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Sorption and diffusion of arenes through poly (ethylene-co-vinyl acetate) membranes

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Abstract The sorption and diffusion of aromatic hydrocarbons through poly (ethylene-co-vinyl acetate) membranes has been investigated in the temperature interval of 25–70 °C using the sorption gravimetric analysis. The carbon–carbon crosslinks are introduced by using benzoyl peroxide (BP). Diffusion through membranes containing different loading of BP was carried out. For all liquids, the equilibrium solvent uptake was influenced by the penetrant size, temperature and crosslinking density. Thermodynamic constants are estimated from the sorption measurements. The values of polymer–solvent interaction parameters obtained from the diffusion experiments have been used to calculate the molecular mass between crosslinks of the network polymer. The transport mechanism was found to follow close Fickian behavior at 28 °C, but at high temperature, mechanism deviates to anomalous mode of transport.

Introduction

The transport of organic liquids through polymers is of technological importance in a variety of applications [1] such as controlled drug release, microelectronics, pervaporation [2], reverse osmosis [3] and food packaging. The sorption behavior has been extensively studied by many researchers [4–7]. These studies reported that the sorption mechanism was found to be a function of structure of both the polymer and the penetrant molecule. Aminabhavi et al. [8] investigated the sorption characteristics of santoprene rubber in presence of aliphatic alkanes. They found that equilibrium penetrant uptake was influenced by size and shape of the penetrant, polymer morphology and temperature. Siddaramaiah et al. [9] have reported the sorption and diffusion of aldehydes and ketones into natural rubber blends. Unnikrishnan et al. [10] examined the role of the nature of crosslinks on the sorption and diffusion of aromatic hydrocarbons through crosslinked natural rubber. Recently in this laboratory, transport of various organic liquids through a variety of polymers has been investigated [11–15].

The principal aim of the present work is to investigate the effect of C–C crosslinks generated by benzoyl peroxide (BP) on the phenomenon of diffusion of aromatic hydrocarbons through EVA. Diffusion through crosslinked EVA was carried out in the temperature interval of 28–70 °C but for the uncrosslinked samples the experiments were carried out only at 28 °C. The effects of penetrant size, temperature and crosslinking density on the sorption behavior have been investigated. The extent of polymer–solvent interactions has been analyzed from the sorption data.

Experimental

Materials

Poly (ethylene-co-vinyl acetate), EVA (Pilene, 1802), used was supplied by polyolefin Industries Limited, Madras, India. The basic characteristics of the copolymer are given in Table 1. The crosslinking agent used was BP (100% active). The solvents, benzene, toluene, and xylene were of

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reagent grade and were distilled, before use, to ensure purity. All other chemicals were of reagent grade.

Sample preparation

The formulations for different mixes are given in Table 2. Samples containing BP are represented, as B. Samples with different loading of BP were also prepared. The mixing was done in a two roll mixing mill having a friction ratio 1:1.4. The cure properties of the samples were studied in a Goettfert Rheometer. The samples were cured to their optimum cure time. The curing was done in a hydraulic press at 120 °C under a load of 24.5×10^4 N. To prepare uncrosslinked samples, the EVA granules were sheeted out in a two roll mixing mill. The sheeted samples were compression molded in a hydraulic press. The uncrosslinked samples are represented as B_0.

Diffusion experiments

Crosslinked and uncrosslinked EVA samples were cut circularly from dried sheets by means of a sharp edged steel die of diameter 1.9×10^{-2} m and the measurements of the thickness were made at several points with an accuracy of $\pm 0.1 \times 10^{-4}$ m by using micrometer screw gauge. These circularly cut EVA samples were weighed initially, and placed in test bottles having air tight stoppers containing 25×10^{-6} m^3 of the respective solvents. The samples were removed periodically, and their surfaces were wiped with a tissue paper to remove the adherent solvent and then weighed quickly on a digital Mettler balance. This procedure was repeated for all liquids until equilibrium swelling was attained. The transport studies were carried out at four different temperatures namely, 28 °C, 40 °C, 50 °C, and 60 °C. A possible chance of error in this method arises during the weighing operation where the sample has to be removed from the bottle. Since the weighing was done within 30–40 s, this error can be neglected. The results of solvent uptake by the polymer are expressed as mol% of the solvent sorbed by 0.1 kg of the polymer (Q_t). The experiments were duplicates or triplicates in most cases and the standard deviation was found to range from 0.07 to 0.1.

