

## ***Absorption of Ester Type Plasticisers by Natural Rubber and Epoxidised Natural Rubber – Diffusion Coefficients and Equilibrium Uptake***

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*The diffusion coefficients of ester plasticisers in natural rubber (NR) and epoxidised natural rubber (ENR) were determined by using the mass uptake method. Diffusion coefficients decrease with increasing viscosity of the plasticiser. They are greater for NR than for ENR, in accord with previous observations that diffusion coefficients decrease with increasing glass transition temperature. Diffusion coefficients do not decrease continuously with increasing crosslink density, rather maximum values are observed at about  $5 \times 10^{-2}$  mol/kg. Thermodynamic diffusion coefficients show the expected continuous decrease with increasing crosslink density.*

The swelling of rubber by liquids is a diffusion-controlled process and as such has been extensively studied and reviewed<sup>1-6</sup>. The present paper is concerned with the absorption of ester plasticisers by natural rubber (NR) and epoxidised natural rubber (ENR). The mathematical aspects of diffusion in different specimen geometries have been analysed in detail by Crank<sup>7</sup>. Here we are concerned only with diffusion into a plane sheet, which is generally the type of test piece used. The diffusion in a plane sheet in the early stages is indicated to that in a semi-infinite medium but the equation<sup>8</sup> normally used in this case is:

$$\frac{M_t}{M_\infty} = \frac{4}{l} \left( \frac{Dt}{\pi} \right)^{1/2} \quad \dots 1$$

where  $D$  is the diffusion coefficient

$M_t$  is the mass of liquid absorbed per unit area of the sheet after immersion for time  $t$

$M_\infty$  is the amount of liquid absorbed per unit area after infinite time

$l$  is the thickness of sheet.

The measurement of diffusion coefficient has been comprehensively reviewed and therefore only an account of the more widely used method suitable for plasticisers as the penetrant is given here. This can be broadly classified as a steady-state method. The steady-state method consists of monitoring the amount of diffusing substance across a polymer liquid interface as a function of time until the rate of transfer of diffusant becomes independent of time. It involves measurement of mass uptake<sup>9-12</sup>, the mass absorbed being plotted against square root of time. In order to correct the effect of lateral swelling, Garrett and Park<sup>13</sup> have suggested that the diffusion coefficient should be multiplied by  $V_r^{4/3}$  where  $V_r$  is the volume fraction of rubber in the swollen vulcanisate. However, it should be noted that this allows only for the change in surface area and not the accompanying changes in surface concentration, although throughout the work the surface concentration was assumed constant.

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The diffusion of a range of ester plasticisers in NR and ENR vulcanisates is described here. The effect of glass transition temperature and crosslink density of the rubber vulcanisate and of the viscosity of the plasticiser on diffusion coefficients is considered.

#### MATERIALS AND METHODS

Natural rubber (SMR L) and ENR having epoxide contents of 50 and 25 mole% (ENR-50 and ENR-25, respectively)<sup>14</sup> were used in the investigation. The plasticisers chosen are non-volatile liquids, and they are detailed in *Table 1*.

The standard mix formulation was the same for each rubber, so as to avoid complications associated with variations in the compounding ingredients. *Table 2* shows the standard mix formulations for the NR and ENR investigated. For simplicity, as well as on the basis of its suitability for ENR, a semi-EV vulcanisation system was used. When investigating the effect of crosslink levels on the diffusion coefficient of plasticisers in NR and ENR-50, the amounts of sulphur and accelerator incorporated into the rubbers were varied (*Table 3*).

Mixes were prepared on a two-roll mill with the rolls set at 30°C and the nip set at 1.2 mm. Sulphur and accelerator were also added.

Vulcanisation was carried out using a compression mould in a steam-heated press, heated to 150°C, to produce a flat vulcanised sheet of uniform thickness. The maximum state of cure was taken as the time to reach the maximum torque on the Monsanto Rheometer curve.

The plasticiser absorption measurements were carried out by using the mass-uptake method. Samples of NR and ENR vulcanisates

to be tested were cut to size, normally 25.4 mm square from a 228 × 228 × 1 mm vulcanised sheet. Each test sample thickness was measured at three different locations on the test piece and the average value recorded as thickness. A small hole (of diameter 0.2 mm) was made near one end of the test piece for insertion of a stainless steel hook which later kept the test piece submerged in the plasticiser. The initial weight of the test piece was recorded. The test piece was then attached to the stainless steel hook and immersed in the required plasticiser at 23°C for a known period, removed, dried on the surface with filter paper, weighed and replaced in the plasticiser. This procedure was repeated for all test pieces in various plasticisers. Each test was continued until equilibrium plasticiser uptake was attained.

