

# Mass Transfer Characteristics of Natural Rubber/Ethylene Vinyl Acetate Blends

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**ABSTRACT:** The transport behavior of natural rubber/ethylene vinyl acetate (NR/EVA) blends has been investigated using aromatic hydrocarbons as probe molecules, in the temperature range of 26–56°C. It has been observed that the solvent uptake decreases with increase in the EVA content of the blends. The blends were crosslinked by three systems, viz. sulfur, dicumyl peroxide (DCP), and a mixture consisting of sulfur and peroxide. The DCP crosslinked system exhibited the lowest solvent uptake. The differences in the transport behavior of the blends, crosslinked by different modes, has been described in terms of the nature of

crosslinks introduced between the macromolecular chains during vulcanization. The mechanism of transport has been found to deviate from the regular Fickian behavior, observed with conventional rubbers, with an increase in EVA in the blends. The dependence of the transport coefficients on blend composition, crosslinking systems, nature of penetrants, and temperature was studied. The blend–solvent interaction parameter, enthalpy, and entropy of sorption have also been estimated from the transport data. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2691–2702, 2003

## INTRODUCTION

The transport characteristics of macromolecular systems have been studied extensively by several researchers.<sup>1–7</sup> The dimensional stability and integrity of polymeric materials in an aggressive liquid environment is highly essential for their successful technological and engineering applications. It is well established that the sorption and diffusion of penetrants through polymers is controlled by the polymer structure, its crosslink density, presence of fillers, nature, and size of penetrants, temperature, etc.<sup>8–10</sup> Solvent transport in elastomers can generally be described by Fick's laws of diffusion. Glassy polymers, however, because of their time-dependant response show non-Fickian or anomalous transport behavior.<sup>11</sup>

Salmawi et al.<sup>12</sup> studied the sorption of dye wastes by poly (vinyl alcohol)/poly (carboxy methyl cellulose) (PVA/CMC) blends grafted through a radiation method. It was found that the sorption of dyes depends on the weight of the blend graft copolymer and not on the volume of the waste solution. Sidharamaiah et al.<sup>13</sup> studied the sorption and diffusion of a number of aldehydes and ketones through different NR blends

of bromobutyl, chlorobutyl, neoprene, ethylene propylene diene monomer, polybutadiene, and styrene butadiene rubber at 25, 40, and 60°C. For all the solvents the polymer blends remained inert, but in the presence of benzaldehyde, they showed degradative reactions at higher temperature. Aminabhavi and Phayde<sup>14</sup> used a new experimental protocol based on the measurements of sorption, desorption, resorption, and redesorption to study the molecular transport of aliphatic alkanes through thermoplastic miscible blends of ethylene–propylene random copolymer and isotactic polypropylene. Our research<sup>15–19</sup> group also conducted investigations on the transport behavior of different liquids through a variety of polymer matrices.

The goal of the present work is to investigate the transport behavior of three aromatic hydrocarbons through natural rubber/ethylene vinyl acetate (NR/EVA) blends in the temperature range of 26–56°C, with particular attention to the effects of blend composition, nature of crosslinks, penetrant size, and temperature. The kinetic and thermodynamic coefficients of transport have also been determined.

## EXPERIMENTAL

### Materials

Natural rubber (NR) used was of ISNR-3L grade, supplied by Rubber Research Institute of India, Kottayam, Kerala. Ethylene vinyl acetate (EVA) was supplied by

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**TABLE I**  
**Formulation of the Mixes (phr)**

Ingredient	Vulcanizing system		
	Sulfur	DCP	Mixed
Polymer	100.0	100.0	100.0
Zinc oxide	5.0	5.0	5.0
Stearic acid	1.5	1.5	1.5
MBTS <sup>a</sup>	0.8	—	0.8
Dicumyl peroxide (40% active)	—	4.0	4.0
Sulfur	2.5	—	2.5

<sup>a</sup> Mercaptobenzothiazyl disulfide

EXXON Chemical Company, Houston, TX. The additives such as sulphur, dicumyl peroxide (DCP), zinc oxide, stearic acid, and mercaptobenzothiazyl disulfide (MBTS) used were of commercial grade. The solvents benzene, toluene, and xylene were obtained from E. Merk (India) Ltd., Mumbai, India. They were of reagent grade (99% pure), and were distilled twice before use to ensure purity.

### Preparation of blends

The NR/EVA blends were prepared on a two roll mixing mill (150 × 300 mm) at a nip gap of 1.3 mm and at a friction ratio of 1 : 1.4. The nip gap, mill speed ratio, time of mixing, and temperature of the rolls were kept the same for all mixes. The formulation of the mixes is given in Table I. The vulcanization behavior of the mixes was followed by using a Monsanto Rheometer R-100 at a rotational frequency of 100 cycles/min. Blanks cut from the uncured samples were marked with the direction of the mill grain and were vulcanized at 160°C in a hydraulic press having electrically heated platens under a pressure of 30 tonnes. Due to the processing difficulty we could not, however, prepare sulfur vulcanized 20/80 NR/EVA and 0/100 NR/EVA samples.

### Sorption experiments

Circular samples of a diameter of 1.9 cm were punched out from the vulcanized NR/EVA blend samples using a sharp steel die, and were used in sorption experiments that monitored liquid sorption gravimetrically. Initially, samples were dried overnight in a vacuum desiccator and the original weights were taken. The thickness of the samples was measured using a dial gauge with an accuracy of ±0.01 mm. They were then immersed in different solvents in air-tight test bottles. At regular intervals, the test samples were removed from the solvent and damp dried for 5–10 s between filter papers to remove the excess solvent on their surfaces. They were then weighed immediately using an electronic balance (Shimadzu,

Libror AEU-210 Japan) that measured reproducibly within ±0.0001 g. The samples were immediately re-immersed in the test liquids to permit the continuation of the kinetic sorption until saturation in excess liquid was established. A possible source of error in this method arises during the weighing operation, where the sample has to be removed from the test bottle. However, because the weighing was done within 30–40 s, the error can be neglected.<sup>20</sup> Similar methodology has been adopted by several researchers.<sup>21–23</sup>

### Morphology studies

Samples for scanning electron micrographs (SEM) were prepared by cryogenically fracturing the samples in liquid nitrogen. The samples were sputter coated with gold and the photographs were taken using a scanning electron microscope (S-2400, Hitachi).

## RESULTS AND DISCUSSION

The results of sorption experiments have been expressed as mol of liquid  $Q_t$  sorbed by 100 g of the blends vs. the square root of time. Each value presented in this article represents an average obtained from at least three experiments.