Results and discussion

Effect of crosslinks on diffusion

The sorption curves, expressed as mol% uptake of the solvent, Q_t vs. square root of time, $t^{1/2}$ have been plotted. Figure 1 shows the benzene uptake of uncrosslinked and crosslinked poly (ethylene-co-vinyl acetate) samples at 28 °C. It is clearly evident that B_1 sample possesses higher solvent uptake than the uncrosslinked (B_0) sample. Similar trends were also observed for the other two solvents. The Q_∞ values are given in Table 3. The low solvent uptake of the uncrosslinked poly (ethylene-co-vinyl acetate) is associated with its crystalline nature. Due to the long-range order, polymer is highly compact and hence the free volume is low. When moderate amounts of BP were introduced, these molecules cause some disorder in the crystal structure by introducing C–C networks. Thus the increased solvent uptake of crosslinked samples is due to the formation of C–C networks introduced by BP molecules. As a result crystallinity is substantially reduced in the crosslinked samples. X-ray diffraction studies of the uncrosslinked and crosslinked EVA were done using the wavelength 1.54×10^{-10} m to support the above data and is represented in Fig. 2.

Figure 3 shows the effect of the number of moles of BP on the equilibrium mol% uptake of the three solvents. The equilibrium mol% uptake of the crosslinked EVA membranes for all solvents decrease in the order $B_1 > B_2 > B_4 > B_6 > B_8$. When the amount of BP is increased, the extent of crosslinking goes up and this prevents the migration of the solvent molecules into the network. As crosslink density increases, the contribution of the crosslink constraints on the penetrant chemical potential becomes stronger and solvent uptake decreases accordingly. In fact, the decreases in crystallinity are offset by the increase in crosslinking density. It has been found that a critical concentration of crosslinker is necessary for

Table 1 Details of the material used

Material	Properties		Source
Poly (ethylene-co-vinyl acetate) (Pilene 1802)	Melt flow index (kg/600 s) (ASTM D 1238)	2×10^{-3}	PIL, Chennai, India
	Density (kg m^{-3}) (ASTM D 1505)	0.94×10^3	
	Vicat softening point (°C) (ASTM D 1525)	59.0	
	Vinyl acetate (%)	18.0	
	Intrinsic viscosity (m^3 kg^{-1}) (ASTM D 2857)	0.017	
	T_g (°C) (ASTM D 3417)	–10	

Table 2 Composition of the mixes

Weight of the polymer (kg)	Weight of BP (kg)	Number of moles of BP	Representation of the samples
0.1	0	0	B_0
0.1	0.001	0.004	B_1
0.1	0.002	0.008	B_2
0.1	0.004	0.016	B_4
0.1	0.006	0.025	B_6
0.1	0.008	0.033	B_8

maximum sorption, followed by a decrease at higher concentration of the crosslinker.

Effect of penetrant properties

From the Q_∞ values (Table 3) and Fig. 4, it is observed that the equilibrium mol% benzene uptake is maximum, while xylene uptake is least and toluene uptake is intermediate. A systematic trend on the sorption of liquids with different molecular weights was observed. When the molecular weight of liquids is increased the solvent uptake of the samples decreased. The decrease of solvent uptake with increasing size of penetrant molecules might be due to the greater activation energy required for activating the sorption process. Similar results were reported earlier in the literature [10]

Mechanism of transport

Table 3 Values of equilibrium sorption (Q_∞) (mol%)

Solvent	Temperature (°C)	B_0	B_1	B_2	B_4	B_6	B_8
Benzene	28	2.51	3.16	3.01	2.88	2.82	2.77
	40		10.13	7.46	5.89	4.91	4.36
	50		13.66	9.73	7.34	6.78	6.18
	70		15.42	11.19	8.08	7.99	7.93
Toluene	28	2.41	3.06	2.93	2.83	2.78	2.62
	40		9.89	5.49	4.77	4.57	4.02
	50		12.59	8.73	6.78	6.21	5.69
	70		14.66	10.19	7.98	7.51	6.46
Xylene	28	1.99	2.93	2.83	2.76	2.69	2.59
	40		9.00	5.26	4.64	4.39	3.95
	50		11.99	8.49	6.59	5.85	5.33
	70		14.29	9.94	7.79	7.30	6.45

In order to investigate the type of transport mechanism, the sorption results were fitted into the following equation [8, 16]

$$\log Q_t/Q_\infty = \log k + n \log t \quad (1)$$

where Q_t and Q_∞ are the mol% solvent uptake at time t and at equilibrium respectively and k is a parameter which depends on the structural characteristics of the polymer in addition to its interaction with the solvent. The value of n indicates the type of the mechanism. The value of $n = 0.5$ indicates Fickian transport while $n = 1$ shows case II (relaxation controlled) transport. The values of n between