The mass uptake,  $M_t$ , per unit original surface area, was plotted against the square root of time of immersion. The diffusion coefficients,  $D$ , of the various plasticisers in the gum NR and ENR vulcanisates are calculated using *Equation 1*.

Physical crosslink densities were calculated from the Mooney-Rivlin constants,  $C_r$ , as determined from equilibrium stress-strain measurements<sup>15</sup> on swollen vulcanisates.  $C_r$  is corrected for swelling<sup>16</sup> by:

$$C_1(\text{dry}) = \frac{C_1(\text{swollen})}{V_r^{1/3}} \quad \dots 2$$

and physical crosslink density is calculated from:

$$[X]_{phys} = \frac{C_1}{\rho RT} \quad \dots 3$$

where  $\rho$  is the density of the vulcanisate  
 $R$  is the universal gas constant  
 $T$  is the temperature at which the equilibrium stress-strain measurements were performed.

TABLE 1. CHARACTERISTICS OF PLASTICISERS

Plasticiser	Mol. weight	Sp.gr. at 25°C	$\delta^a$ (MPa) <sup>1/2</sup>	Viscosity mPa.s
Dimethyl phthalate (DMP)	194	1.192	21.9	11.0
Diethyl phthalate (DEP)	222	1.118	20.5	10.0
Dibutyl phthalate (DBP)	278	1.049	19.0	20.0
Dioctyl phthalate (DOP)	390	0.978	16.2	54.8
Diisodecyl phthalate (DiDP)	446	0.962	14.7	81.8
Tributoxyethyl phosphate (TBEP)	344	1.020	19.2	12.2
Tricresyl phosphate (TCP)	368	1.158	19.2	69.5
Dioctyl sebacate (DOS)	426	0.913	17.6	17.8
Diisodecyl adipate (DiDA)	426	0.912	16.8	20.1
Reomol <sup>b</sup> BCD <sup>d</sup>	436	1.018	18.9	13.8
Reomol <sup>b</sup> MD <sup>e</sup>	—	0.917	—	21.5
Reomol <sup>b</sup> 249 <sup>f</sup>	—	1.059	—	22.2
Reofos <sup>b</sup> 65 <sup>g</sup>	—	1.164	—	66.3
Diolpate <sup>c</sup> 7017 <sup>h</sup>	—	1.065	—	250
Diolpate <sup>c</sup> 171 <sup>h</sup>	—	1.075	—	850

<sup>a</sup>Solubility parameter<sup>b</sup>Ciba-Geigy Industrial Chemicals<sup>c</sup>Macpherson Polymers<sup>d</sup>Di-(butoxyethoxyethyl) adipate<sup>e</sup>Ester of mixed adipic, glutaric and succinic acids with iso-decanol<sup>f</sup>A modified phosphate<sup>g</sup>Isopropylated phenyl phosphate<sup>h</sup>Polymeric esters

TABLE 2. BASE FORMULATIONS

Reference number	A1	A2	A3
SMR L	100	—	—
ENR-25	—	100	—
ENR-50	—	—	100
Calcium stearate <sup>a</sup>	—	3	3
Zinc oxide	5	5	5
Stearic acid	2	2	2
TMQ <sup>b</sup>	2	2	2
Sulphur	Variable	Variable	Variable
MBS <sup>c</sup>	Variable	Variable	Variable

<sup>a</sup>Stabiliser<sup>b</sup>Poly-2,2,4-trimethyl,2-dihydroquinoline, *Flectol H*, Monsanto<sup>c</sup>2-(Morpholinothio) benzothiazole

TABLE 3. FORMULATIONS FOR THE INVESTIGATION OF THE EFFECT OF CROSSLINK LEVEL ON DIFFUSION COEFFICIENT OF PLASTICISERS IN NR AND ENR-50