Figure 1 shows the liquid sorption behavior of different NR/EVA blend systems at 26°C, vulcanized using DCP. The penetrant used was benzene. It is clear from the figure that the liquid uptake tendency decreases with increase in EVA content in the blends. Pure EVA shows the lowest solvent uptake. EVA is a semicrystalline polymer. The crystalline regions of EVA put up stiffer resistance to the penetrant molecules leading to a lower solvent uptake. Upon blending with amorphous NR, the flexibility of EVA matrix increases due to enhanced macromolecular chain rearrangements. This results in higher penetrant ingress into the matrix, which regularly increases with increase in the weight percent of NR in the blends. A schematic representation of the reduction in crystallinity of EVA upon blending with NR is given in Figure 2, where the dotted lines represent the NR chains that migrate into the crystalline regions of pure EVA. The difference in the solvent uptake behavior can also be explained in terms of the difference in the solubility parameter ( $\delta$ ) values. The greater the difference in solubility parameter values, the lesser is the affinity of a polymer to a solvent. The difference in the solubility parameters of the solvent and the polymer blend ( $\delta_s - \delta_p$ ) has been plotted against the equilibrium sorption values in Figure 3. It is clear from the figure that as ( $\delta_s - \delta_p$ ) increases, the equilibrium sorption value  $Q_\infty$  decreases.

Figure 4 shows the sorption curves of 60/40 NR/EVA blends vulcanized by sulfur, DCP, and a mixed

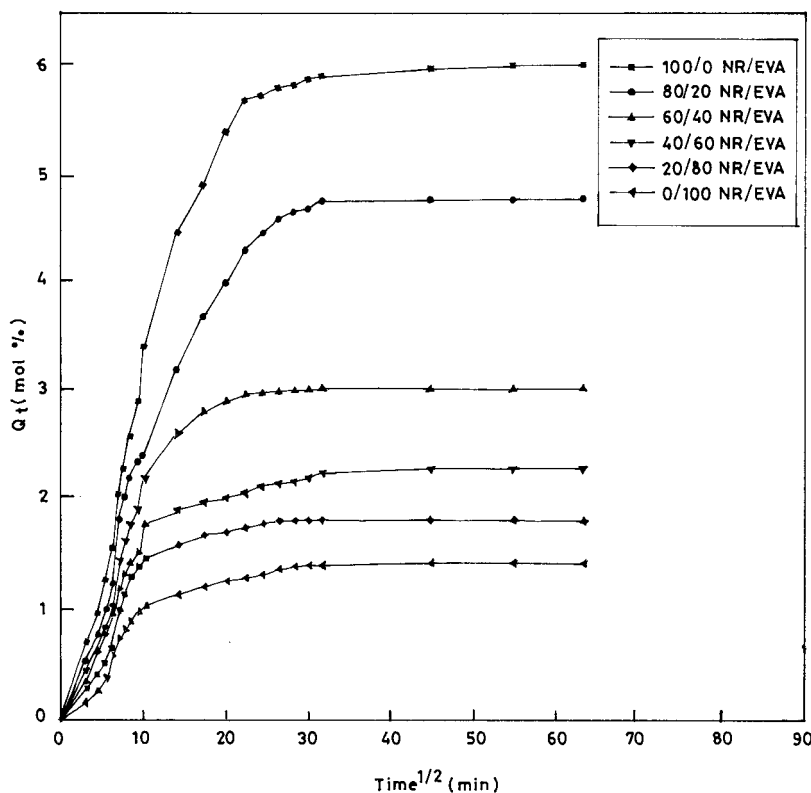


Figure 1 Mol % uptake of benzene by different blend systems crosslinked with DCP at 26°C.

system. The solvent used was benzene. It is found that the liquid sorption behavior follows the order sulfur > mixed > DCP. We observed the same order for our

earlier systems also<sup>18,24,25</sup> The differences in the solvent uptake behavior for a given blend composition, with different crosslinking systems, is due to the different types of crosslinks present in them. The sulfur vulcanization introduces flexible polysulfidic linkages between the macromolecular chains. This allows the easy accommodation of penetrant molecules within the matrix. The DCP vulcanized system has only rigid C—C linkages that do not allow the chains to rearrange under solvent stress. This accounts for the lowest solvent uptake by DCP cured blend systems. The mixed system having polysulfidic as well as rigid C—C linkages occupy an intermediate position in its solvent uptake behavior.

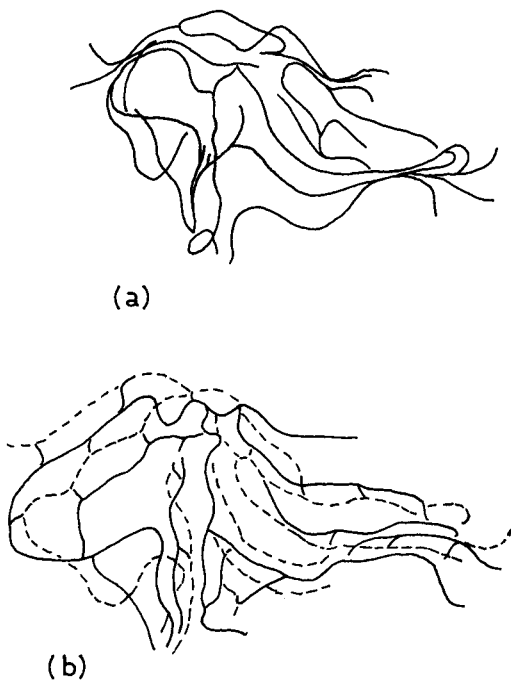


Figure 2 Schematic representation of reduction in crystallinity of EVA upon blending with NR (a) EVA, (b) the NR/EVA blend.