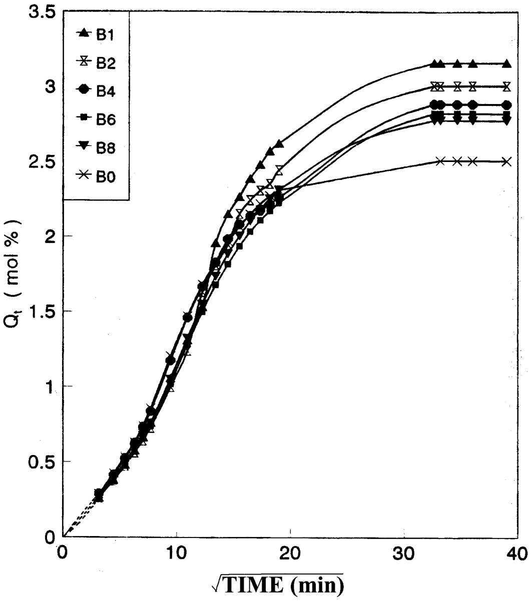

Fig. 1 Mol % benzene uptake of uncrosses linked and cross-linked EVA samples at 28 °C

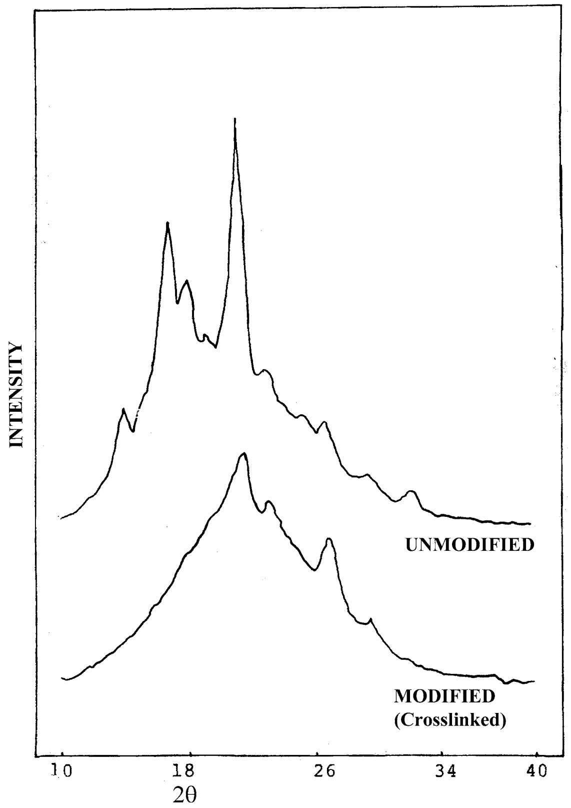

Fig. 2 X-ray diffraction patterns of neat (unmodified) and cross-linked membranes

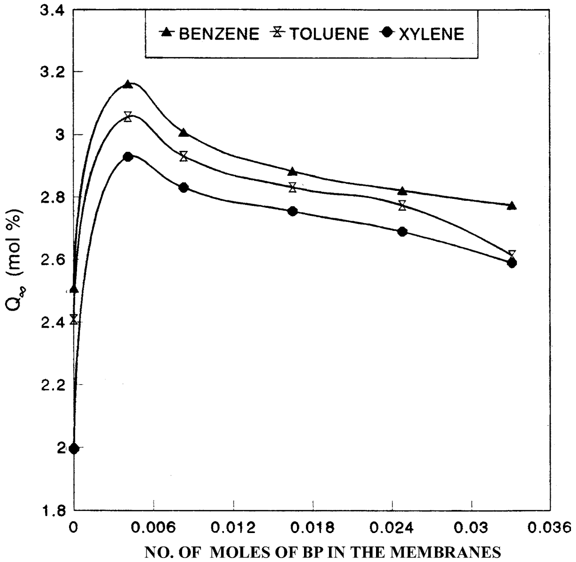

Fig. 3 Effect of the number of moles of BP on the equilibrium mol % uptake of solvents

0.5 and 1 indicate an anomalous mode of transport. Also there have been reports of $n > 1$ which is called super case II [17].

The values of n and k for all samples in the three solvents were determined by regression analysis of the linear portion of plots log (Q_t/Q_∞) versus log t. To assure linearity, the values up to 50% of the equilibrium uptake were only used. The estimated values of n and k are compiled in Table 4. At 28 °C, the values of n are close to 0.5 for the crosslinked and uncrosslinked samples in all the three solvents. Hence they all show the Fickian mode of transport. However, at high temperatures, the values of n vary between 0.73 and 0.97 suggesting that the mechanism appear to follow an anomalous mode of transport.