Rubber type	A1, Table 2						A3, Table 2					
Mix number	B1	B2	B3	B4	B5	B6	B7	B8	B9	B10	B11	B12
Base mix	100	109	109	109	109	109	100	112	112	112	112	112
Sulphur (p.h.r.)	-	0.6	1.0	1.5	2.4	3.5	-	0.6	1.0	1.5	2.4	3.5
MBS (p.h.r.)	-	0.6	1.0	1.5	2.4	3.5	-	0.6	1.0	1.5	2.4	3.5

The polymer-solvent interaction parameter,  $\chi$ , was determined for two of the plasticisers with both NR and ENR-50 from the  $C_1$  values by substitution of equation in the Flory-Rehner<sup>17</sup> relationship:

$$-1n(1 - V_r) - V_r - \chi V_r^2 = 2C_1 V_0 V_r^{1/3} \quad \dots 4$$

where  $V_0$  is the molar volume of the plasticiser.

## RESULTS

For each plasticiser,  $M_t$  was plotted against the square root of time for each test. The mass uptake of plasticiser per unit area has been corrected for lateral increase in the dimensions of the test piece which occurs as a result of swelling. This is done by multiplying the weight change by  $(V_r^{2/3}/A_0)$  where  $A_0$  is the total unswollen area of the sample.

For convenience, results are presented graphically in two major groups. Typical examples of each group are depicted in *Figures 1* and *2*. *Figure 1* shows examples of plasticisers in which the equilibrium uptake by the ENR-50 vulcanisate is much higher than that of NR, whilst *Figure 2* shows examples of the opposite. It can be seen that the mass uptake curve for a sheet of rubber vulcanisate, when plotted against the square root of time, is linear in the early stages of swelling, becoming increasingly concave to the abscissa at longer times and finally approaching an equilibrium value. The diffusion coefficient is calculated

from the initial linear portion of the curve using *Equation 4*, and values for the various plasticisers in gum NR and ENR vulcanisates are presented in *Table 4*.

The results in *Table 4* show that, in general, the diffusion coefficient of the various plasticisers in the gum ENR-50 vulcanisates are significantly lower than those in NR at similar absorption times. The reason for this could well be the high glass transition temperature ( $T_g$ ) of the ENR-50 ( $T_g, -18^\circ\text{C}$ ) compared with that of NR ( $T_g, -72^\circ\text{C}$ ) — a possible explanation being a free volume effect, since the ease of movement of the rubber segments, which determines the rate of progress of the diffusing molecule, is related to the  $T_g$  of the rubber. A comparison of the diffusion coefficient of some plasticisers in ENR-25 and ENR-50 was carried out and the results obtained are given in *Table 5*. Diffusion coefficients are higher in ENR-25 ( $T_g, -45^\circ\text{C}$ ) than in ENR-50 but lower than in NR. These results confirm a relationship between the diffusion coefficient of the liquid and the  $T_g$  of the rubber, although the relationship is non-linear.

It has been suggested<sup>3-8</sup> that the presence of polar or sterically-hindered groups in the polymer molecules, leads to a low diffusion coefficient. Van Amerongen<sup>2</sup> demonstrated this by diffusing various penetrants into NBR copolymers and showed that diffusivity