Figure 5(a) shows the SEM photographs of 80/20 NR/EVA blend, vulcanized by the sulfur system, where the EVA phase is found to be dispersed as domains in the continuous NR phase. Figure 5(b) and (c) show the transformation of morphology with the incorporation of 40 and 60 wt % of EVA respectively into the NR matrix. With the increase in EVA content in the matrix, the domain size of the dispersed phase decreases, and a more continuous morphology is attained. In other words, the free volume of the blends decreases with an increase in EVA content. Figure 5(a), (d) and (e) shows a comparison between the phase morphology of 80/20 NR/EVA blends vulcanized by the sulfur, mixed, and DCP systems, respectively. It is clear from the photographs that a fine and

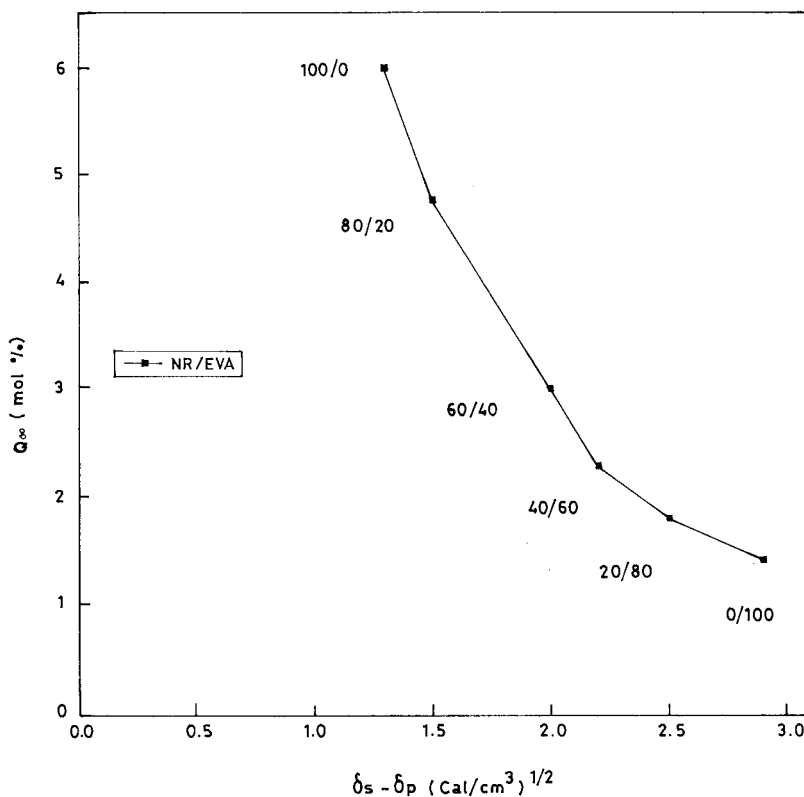


Figure 3 Variation of  $Q_\infty$  with  $(\delta_s - \delta_p)$  values for the NR/EVA blend-benzene system.

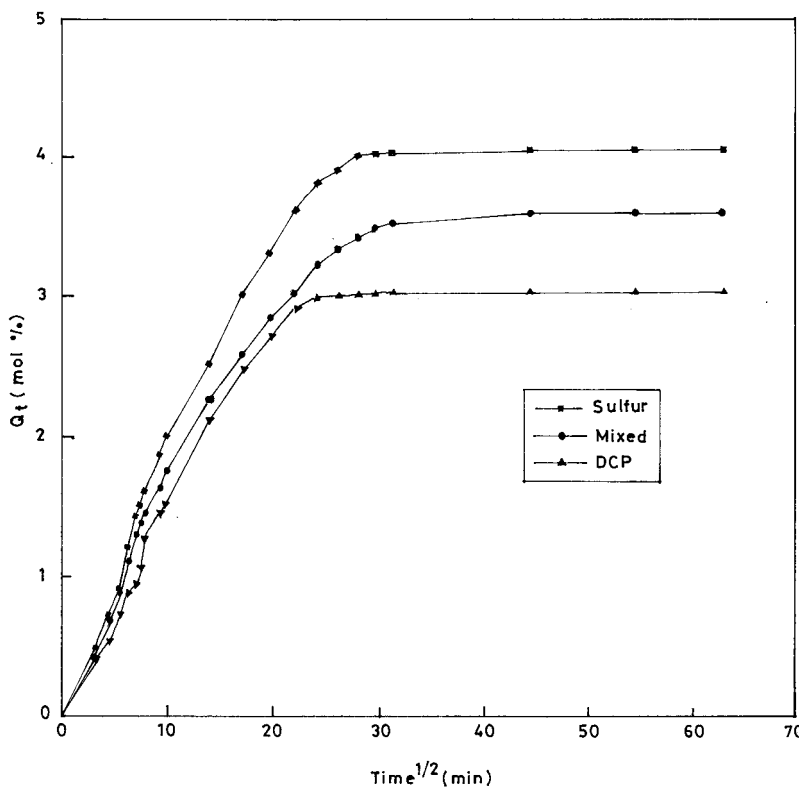
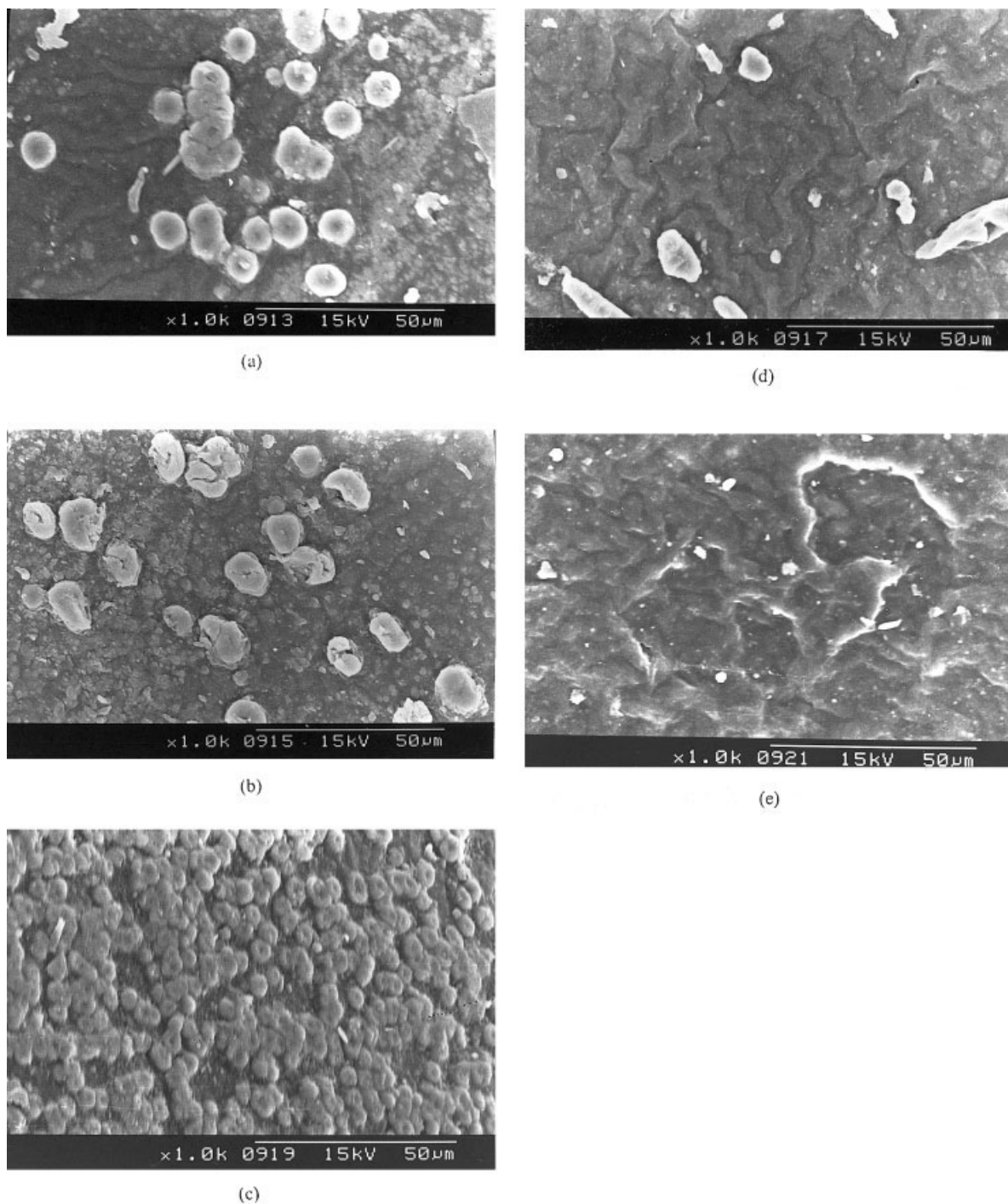