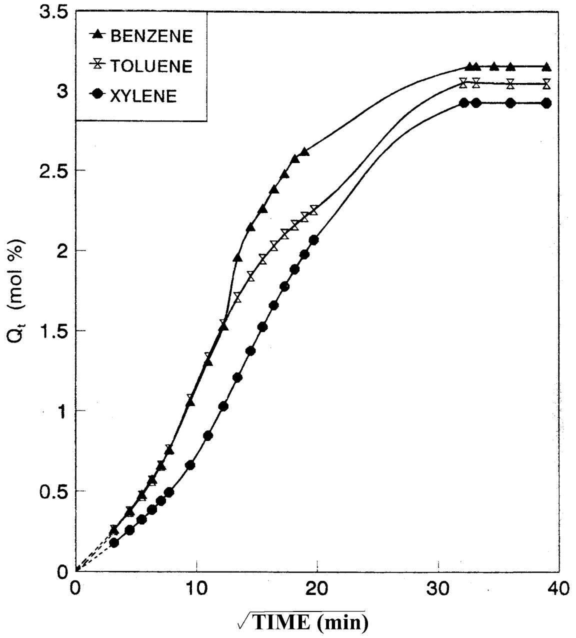

Fig. 4 Mol % solvent uptake of B_1 sample at 28 °C

Transport coefficients

From the slope θ of the initial linear portion of the sorption curves (Q_t vs. $t^{1/2}$) the diffusion coefficient, D, was calculated using the equation [8, 18]

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

where, h is the thickness of the polymer sample and Q_∞ is the equilibrium mol% uptake. Since significant swelling of polymer samples was observed during sorption experiments in all solvents, correction to diffusion coefficients under swollen conditions was essential. This was done by calculating the intrinsic diffusion coefficient D^*, from the volume fraction of polymer in the swollen sample using the relation [19].

$$D^* = \frac{D}{\phi^{7/3}} \tag{3}$$

The modified diffusion coefficient values known as intrinsic diffusion coefficient are given in the Table 5. The D^* values decreases regularly from B_1 to B_8 for the crosslinked samples. Thus when the extent of crosslinking increases, the intrinsic diffusion coefficient values decrease. Also, it is noticeable that in each system, D^* value increases with temperature. The increase of D with temperature invariably points out the activation of the diffusion process at higher temperatures.

The permeation of a penetrant into a polymer membrane depends on the diffusivity as well as on the sorption. Hence sorption coefficient is calculated using the equation [13]

$$S = \frac{M_\infty}{M_0} \tag{4}$$

where, M_∞ is the mass of the solvent at equilibrium swelling and M_0 is the initial polymer mass. The values of S are given in the Table 6. For the crosslinked systems, S is found to be maximum for B_1 and minimum for B_8 in all the three solvents. The maximum sorption coefficient for the B_1 system reveals that the flexible polymer chains better accommodate the sorbed molecules. The B_8 system shows the least capability to accommodate the solvent molecules. When the amount of BP increases, the extent of crosslinking becomes too high and this prevents sorption. The very low sorption of uncrosslinked system is due to the crystallinity of the polymer. Thus by the introduction of C–C crosslinks, the sorption first increases and when extent

Table 4 Analysis of sorption data of aromatic hydrocarbons in EVA at different temperatures

Solvent	Temperature (°C)	n						$k \times 10^{-2}$					
		B_0	B_1	B_2	B_4	B_6	B_8	B_0	B_1	B_2	B_4	B_6	B_8
Benzene	28	0.56	0.56	0.55	0.55	0.57	0.55	3.12	2.26	2.46	2.77	2.82	2.8
	40		0.75	0.75	0.76	0.77	0.67		0.52	0.71	0.97	1.09	1.52
	50		0.91	0.85	0.85	0.80	0.79		0.34	0.59	0.77	0.89	1.01
	70		0.95	0.91	0.83	0.97	0.82		0.49	0.77	1.22	0.78	1.15
Toluene	28	0.54	0.56	0.57	0.57	0.57	0.56	3.52	2.29	2.28	2.34	2.52	2.58
	40		0.76	0.71	0.73	0.73	0.72		0.48	0.97	1.08	1.15	1.31
	50		0.92	0.86	0.78	0.76	0.75		0.36	0.58	0.89	1.03	1.23
	70		0.93	0.90	0.79	0.80	0.81		0.72	0.84	1.34	1.39	1.58
Xylene	28	0.42	0.55	0.55	0.55	0.56	0.56	4.75	1.70	1.74	1.91	1.97	1.93
	40		0.84	0.82	0.79	0.72	0.73		0.31	0.52	0.69	0.65	0.78
	50		0.86	0.82	0.78	0.73	0.79		0.30	0.46	0.68	0.80	0.93
	70		0.90	0.85	0.82	0.81	0.80		0.43	0.98	0.94	1.19	1.07

