6.93
	65	10.06	9.13	10.92	8.13

Swelling parameters

Swelling coefficient (α) is an index of the ability with which the sample swells and is determined by the equation[20]

$$\alpha = \frac{M_\infty - M_0}{M_0} \times \frac{1}{P_s} \qquad (11)$$

M_∞ is the mass of the swollen rubber sample (i.e., equilibrium saturation). M_0 has the same meaning as before. P_s is the density of solvent used. The values are shown in *Table 9*. The swelling coefficient values change in all the solvents as in the order EV > mixed > CV > DCP. This suggests that the swelling is highest for EV sample and lowest for DCP system.

Hayes[27] estimated the rubber–solvent interaction parameter (χ) by using the Flory–Rehner equation:

$$-[\ln(1 - v_r) + v_r + \chi v_r^2] = \nu v_s(v_r^{1/3} - 2v_r \mathrm{f}) \qquad (12)$$

where v_s is the molar volume of solvent.

We have followed the procedure suggested by Hayes[27] and estimated the χ parameter from the Flory–Rehner equation. For CV system, samples crosslinked at different cure times ($>t_{100}$, t_{100}, t_{90}, t_{50} and t_{20}) were used to compute interaction parameter. The swelling data in two solvents (v_r) for each vulcanizate were equated assuming no change in effective number of crosslinks (ν) with solvent. The functionality of crosslinks (f) assumed was four[27].

As an example, for CV system the samples crosslinked at different cure times ($>t_{100}$, t_{100}, t_{90}, t_{50} and t_{20}) were subjected to swelling experiments in *p*-xylene and mesitylene. By equating the swelling data in these two solvents, we get the following equations[27] corresponding to $>t_{100}$ (13), t_{100} (14), t_{90} (15), t_{50} (16), t_{20} (17).

$$\chi_1 = 0.0397 + \chi_2\, 0.9278 \qquad (13)$$

$$\chi_1 = 0.0092 + \chi_2\, 0.9800 \qquad (14)$$

$$\chi_1 = 0.0519 + \chi_2\, 0.9084 \qquad (15)$$

$$\chi_1 = 0.0256 + \chi_2\, 0.9502 \qquad (16)$$

$$\chi_1 = 0.0241 + \chi_2\, 0.9523 \qquad (17)$$

By regression analysis, the values of χ_1 (*p*-xylene) and χ_2 (mesitylene) obtained are $\chi_1 = 0.594$ and $\chi_2 = 0.597$. By

Table 9 Values of swelling parameters (SBR samples cured to a rheometric torque of 20 dN.m)

	Swelling coefficient (α)				Interaction parameter (χ)			
Solvent	EV	Mixed	CV	DCP	EV	Mixed	CV	DCP
Benzene	8.697	5.209	5.004	4.052	0.569	0.768	0.619	0.737
Toluene	8.863	5.470	5.242	4.107	0.576	0.817	0.629	0.770
p-Xylene	9.073	5.384	5.337	4.368	0.556	0.593	0.594	0.616
Mesitylene	8.644	5.362	5.129	3.848	0.559	0.597	0.598	0.623

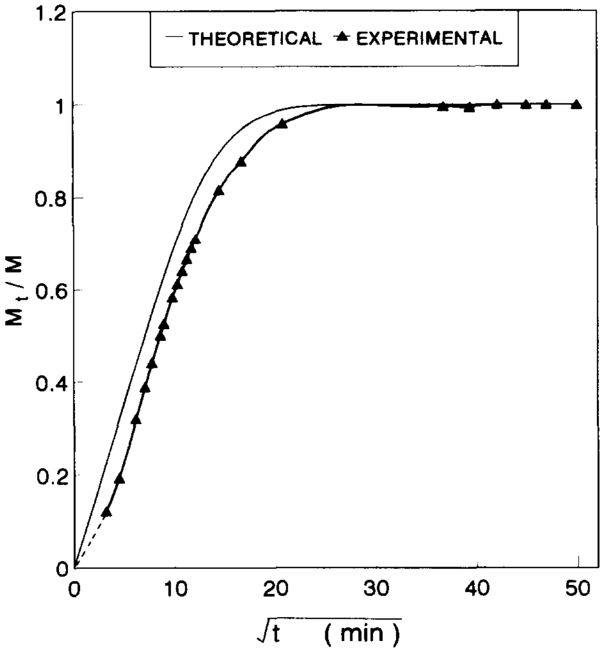

Figure 11 Comparison between experimental and theoretical sorption curves of EV sample in toluene