Figure 4 Mol % uptake of benzene by 60/40 NR/EVA blends with different crosslinking systems at 26°C.



**Figure 5** Scanning electron micrographs of (a) 80/20 NR/EVA (Sulfur system), (b) 60/40 NR/EVA (Sulfur system), (c) 40/60 NR/EVA (Sulfur system), (d) 80/20 NR/EVA (Mixed system), and (e) 80/20 NR/EVA (DCP system).

more uniform phase distribution is exhibited by the DCP vulcanized samples. The domain size of the dispersed phase has been found to decrease in the order sulfur > mixed > DCP. This accounts for the observed solvent uptake behavior of the blends, with different vulcanizing systems.

To test how well the observed solvent uptake behavior correlates with the crosslink distribution in the

matrix, we calculated the molecular mass between crosslinks  $M_c$  using the Flory-Rehner equation,<sup>26</sup>

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

where  $\rho_p$  is the density of the matrix,  $V$  is the molar volume of the solvent,  $\phi$  is the volume fraction of the

**TABLE II**  
Values of  $M_c$

NR/EVA	Vulcanizing system	$M_c$		
		Benzene	Toluene	Xylene
100/0	Sulfur	12454.34	10640.61	9997.63
	Mixed	6436.41	4733.88	3123.50
	DCP	5102.20	3604.76	2046.87
80/20	Sulfur	9523.25	6379.01	5854.36
	Mixed	5539.80	3348.61	2867.43
	DCP	4034.61	3108.99	1630.55
60/40	Sulfur	7399.16	4326.60	3277.86
	Mixed	4205.64	3078.09	1569.45
	DCP	3034.61	2976.12	1034.73
40/60	Sulfur	6539.27	4068.00	2378.90
	Mixed	3012.77	2480.17	1017.34
	DCP	1945.34	1679.22	1007.12
20/80	Mixed	2435.01	1813.96	965.98
	DCP	1246.40	1027.15	908.78
0/100	Mixed	1654.75	1561.11	789.90
	DCP	989.52	749.27	703.34

polymer blend in the fully swollen state, and  $\chi$  is the blend-solvent interaction parameter determined as described later. The estimated values of  $M_c$  are given in Table II. It is seen that the  $M_c$  values decrease with increase in the EVA content in the blends. The semi-crystalline EVA phase could induce physical crosslinks in addition to the permanent chemical crosslinks in the matrix. It is also observed that the  $M_c$  values for a given solvent decreases quantitatively in

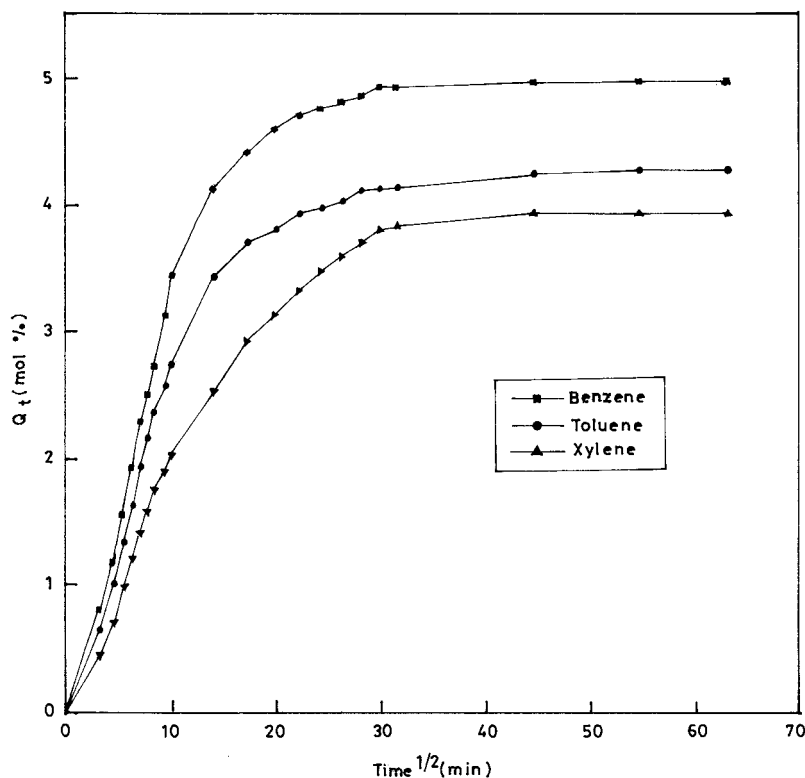
the order sulfur > mixed > DCP, which is exactly in compliance with the order noted for the  $Q_t$  values.