of crosslinking is too high sorption decreases. The sorption coefficients of the crosslinked samples are found to increase with increase in temperature for all solvents. Thus sorption is activated by temperature. Permeation is a collective process of diffusion and sorption and hence permeation coefficient, P, can be defined as [17, 18]

$$P = D^{*} \times S \tag{5}$$

where, D^* is the intrinsic diffusion coefficient and S, the sorption coefficient. Table 6 gives the values of P. The permeability coefficient shows the net effect of sorption and diffusion. The temperature activates permeation too. It can be seen from the Table 6 that permeation coefficients increase with rise in temperature.

Effect of temperature

Diffusion experiments were conducted at 40 °C, 50 °C and 70 °C besides 28 °C in order to follow the effect of temperature on the diffusion mechanism in EVA. As temperature increases the maximum solvent uptake (Q_∞) also increases. The Q_∞ values at high temperature are given in the Table 3. The Q_∞ value increases with temperature indicating that temperature activates the solvent uptake. The plots of Q_t vs. $t^{1/2}$ at various temperatures for the B_1 system are shown in Fig. 5. The solvent used is benzene. It has been observed that the slope of the linear portion increases with temperature indicating that the transport process is temperature activated. The shape of the curves at high temperatures is different from those at 28 °C. This indicates that at high temperature the solvent transport occurs by different mechanism. This is clearly manifested in the values of n. From Table 4 it can be seen that at high temperature, diffusion follows anomalous mode of transport whereas at 28 °C diffusion follows Fickian mode. For the uncrosslinked system the high temperature diffusion experiments were not possible because the solvent dissolved the samples. There is an increase in the intrinsic diffusion coefficient (D^*) at values with increase in temperature. Table 5 gives the values of D^* at higher temperatures. It can be seen that the temperature activates diffusion process.

According to Huang [11] the thermodynamic sorption constant (K_s) is defined as

$$K_S = \frac{\text{No. of mols of solvent sorbed at equilibrium}}{\text{Mass of the polymer sample}} \tag{6}$$

Thermodynamic sorption constant is a measure of the solvent uptake by the polymer. The values of K_s were estimated and given in Table 7. The highest values are obtained for B_1 system and lowest for B_0 system. The low values of K_s for B_0 system are associated with crystallinity of the polymer. With the introduction of BP, disorder is created in the crystal lattice due to the formation of C–C networks. Thus polymer chains become flexible and hence solvent uptake increases. For the crosslinked samples values of K_s decrease in the order $B_1 > B_2 > B_4 > B_6 > B_8$. The observed reverse trend is due to the formation of large

Table 5 Values of $D^* \times 10^6$ ($m^2 s^{-1}$) at different temperatures for EVA samples

Solvent	Temperature (°C)	B_0	B_1	B_2	B_4	B_6	B_8
Benzene	28	0.025	0.049	0.042	0.039	0.039	0.038
	40		13.30	3.89	1.67	0.83	0.45
	50		146.5	31.3	9.27	6.32	4.45
	70		940.5	216.1	39.7	36.4	33.2
Toluene	28	0.013	0.11	0.09	0.09	0.09	0.08
	40		35.20	3.35	1.81	1.58	0.90
	50		361.9	59.6	16.6	11.0	7.90
	70		2980.4	394.5	87.9	77.85	41.9
Xylene	28	0.019	0.13	0.09	0.09	0.09	0.08
	40		36.72	3.54	1.76	1.48	0.95
	50		263.5	49.0	15.4	8.50	5.80
	70		2569.5	344.9	119.1	89.0	43.9

Table 6 Values of sorption coefficients (S) and permeation coefficients ($P \times 10^8$ m^2 s^{-1})