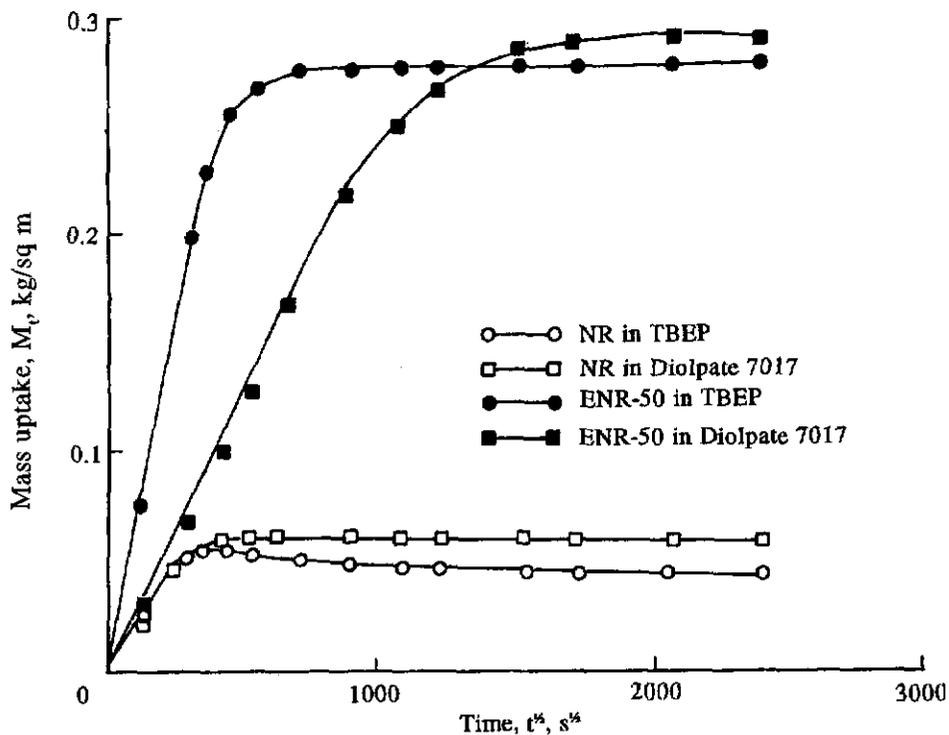


Figure 1. Typical mass uptake curves for NR and ENR-50 vulcanisates which swell ENR-50 more than NR.

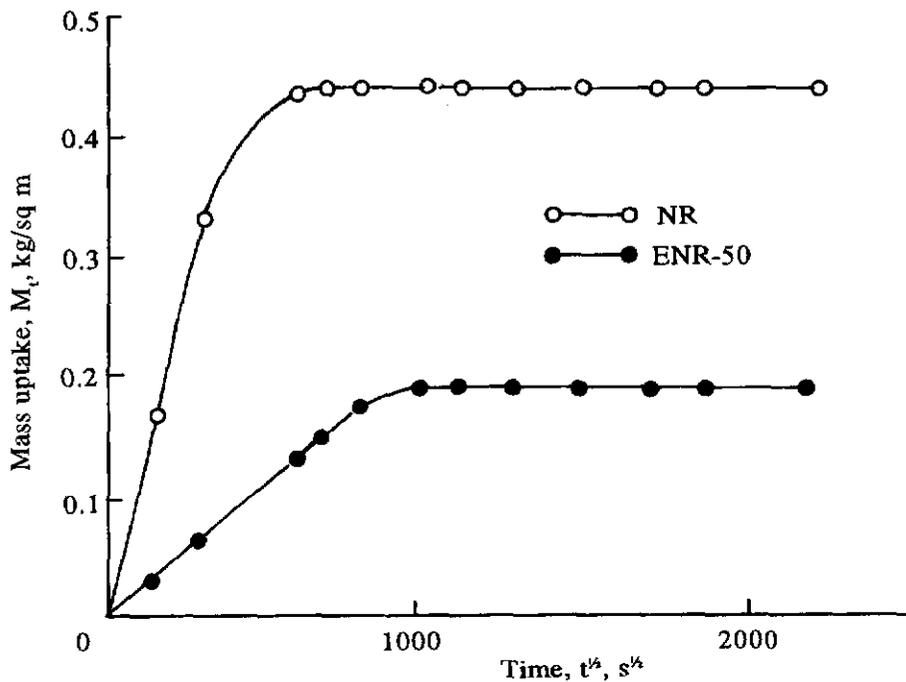


Figure 2. Typical mass uptake curves for NR and ENR-50 vulcanisates in DOS which swells NR more than ENR-50.

TABLE 4 DIFFUSION COEFFICIENT OF VARIOUS PLASTICISERS IN NR AND ENR-50 GUM VULCANISATES

Plasticiser	NR vulcanisates		ENR-50 vulcanisates	
	$V_r^a$	$D \times 10^{12}$ (m <sup>2</sup> /s)	$V_r^a$	$D \times 10^{12}$ (m <sup>2</sup> /s)
DMP	0.780	4.55	0.291	2.32
DEP	0.893	5.79	0.272	2.74
DBP	0.683	4.24	0.255	2.06
DOP	0.455	1.94	0.323	0.28
DiDP	0.419	1.13	0.631	0.22
TBEP	0.873	9.30	0.353	1.73
TCP	0.901	3.24	0.346	0.96
DOS	0.334	5.47	0.492	0.53
DiDA	0.346	5.14	0.461	0.38
<i>Reomol BCD</i>	0.874	12.0	0.357	2.65
<i>Reomol MD</i>	0.348	4.47	0.457	0.38
<i>Reomol 249</i>	0.556	5.34	0.259	1.22
<i>Reomol 65</i>	0.886	1.93	0.297	0.23
<i>Diolpate 7017</i>	0.827	3.59	0.371	0.27
<i>Diolpate 171</i>	0.866	1.52	0.41	0.08