In Figure 6, the effect of penetrant size on the sorption and diffusion of three aromatic hydrocarbons through the 80/20 NR/EVA systems vulcanized by sulfur is presented. It follows from the graphs that there is a regular trend in the sorption behavior of aromatics through the NR/EVA matrices. The  $Q_t$  values decrease with increase in the molecular mass of the penetrant. The same trend is also observed with the other two vulcanizing systems viz., DCP and mixed, for all blend systems. The effect of molecular mass of the solvent on the maximum mol % uptake  $Q_\infty$  is illustrated in Figure 7.

To find the mechanism of transport, the dynamic swelling data have been fitted to the equation<sup>27</sup>

$$\log(Q_t/Q_\infty) = \log k + n \log t \quad (2)$$

where  $Q_t$  is the mol % sorption at time  $t$  and  $Q_\infty$  that at equilibrium. The constant  $k$  depends of the structural characteristics of the polymer in addition to its interaction with the solvents. The magnitude of the  $n$  denotes the transport mode. For normal Fickian mode of transport [Case I] where the rate of polymer chain relaxation is higher compared to the diffusion rate of the penetrant, the value of  $n = 0.5$ . When  $n = 1$ , the transport process is said to be Case II (relaxation-controlled) where the chain relaxation is slower than



**Figure 6** Mol % uptake of solvents at 26°C by 80/20 NR/EVA blends.

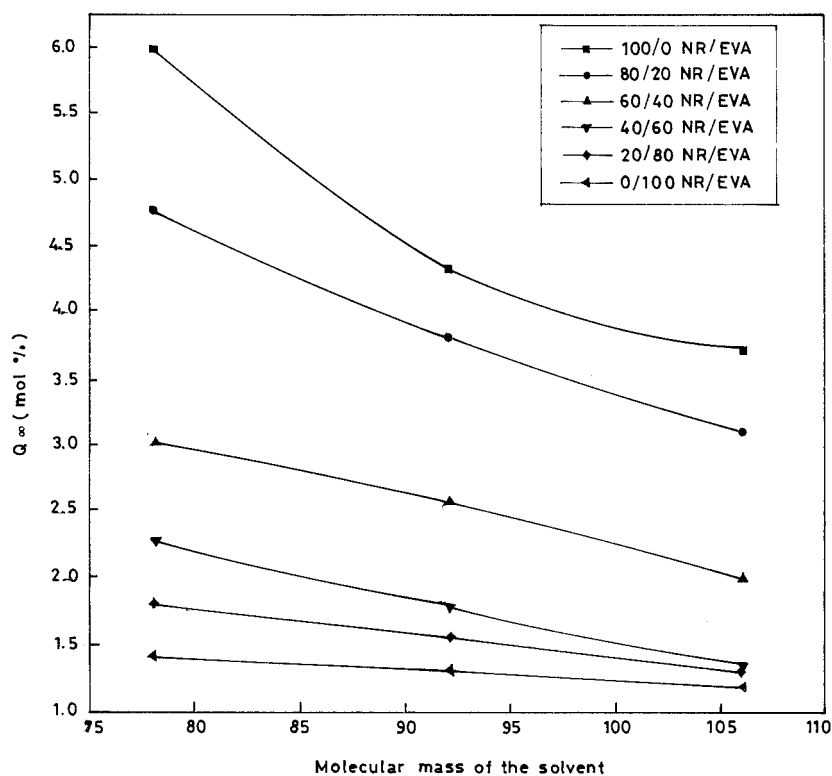


Figure 7 The effect of molecular mass of the solvent on the maximum mol % uptake of different blends vulcanized by DCP.

the liquid diffusion. If the value of  $n$  is in between 0.5 and 1, the mode of transport is classified as anomalous. The estimated values of  $n$  and  $k$  are compiled in Table III. The  $n$  values are accurate to  $\pm 0.01$  units. It is seen that the  $n$  values are in between 0.5 and 1 for all the systems under investigation, suggesting an anomalous mode of transport. It is interesting to note that the  $n$  values regularly increase with increase in EVA content in the blends in a given solvent. The crystal-

linity of EVA effectively reduces the macromolecular chain flexibility and the available free volumes in the NR matrix, thereby causing the mechanism to shift gradually to the non-Fickian mode.

The kinetic parameter, diffusion coefficient  $D$  for the different systems, under investigation was estimated by<sup>28</sup>

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

TABLE III  
Values of  $n$  and  $k$

NR/EVA	Vulcanizing system	$n$			$k \times 10^2$ (g/g min <sup>n</sup> )		
		Benzene	Toluene	Xylene	Benzene	Toluene	Xylene
100/0	Sulfur	0.56	0.57	0.56	3.06	2.76	2.44
	Mixed	0.59	0.56	0.58	3.80	3.04	2.74
	DCP	0.57	0.56	0.57	4.20	3.83	3.25
80/20	Sulfur	0.61	0.60	0.59	2.94	2.56	2.17
	Mixed	0.60	0.62	0.60	3.71	3.01	2.79
	DCP	0.61	0.61	0.62	4.03	3.74	3.39
60/40	Sulfur	0.62	0.62	0.60	2.61	2.20	2.07
	Mixed	0.63	0.61	0.61	3.66	3.22	3.17
	DCP	0.60	0.62	0.63	3.91	3.48	3.30
40/60	Sulfur	0.66	0.66	0.67	2.41	2.12	2.00
	Mixed	0.66	0.64	0.67	3.07	2.83	2.50
	DCP	0.64	0.64	0.66	3.33	3.07	2.98
20/80	Mixed	0.69	0.68	0.68	2.87	2.31	2.02
	DCP	0.69	0.66	0.69	3.02	2.70	2.50
0/100	Mixed	0.76	0.75	0.79	2.23	1.91	1.67
	DCP	0.75	0.77	0.74	2.72	2.47	2.22