Solvent	Temp (°C)	S						$P \times 10^8$					
		B_0	B_1	B_2	B_4	B_6	B_8	B_0	B_1	B_2	B_4	B_6	B_8
Benzene	28	1.9	2.5	2.3	2.2	2.2	2.1	0.005	0.012	0.009	0.0087	0.0085	0.0082
	40		7.9	5.8	4.6	3.8	3.4		10.50	2.26	0.768	0.318	0.153
	50		10.7	7.6	5.7	5.3	4.8		156.2	23.7	5.316	3.34	2.14
	70		12.0	8.7	6.3	6.2	6.1		1132.6	188.8	25.05	22.7	20.5
Toluene	28	2.2	2.8	2.7	2.6	2.5	2.4	0.002	0.031	0.024	0.023	0.02	0.019
	40		9.1	5.1	4.4	4.2	3.7		32.07	1.69	0.795	0.665	0.33
	50		11.6	8.0	6.2	5.7	5.2		420.0	47.9	10.37	6.29	4.12
	70		13.5	9.4	7.3	6.9	5.9		4025.3	370.2	64.63	53.8	24.9
Xylene	28	2.1	3.1	3.0	2.9	2.8	2.7	0.004	0.040	0.027	0.026	0.025	0.022
	40		9.6	5.6	4.9	4.7	4.2		35.1	1.97	0.86	0.689	0.398
	50		12.7	9.0	6.9	6.2	5.7		335.4	44.17	10.76	5.27	3.28
	70		15.1	10.6	8.3	7.8	6.8		3897.9	364.0	98.48	69.00	30.07

extent of crosslinks. When the amount of BP increases the extent of crosslinking too increases and hence the solvent uptake decreases. As the size of the penetrant molecules increase the sorption constant decreases for all the system. It was also found that sorption constant increase with the rise in temperature for all the systems studied. From the values of K_s, the standard entropy (ΔS^0) and standard enthalpy (ΔH^0) for the crosslinked EVA samples was calculated using Van't Hoffs equation [20]

$$\log K_S = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \tag{7}$$

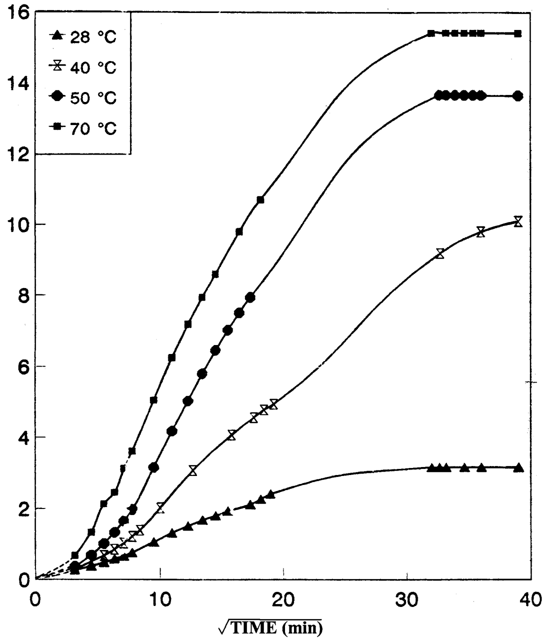

Fig. 5 Temperature dependence of mol % uptake of B_1 sample

The standard free energy change (ΔG^0) for the diffusion process was calculated using the equation.

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

Table 8 gives the values of ΔS^0, ΔH^0 and ΔG^0. Entropy values are found to be positive and thus entropy factor favors the spontaneity of the process. Entropy change is highest for B_1 system and least for B_8 system. Thus entropy change decreases when the degree of crosslinking becomes higher. There is no systematic trend for entropy change with increasing size of the penetrants. For all the systems, the entropy change is minimum in toluene and maximum in benzene. Standard enthalpy values are positive suggesting that sorption is dominated by Henry's law. The heat of sorption is highest for B_1 system and least for B_8 system in all solvents.

The value of free energy change is maximum for B_8 system and least for B_1 system. Therefore it can be stated that the sorption process is more spontaneous in B_1 system and less feasible in B_8 system. The values of standard free energy change increase with the molecular size of penetrants for all the systems studied.

Volume fraction

The volume fraction (ϕ) of the solvent swollen polymer is calculated using the equation [4]

$$\phi = \frac{W_1/\rho_1}{W_1/\rho_1 + W_2/\rho_2} \tag{9}$$

where, W_1 and ρ_1 are the weight and density of the polymer sample respectively and W_2 and ρ_2 are the weight and density of the solvent respectively. Table 9 gives the values of ϕ. The value of volume fraction is a measure of the crosslinking density and it can be concluded that as the

Table 7 Thermodynamic sorption constants (K_s, mol kg^{-1})