<sup>a</sup>Volume fraction of rubber in the swollen vulcanisate at equilibrium uptake

TABLE 5 COMPARISON OF DIFFUSION COEFFICIENTS OF VARIOUS PLASTICISERS IN NR, ENR-25 AND ENR-50 GUM VULCANISATES

Plasticiser	Diffusion coefficient $\times 10^{12}$ (m <sup>2</sup> /s)		
	NR	ENR-25	ENR-50
TBEP	9.30	3.65	1.73
<i>Reomol BCD</i>	12.0	3.89	2.65
<i>Reomol 249</i>	5.34	3.20	1.22
<i>Reofos 65</i>	1.93	0.53	0.23
<i>Diolpate 171</i>	1.52	0.41	0.08
<i>Diolpate 7017</i>	3.59	0.67	0.27

decreased strongly on increasing the nitrile group content in the copolymers. These groups also reduce segmented mobility at a given temperature and give increased  $T_g$ . Southern<sup>12</sup> found a low rate of diffusion of n-decane in

butyl rubber. He suggested that the low diffusion coefficient could be attributed to the steric hindrance of the gum-dimethyl groups in the polymer chain. A similar effect may be proposed for ENR. A comparison of the

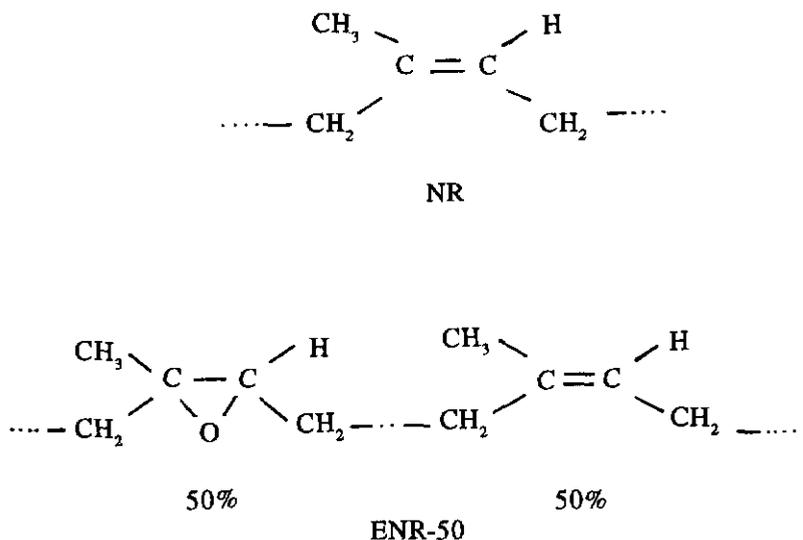


Figure 3. Structural units present in NR and ENR-50.

structures of NR and ENR (Figure 3) shows that both rubbers have a similar structure except that double bonds are replaced by the bulkier epoxy (polar) groups in ENR. Double bonds prevent rotation as effectively as epoxide, but the latter has an additional effect because it is bulkier. Consideration should also be given to the possibility that polar interactions between the liquid and epoxide groups during diffusion may reduce the coefficient as the epoxide content of the rubber increases.

A lower diffusion coefficient in ENR-50, however, does not necessarily mean a slower rate of absorption of plasticisers by ENR-50 since the rates of absorption, as shown by the slope of the linear portion of the curve  $M_t$  vs  $t^{1/2}$ , in ENR-50 and NR vary considerably. The results in Table 4 show that plasticisers such as TBEP, TCP, Reomol 249, Reomol BCD, Reofos 65 and the two Diolpates exhibit higher rates in ENR-50 than in NR. The main reason

is that the final mass uptake,  $M_t$  of these plasticisers by the ENR-50 vulcanisate is higher, i.e. much more plasticiser is absorbed before equilibrium is reached.