TABLE IV  
Values of Diffusion and Permeation Coefficients at 26°C

NR/EVA	$D^* \times 10^5$ (cm <sup>2</sup> /s)			$P \times 10^8$ (cm <sup>2</sup> /s)		
	Benzene	Toluene	Xylene	Benzene	Toluene	Xylene
100/0 sulfur	5.2	5.0	4.2	26.8	20.7	18.8
100/0 mixed	4.8	4.3	2.9	17.3	14.5	11.0
100/0 DCP	4.2	3.6	2.4	14.3	11.8	9.8
80/20 sulfur	3.1	2.4	2.1	8.7	6.9	4.7
80/20 mixed	2.9	2.2	1.9	8.3	7.5	5.7
80/20 DCP	2.6	2.0	1.7	7.0	6.5	5.4
60/40 sulfur	2.4	1.9	1.6	7.8	6.8	4.8
60/40 mixed	2.3	1.8	1.2	5.5	4.0	3.8
60/40 DCP	2.2	1.6	1.1	4.9	4.5	3.8
40/60 sulfur	2.0	1.4	1.0	5.0	4.6	3.9
40/60 mixed	1.9	1.3	0.9	3.9	3.3	3.0
40/60 DCP	1.8	1.1	0.8	3.4	3.0	2.9
20/80 mixed	1.7	1.0	0.6	3.1	2.9	2.3
20/80 DCP	1.5	0.9	0.5	2.0	1.9	1.9
0/100 mixed	1.0	0.7	0.4	1.8	1.8	1.3
0/100 DCP	0.7	0.6	0.3	1.6	1.3	1.1

where  $h$  is the sample thickness,  $\theta$  is the slope of the linear portion of the sorption curves before attaining 50% of equilibrium, and  $Q_\infty$  has the same meaning as in eq. (2). Because significant swelling was observed during sorption experiments in all solvents, corrections to diffusion coefficients under swollen conditions were essential. This was done by calculating the intrinsic diffusion coefficient  $D^*$  from the volume fraction  $\phi$  of the blends in the swollen sample using the relation<sup>29</sup>

$$D^* = \frac{D}{\phi^{7/3}} \quad (4)$$

The values of  $D^*$  are given in Table IV. It can be seen that the  $D^*$  values regularly decrease with increase in EVA content in the blends, in a given solvent. It is also found that the  $D^*$  values are highest for sulfur vulcanized samples for a given blend ratio and solvent. The  $D^*$  values show a regular decrease with increase in molecular weight of the probe molecules. The change in the values of  $D^*$  with blend composition for the three solvents is shown in Figure 8.

The permeation process through any matrix is a combination of sorption and diffusion, and hence, the permeation coefficient depends on sorption coefficient and diffusion coefficient. The permeation coefficient  $P$  for all the systems under investigation was computed as<sup>30</sup>

$$P = D^*S \quad (5)$$

where  $D^*$  is the intrinsic diffusion coefficient and  $S$  is the sorption coefficient, which is the ratio of the mass of the penetrant molecule at equilibrium swelling to the mass of the polymer sample. The calculated values

of  $P$  are also given in Table IV. It is observed that the  $P$  values of the blend-solvent systems follow the same trend as that of intrinsic diffusion coefficient, all in terms of blend ratio, crosslinking agent, penetrant size, and temperature.

To examine the influence of temperature on the transport process, the sorption experiments were conducted at 36, 46, and 56°C, in addition to those at 26°C in all solvents. The diffusion curves of the 60/40 NR/EVA sulfur systems in benzene at 26, 36, 46, and 56°C are given in Figure 9. The disruption of long-range order in the crystalline regions of EVA coupled with the enhanced macromolecular flexibility of the matrix at elevated temperature accounts for the observed activation of the transport process through the present blend systems. The variation in the values of  $D^*$  with temperature for the 80/20 NR/EVA sulfur blend system is given in Figure 10.

The values of  $D^*$  at different temperatures have been used to estimate the activation energy for transport from the Arrhenius-type relation<sup>31</sup>

$$\log D^* = \log D_0^* - \frac{E_D}{2.303RT} \quad (6)$$

where  $D_0^*$  is the preexponential factor,  $R$  the universal gas constant, and  $T$  the temperature on the absolute scale. Typical Arrhenius plot of  $\log D^*$  vs.  $1/T$  is given in Figure 11. The calculated values of  $E_D$  are given in Table V. The activation energy values have been found to decrease with increase in EVA content in the blends for a given solvent. This clearly indicates the higher temperature sensitivity of blends with lower EVA content. Another interesting observation is the variation in the activation energy values of a given



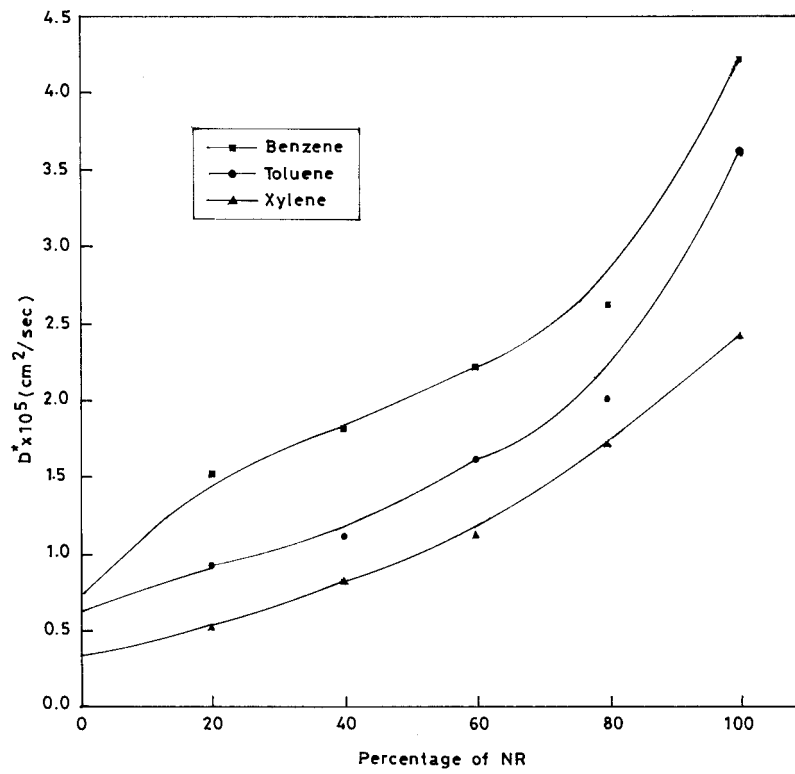


Figure 8 Variation of diffusion coefficient values with respect to the blend composition.