Solvent	Temperature (°C)	B_0	B_1	B_2	B_4	B_6	B_8
Benzene	28	25.1	31.6	30.1	28.8	28.2	27.7
	40		101.2	74.6	58.9	49.1	43.6
	50		136.5	97.3	73.4	67.8	61.8
	70		154.2	111.8	80.7	79.9	79.3
Toluene	28	24.1	30.5	29.3	28.3	27.8	26.2
	40		98.9	54.9	47.7	45.7	40.2
	50		125.9	87.2	67.8	62.1	56.9
	70		146.6	101.8	79.8	75.1	64.6
Xylene	28	19.9	29.2	28.3	27.5	26.9	25.9
	40		90.0	52.6	46.3	43.8	39.5
	50		119.8	84.9	65.8	58.5	53.3
	70		142.9	99.4	77.9	73.0	64.5

volume fraction values decrease the crosslinking density also decreases. For the crosslinked systems volume fraction is maximum for B_8 system. Thus it is clearly evident that when the amount of BP used for crosslinking was increased degree of crosslinking also increased. The highest value for B_8 system indicates that the maximum number of crosslinks was formed in B_8 system. Therefore the solvent uptake behavior follows the order $B_1 > B_2 > B_4 > B_6 > B_8$. The values of volume fraction decreased when temperature was increased. Similar trends were observed for all system in all other solvents also.

The polymer–solvent interaction parameter (χ) has been calculated using the equation [10]

$$\chi = \frac{(\mathrm{d}\phi/\mathrm{d}T)\{[\phi/(1-\phi)] + N\ln(1-\phi) + N\phi\}}{2\phi(\mathrm{d}\phi/\mathrm{d}T) - \phi^2 N(\mathrm{d}\phi/\mathrm{d}T) - \phi^2/T} \tag{10}$$

where, ϕ is the volume fraction of the polymer in the solvent swollen sample and N is calculated from using the equation [10]

Table 8 Thermodynamic parameters standard free energy ΔG^0 (kJ mol^{-1}), entropy ΔS^0 (J mol^{-1}) and enthalpy ΔH^0 (kJ mol^{-1})

Solvent	Samples	ΔG^0	ΔS^0	ΔH^0
Benzene	B_1	8.23	84.84	33.76
	B_2	8.45	64.66	27.91
	B_4	8.62	44.19	21.92
	B_6	8.72	44.33	22.26
	B_8	8.82	44.23	22.13
Toluene	B_1	8.34	83.12	33.35
	B_2	8.55	59.49	26.45
	B_4	8.70	44.01	21.95
	B_6	8.79	40.71	21.04
	B_8	8.92	34.06	19.17
Xylene	B_1	8.46	83.83	33.69
	B_2	8.64	59.96	26.68
	B_4	8.78	43.99	22.02
	B_6	8.89	40.44	21.06
	B_8	8.99	34.14	19.26

Table 9 Values of volume fraction (ϕ) of the swollen polymer

Solvent	Temperature (°C)	B_0	B_1	B_2	B_4	B_6	B_8
Benzene	28	0.32	0.27	0.28	0.29	0.30	0.30
	40		0.11	0.13	0.16	0.19	0.21
	50		0.08	0.11	0.14	0.15	0.16
	70		0.07	0.09	0.12	0.13	0.13
Toluene	28	0.29	0.24	0.25	0.26	0.26	0.27
	40		0.09	0.15	0.17	0.18	0.19
	50		0.07	0.10	0.13	0.14	0.15
	70		0.06	0.08	0.11	0.12	0.13
Xylene	28	0.30	0.22	0.23	0.24	0.24	0.25
	40		0.08	0.13	0.15	0.16	0.18
	50		0.06	0.09	0.11	0.13	0.14
	70		0.05	0.07	0.09	0.10	0.12

$$N = \frac{\phi^{2/3}/3 - 2/3}{\phi^{1/3} - 2\phi/3} \tag{11}$$

The values of χ are a measure of the polymer–solvent interaction. As χ increases solvent interaction with the polymer decreases. The values of χ for EVA benzene systems are given in Table 10. Among the different crosslinked samples, the value of χ follows the order: $B_8 > B_6 > B_4 > B_2 > B_1$. The values are lowest for the B_1 system compared to all other systems in all the three solvents. This clearly shows the higher interaction of B_1 system with the penetrants than all other samples. The B_8 samples showed the lowest interaction with penetrants. Thus the polymer–solvent interaction parameter supports the different sorption behavior of crosslinked samples.

Molecular mass between crosslinks

The molecular mass between the crosslinks [M_c {chem.}] of the network polymer was estimated using the equation developed from Flory–Rehner theory [21].

$$M_\mathrm{C} = \frac{-\rho_\mathrm{p} V \phi^{1/3}}{[\ln(1-\phi) + \phi + \chi\phi^2]} \tag{12}$$

where, ρ_p is the density of the polymer, V the molar volume of solvent, χ the polymer–solvent interaction parameter and ϕ the volume fraction of the polymer. The calculated M_c values are placed in Table 11. It is interesting to see that the M_c for a given solvent decreases from B_1 to B_8. This

Table 10 Values of interaction parameter (χ)

Solvent	B_1	B_2	B_4	B_6	B_8
Benzene	0.614	0.619	0.623	0.625	0.626
Toluene	0.598	0.600	0.603	0.604	0.609
Xylene	0.581	0.585	0.587	0.588	0.589

indicates clearly that the samples have different degrees of crosslinking. The highest value for B_1 system shows that crosslinks are farthest and hence more space is available for solvents. The low M_c values for B_8 indicate high extent of crosslinking in this system.