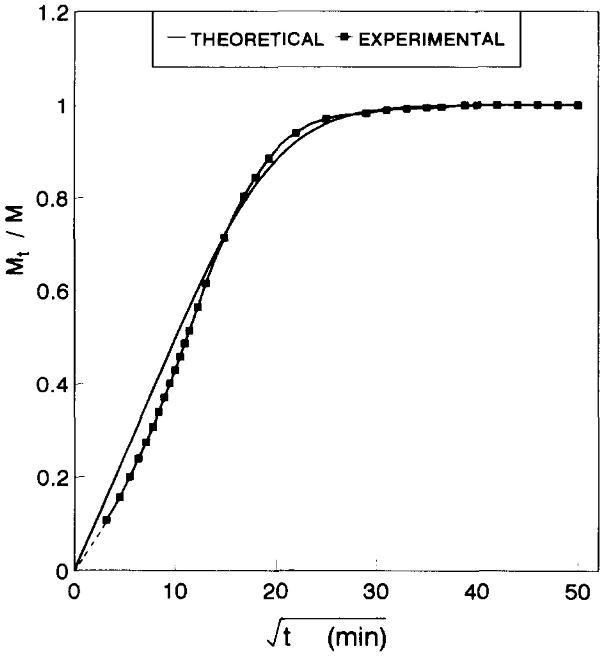

Figure 12 Comparison between experimental and theoretical sorption curves of peroxide sample in toluene

adopting this method the χ for different vulcanized samples were estimated and are shown in *Table 9*. Among all the samples considered, the EV samples had lowest value of χ, and thereby exhibit strongest interaction with solvents. *p*-Xylene has the maximum interaction with EV sample. This is also supported by the high swelling coefficient values of EV samples, particularly in *p*-xylene. In *p*-xylene and mesitylene the interaction parameter values are in the same order as that of extent of swelling, i.e., in the order EV > mixed > CV > DCP. However, in benzene and toluene the χ values are not of the same order as that of extent of swelling.

Comparison with theory

Experimental diffusion results were compared with those of theoretical predictions. The theoretical diffusion curves were simulated using the relation[20]

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{n=\infty}\frac{1}{(2n+1)^2} \times \exp\left[-D(2n+1)^2\pi^2 t/h^2\right] \qquad (18)$$

where M_t and M_∞ are the mass of solvent uptake at time t and at equilibrium; h is the initial sample thickness. This equation truly represents a Fickian mode of diffusion. Experimentally determined diffusivity (D) values are substituted in the above relation. The resulting curves obtained are shown in *Figure 11* and *Figure 12*.

In *Figure 11*, a comparison of experimental and theoretical diffusion curves of efficiently vulcanized sample in toluene is shown. Both theoretical and experimental results are not in very good agreement. The same trend could also be observed in other solvents. CV and mixed systems also showed similar behaviour. *Figure 12* represents the comparison of diffusion results of peroxide vulcanized sample in toluene. Here, the overall agreement is fairly good. The deviation from theoretical prediction for EV, CV and mixed systems is due to the fact that, in these systems, the mechanism of sorption is anomalous. This is evident from the value of n (*Table 4*). However, the mechanism of sorption of peroxide system is very close to Fickian mode. Therefore, the experimental diffusion data are in good agreement with the theoretical predictions. Thus, the theoretical analysis further strengthened the anomalous diffusion behaviour of CV, mixed and EV systems.

CONCLUSIONS

Nature of crosslinking systems plays a central role in the swelling behaviour of the SBR in aromatic hydrocarbons. The maximum solvent uptake values decrease for different systems in the order of EV > mixed > CV > DCP. This is attributed mostly to the extent of crosslinking, which is read directly from volume fraction values of swollen rubber. Thus, efficiently vulcanized samples exhibit highest solvent uptake because of their lower crosslinking density. With an increase in the penetrant size, there is a decrease in the maximum solvent uptake values. There is an inverse dependence on diffusivity on penetrant size and molar volume. In all the cases mechanism of sorption follows an anomalous trend. Temperature was found to activate the diffusion process, which was supported by higher D values and slope values at higher temperatures. As the temperature increases the equilibrium solvent uptake decreases marginally owing to the greater rate of desorption. By using the Van't Hoff relationship entropy and enthalpy of sorption were estimated. The first-order rate equation was found to fit for crosslinked SBR–solvent systems. Rubber–solvent interaction parameter (χ) was computed according to the method suggested by Hays using the Flory–Rehner equation. The χ parameter indicated strong interaction of EV system with all solvents. For peroxide-vulcanized samples the theoretical diffusion results were in good agreement with the experimental.