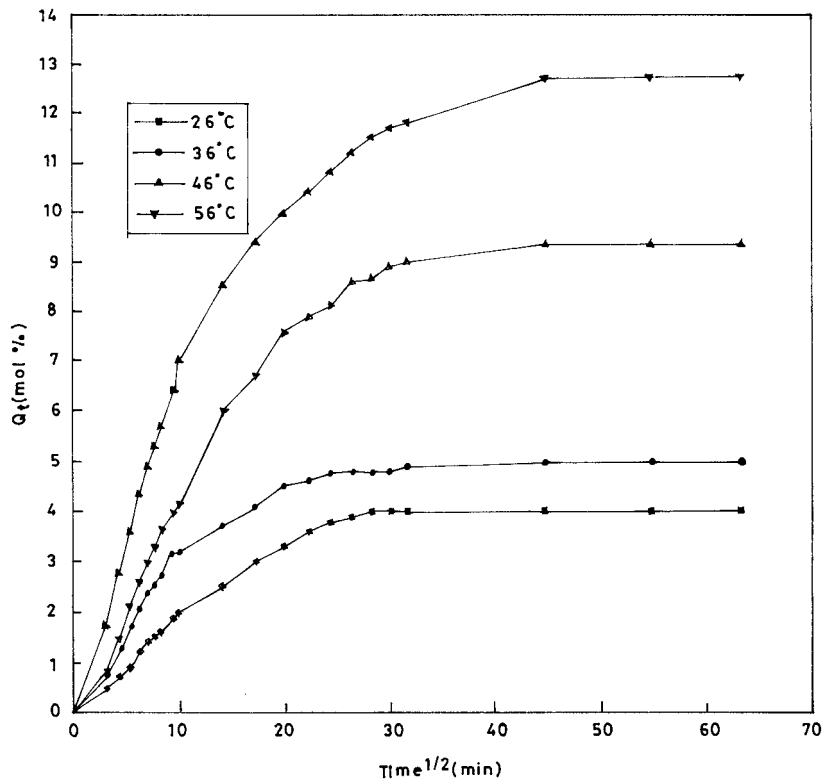


Figure 9 Mol % uptake of benzene by 60/40 NR/EVA blend at 26, 36, 46, and 56°C.

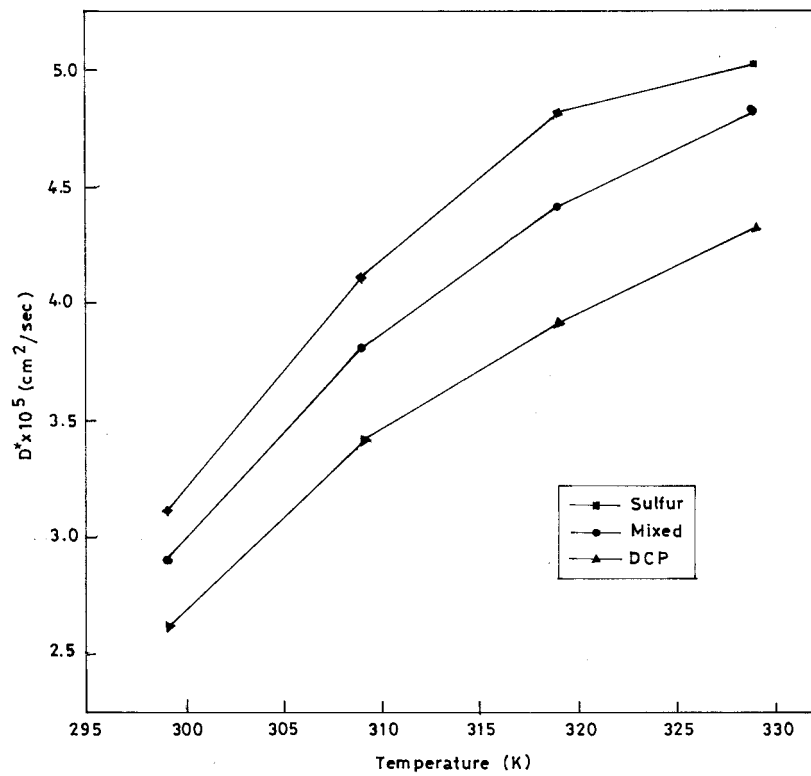


Figure 10 The variation of diffusion coefficient values with temperature for 80/20 NR/EVA system vulcanized with different systems.

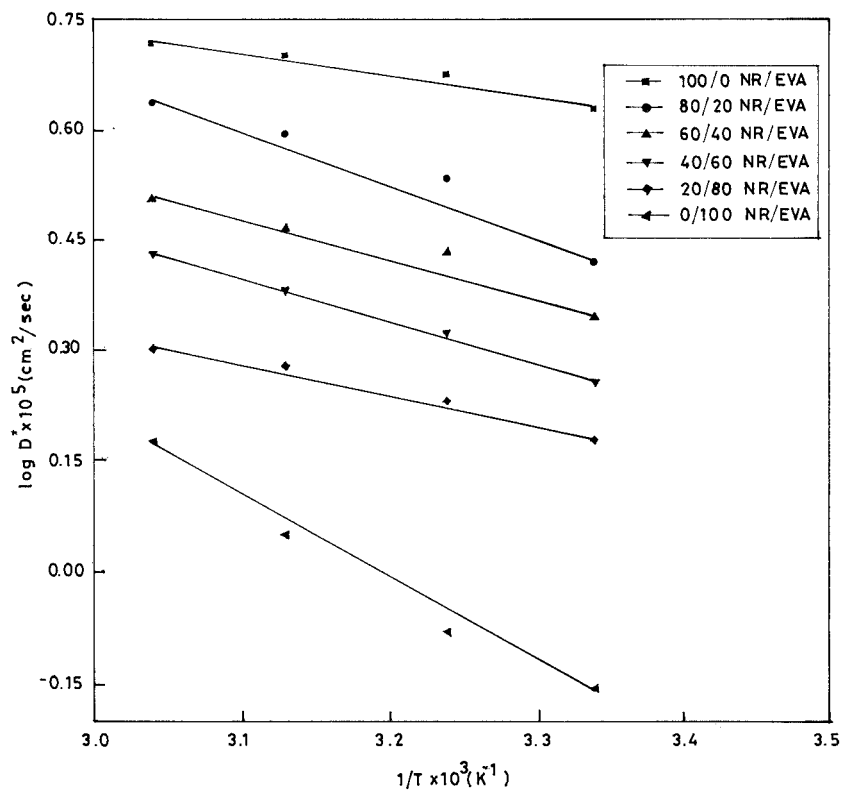


Figure 11 Arrhenius plot of  $\log D^*$  vs.  $1/T$  for different NR/EVA blends crosslinked with DCP, in benzene.