Flory and Rehner [22] relations were developed for a network deforming affinely, i.e., the components of each chain vector transform linearly with macroscopic deformation and the junction points are assumed to be embedded in the network without fluctuations. The molecular weight between crosslinks (M_c) for the affine limit of the model [M_c (aff)] was calculated using the formula.

$$M_\mathrm{c}\,(\mathrm{aff}) = \frac{\rho_\mathrm{p} V \phi_{2\mathrm{c}}^{2/3} \phi_{2\mathrm{m}}^{1/3} \left(1 - \mu \big/ v\phi_{2\mathrm{m}}^{1/3}\right)}{-\left[\ln(1 - \phi_{2\mathrm{m}}) + \phi_{2\mathrm{m}} + \chi\phi_{2\mathrm{m}}^{2}\right]} \tag{13}$$

where μ and V are the number of effective chains and junctions; ϕ_{2m}, the polymer volume fraction at swelling equilibrium; ϕ_{2c}, the polymer volume fraction during crosslinking.

James and Guth [23] proposed the phantom network model where the chain may move freely through one another. According to the theory the molecular weight between crosslinks for the phantom limit of the model [M_c (ph)] was calculated by

$$M_\mathrm{c}\,(\mathrm{aff}) = \frac{(1 - 2/x)\ \rho_\mathrm{p} V \phi_{2\mathrm{c}}^{2/3} \phi_{2\mathrm{m}}^{1/3}}{\left[\ln(1 - \phi_{2\mathrm{m}}) + \phi_{2\mathrm{m}} + \chi\phi_{2\mathrm{m}}^{2}\right]} \tag{14}$$

where x is the junction functionality, the values are given in Table 11. It is seen that M_c (chem.) values are close to M_c (aff). This suggests that in the highly swollen state of B_1, B_2, B_4, B_6 and B_8 the network deforms affinely.

Conclusion

The effect of carbon–carbon crosslinks on the sorption and diffusion of aromatic hydrocarbons through poly (ethylene-co-vinyl acetate) has been investigated by sorption gravimetric analysis. Such a study is important in applications including pervaporation, barrier packaging, etc. It is found that carbon–carbon crosslinks produced by BP has profound influence on the transport process though EVA. The uncrosslinked EVA system possesses the lowest solvent uptake due to its crystalline nature. The crosslinked sample B_1 possess high solvent uptake value than that of neat EVA. With the introduction of BP, the long-range order present in EVA is disrupted due to formation of C–C networks. This has been supported by wide-angle X-ray scattering studies. But for the crosslinked samples solvent uptake decreases in the order $B_1 > B_2 > B_4 > B_6 > B_8$. This is mainly due to the increase in the extent of crosslinking. Thus it is clear that an optimum amount of BP is necessary for maximum sorption. With an increase in the penetrant size, there is a decrease in the maximum solvent uptake values. It was found that the temperature activates the diffusion process which was supported by the higher D^* values and slope values at higher temperatures. The value of equilibrium mol% uptake also increases with the rise in temperature. The values of entropy change were calculated using Van't Hoffs equation.

The mechanism of transport was found to be close to the normal Fickian behavior at 28 °C but at high temperature, mechanism deviates to anomalous mode. Using Flory–Rehner theory the polymer–solvent interaction parameter has been estimated. The calculated values of interaction parameter indicate the highest interaction of B_1 (EVA containing 1% crosslinking agent) system with all the solvents used in this work. The polymer morphology has been analyzed by the estimation of the molar mass between crosslinks.

Table 11 Values of molecular weight between crosslinks (kg mol^{-1})

M_c	Solvent	B_1	B_2	B_4	B_6	B_8
M_c (chem.)	Benzene	9.83	22.92	34.72	46.54	56.06
	Toluene	8.18	14.47	18.64	21.51	32.73
	Xylene	6.09	11.23	14.48	19.17	27.89
M_c (aff)	Benzene	9.76	22.62	33.82	44.76	53.25
	Toluene	8.13	14.28	18.16	20.67	31.09
	Xylene	6.05	11.09	14.10	18.44	26.49
M_c (ph)	Benzene	4.88	11.31	16.91	22.38	26.63
	Toluene	4.06	7.14	9.08	10.34	15.54
	Xylene	3.02	5.54	7.05	9.22	13.25

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