ACKNOWLEDGEMENTS

The authors thank Mr M. Mathew of RRII, Kottayam, India for providing experimental facilities and also Mr Unnikrishnan, Mahatma Gandhi University, for his valuable help. One of the authors (S.C.G.) is grateful to the University Grants Commission, New Delhi, for awarding a UGC-JRF Fellowship.

REFERENCES

1 Naylor, T. D. in 'Comprehensive Polymer Science' (Eds. C. Booth and C. Price), Pergamon Press, New York, 1989, p. 643
2 Crank, J. and Park, G. S. 'Diffusion in Polymers', Academic Press, London, 1968
3 Berens, A. R. and Hopfenberg, H. B. *Polymer* 1978, **19**, 489
4 Smith, M. J. and Peppas, N. A. *Polymer* 1985, **26**, 569
5 Odani, H., Uchikura, M., Taira, K. and Kurata, M. *J. Macromol. Sci. Phys.* 1980, **B17**(2), 337
6 Yi-Yan, Fielder, R. M. and Koros, W. J. *J. Appl. Polym. Sci.* 1980, **25**, 1755
7 Errede, L. A. *Macromolecules* 1986, **19**, 654
8 Rennar, N. and Opperman, W. *Colloid Polym. Sci.* 1992, **270**, 527
9 Schneider, N. S., Illinger, J. L. and Cleaves, M. A. *Polym. Eng. Sci.* 1986, **26**, 22
10 Aithal, U. S., Aminabhavi, T. M. and Cassidy, P. E. *Polym. Preprints* 1989, **30**(1), 17
11 Harogoppad, S. B. and Aminabhavi, T. M. *J. Appl. Polym. Sci.* 1991, **42**, 2329
12 Harogoppad, S. B., Aminabhavi, T. M. and Balundgi, R. H. *J. Appl. Polym. Sci.* 1992, **44**, 1687
13 Aminabhavi, T. M. and Munnolli, R. S. *Polym. Plast. Technol. Eng.* 1992, **31**(9 and 10), 850
14 Unnikrishnan, G. and Thomas, S. *Polymer* 1994, **35**(25), 5504
15 Mathew, A. P., Packiriswamy, S. and Thomas, S. *Polymer* 1995, **36**, 4935
16 Chiang, K. T. and Setton, M. V. *J. Polym. Sci. Polym. Phys. Ed.* 1977, **15**, 1927
17 Aithal, U. S., Aminabhavi, T. M. and Cassidy, P. E. *J. Membr. Sci.* 1990, **50**, 225
18 Morrell, S. H. in 'Rubber Technology and Manufacture' (Eds. C. M. Blow and C. Hepburn), 2nd edition, Butterworths, London, 1982, Ch. 5
19 Porter, M. *Kaut. Gummi. Kunst.* 1969, **22**(8), 419
20 Aithal, U. S. and Aminabhavi, T. M. *J. Chem. Educ.* 1990, **67**, 82
21 Lucht, L. M. and Peppas, N. A. *J. Appl. Polym. Sci.* 1987, **33**, 1557
22 Chiou, J. S. and Paul, D. R. *Polym. Eng. Sci.* 1986, **26**, 1218
23 Harogoppad, S. B. and Aminabhavi, T. M. *Macromolecules* 1991, **24**, 2595
24 Aminabhavi, T. M. and Khinnavar, R. S. *Polymer* 1993, **34**, 1006
25 Hung, G. W. C. *Microchem. J.* 1974, **19**, 130
26 Aminabhavi, T. M. and Harogoppad, S. B. *J. Chem. Educ.* 1994, **68**, 343
27 Hayes, R. A. *Rubber Chem. Technol.* 1986, **59**, 138