**TABLE V**  
Values of Activation Energy

NR/EVA	Vulcanizing system	$E_D$ (kJ/mol)		
		Benzene	Toluene	Xylene
100/0	Sulfur	11.9	12.6	13.7
	Mixed	11.4	12.0	13.1
	DCP	11.1	11.5	12.2
80/20	Sulfur	10.8	11.1	12.6
	Mixed	10.1	10.8	11.9
	DCP	9.6	10.2	11.0
60/40	Sulfur	10.2	10.7	11.4
	Mixed	9.6	10.1	10.7
	DCP	9.0	9.6	10.2
40/60	Sulfur	8.5	9.6	10.3
	Mixed	8.8	9.2	9.8
	DCP	8.2	8.8	9.3
20/80	Mixed	7.1	8.3	9.0
	DCP	6.6	7.0	7.9
0/100	Mixed	5.9	6.6	7.4
	DCP	5.1	5.8	6.5

blend system having different crosslinking agents, for a particular solvent. The DCP crosslinked blends exhibit lower activation energy and the sulfur-vulcanized systems show the highest. The temperature sensitivity of sulfur vulcanized elastomer systems, having polysulfidic linkages, is well known.<sup>32</sup>

From the amount of penetrant sorbed by a given mass of the blend, the equilibrium sorption constant  $K_s$  has been computed as

$$K_s = \frac{\text{No. of mol of penetrant sorbed}}{\text{Unit mass of the blend}} \quad (7)$$

From the values of  $K_s$ , enthalpy  $\Delta H$ , and the entropy  $\Delta S$  of sorption have been determined using the Van't Hoff relation<sup>33</sup>

$$\log K_s = \frac{\Delta S}{2.303R} - \frac{\Delta H_s}{2.303RT} \quad (8)$$

The obtained values of  $\Delta H_s$ , given in Table VI, are negative in all cases, which become more negative from DCP to CV samples in a given solvent, and for a particular blend ratio. These values also exhibit a regular increase from benzene to xylene for a given sample. These trends suggest an increased exothermicity of sorption process from the DCP to sulfur vulcanized samples and a decreased exothermicity with an increase in molecular size of the penetrant for a given sample. The  $\Delta S$  values also show a regular trend, that is, a decrease from CV to DCP samples for a given penetrant.

To follow the extent of blend-penetrant interaction, we have calculated the interaction parameter  $\chi$  using the relation<sup>33</sup>

$$\chi = \frac{(d\phi/dT)\{[\phi/(1-\phi)] + N \ln(1-\phi) + N\phi\}}{2\phi(d\phi/dT) - \phi^2 N(d\phi/dT) - \phi^2/T} \quad (9)$$

where  $\phi$  is the volume fraction of the blend in the swollen sample,  $N$  has been calculated using  $\phi$  as follows:

$$N = \frac{[\phi^{2/3}/3 - 2/3]}{[\phi^{1/3} - 2\phi/3]} \quad (10)$$

The values of  $\chi$  obtained for different blend-solvent systems are tabulated in Table VII. The  $\chi$  values are lowest for pure NR compared to all other systems in a given penetrant, indicating higher interactions. The  $\chi$  values increase regularly with an increase in EVA content in the blends. The decrease in the values of interaction parameter with an increase in molecular

**TABLE VI**  
Values of  $\Delta H$  and  $\Delta S$

NR/EVA		$\Delta S$ (J/mol/k)			$-\Delta H$ (kJ/mol)		
		Benzene	Toluene	Xylene	Benzene	Toluene	Xylene
100/0	Sulfur	13.89	12.65	11.08	1.98	1.95	1.87
	Mixed	12.45	11.30	10.09	1.86	1.69	1.40
	DCP	10.76	10.56	10.24	1.52	1.41	1.29
80/20	Sulfur	11.54	10.99	10.43	1.50	1.46	1.41
	Mixed	10.96	10.73	8.52	1.43	1.37	1.31
	DCP	10.01	9.96	7.23	1.40	1.29	1.22
60/40	Sulfur	9.49	8.76	7.84	1.33	1.26	1.20
	Mixed	9.01	8.05	6.64	1.27	1.19	1.11
	DCP	8.56	7.69	6.45	1.21	1.13	1.06
40/60	Sulfur	8.84	8.00	7.67	1.28	1.21	1.16
	Mixed	8.09	7.50	7.10	1.22	1.12	1.07
	DCP	7.78	7.00	6.63	1.16	1.07	1.02
20/80	Mixed	7.48	7.10	6.56	1.10	1.06	1.02
	DCP	7.11	6.86	6.31	1.09	1.05	1.00
0/100	Mixed	6.30	5.78	5.02	0.96	0.91	0.87
	DCP	6.00	5.23	4.81	0.89	0.82	0.77

TABLE VII  
Values of Interaction Parameter

NR/EVA	Vulcanizing system	$\chi$		
		Benzene	Toluene	Xylene
100/0	Sulfur	0.44	0.39	0.37
	Mixed	0.56	0.45	0.41
	DCP	0.60	0.51	0.46
80/20	Sulfur	0.63	0.54	0.45
	Mixed	0.67	0.60	0.52
	DCP	0.70	0.66	0.57
60/40	Sulfur	0.74	0.69	0.57
	Mixed	0.78	0.73	0.60
	DCP	0.83	0.76	0.64
40/20	Sulfur	0.85	0.77	0.74
	Mixed	0.91	0.82	0.78
	DCP	0.98	0.90	0.86
20/80	Mixed	1.02	0.94	0.88
	DCP	1.07	0.98	0.91
0/100	Mixed	1.10	0.98	0.84
	DCP	1.14	1.03	0.96

mass of the penetrant, for a given sample, is due to the differences in the values of solubility parameter. Such findings have been reported in the earlier literature.<sup>34</sup>

### CONCLUSION

The transport behavior of NR-EVA blends with different vulcanizing systems has been examined using benzene, toluene, and xylene as probe molecules in the temperature range of 26–56°C. The significant observation of reduction in solvent sorption with an increase in EVA content has been explained on the basis of decrease in free volume and an increase in crystallinity of the blends. The examination of the influence of vulcanizing systems on the sorption and diffusion behavior of the blends shows that the solvent uptake follows the trend sulfur > mixed > DCP system. The differences in the solvent uptake behavior exhibited by the samples vulcanized by the three different techniques have been interpreted in terms of the difference in the nature of crosslinks in the macromolecular networks. The diffusion coefficient values, determined by considering isotropic swelling in the samples, decrease with an increase in EVA content in the blends. The transport data were used to estimate the activation energy, the enthalpy, and the entropy of sorption. The computed activation energy values have been found to be lower for samples with higher EVA content, which clearly indicate their lower temperature susceptibility. The computed blend–solvent interac-

tion parameter values indicate a regular decrease in interaction between the blends, and penetrants with an increase in the EVA content.

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