The results in Table 4 also show that there are differences in the diffusion coefficients of various plasticisers for a particular rubber. The dependence of diffusion coefficient on viscosity of the plasticiser is illustrated in Figure 4. The plots show slight scatter, however, in general there is a trend of decreasing  $D$  with decreasing liquid viscosity. This is consistent for both rubbers. A similar correlation was observed by Southern and Thomas<sup>12</sup> in their work on the diffusion of a wide range of liquids in natural rubber. The explanation is that viscosity reflects the effective radius of the molecule. In the present work, the plasticisers swell the rubber considerably, and the mobile species will have a plasticising action which will reduce the

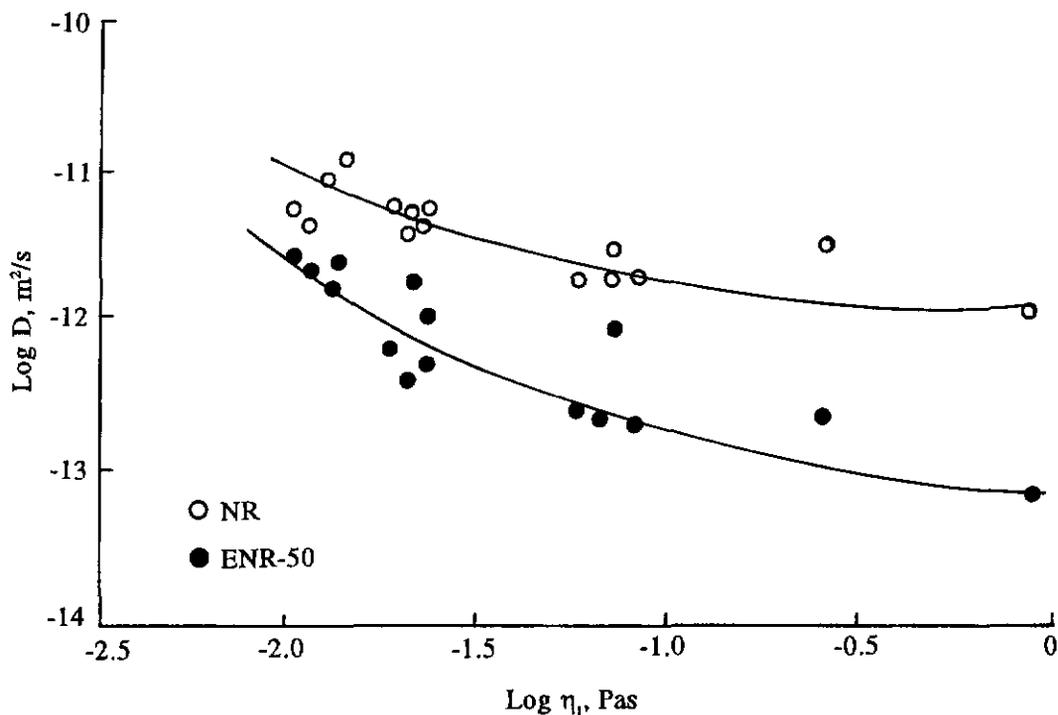


Figure 4. Dependence of diffusion coefficient,  $D$ , on liquid viscosity for various plasticisers in NR and ENR-50 vulcanisates at 25°C.

internal viscosity of the rubber. This effect is greater, the lower the liquid viscosity and the higher the swelling, and therefore explains the observed correlation of  $D$  with liquid viscosity.

The dependence of diffusion coefficient on the crosslink density of the vulcanisate was also investigated. Physical crosslink densities were calculated from Mooney-Rivlin constants estimated from equilibrium stress-strain measurements on swollen vulcanisates. Swollen vulcanisates were preferred in order to decrease the dependence of reduced stress on extension ratio and to increase the relaxation rate of the ENR-50 vulcanisates. Two plasticisers were used as swelling agents, *TBEP* and *Reomol*

*BCD*. For NR vulcanisates, there was excellent accord between crosslink densities obtained using the two plasticisers (*Table 6*). However, agreement between the two sets of values is not as good for the ENR-50 vulcanisates, the differences ranging from 5.2 to 9.6%. The main source of the discrepancy is with the difficulty in assessing the exact equilibrium condition using the standard time during the stress-strain measurements for the ENR vulcanisates. The dependence of  $D$  on crosslink density is shown in *Figure 5*. For both polymers,  $D$  initially increases with increasing crosslink density, reaches a maximum and then decreases. The crosslink density at which the maximum value of  $D$  occurs differs for the two

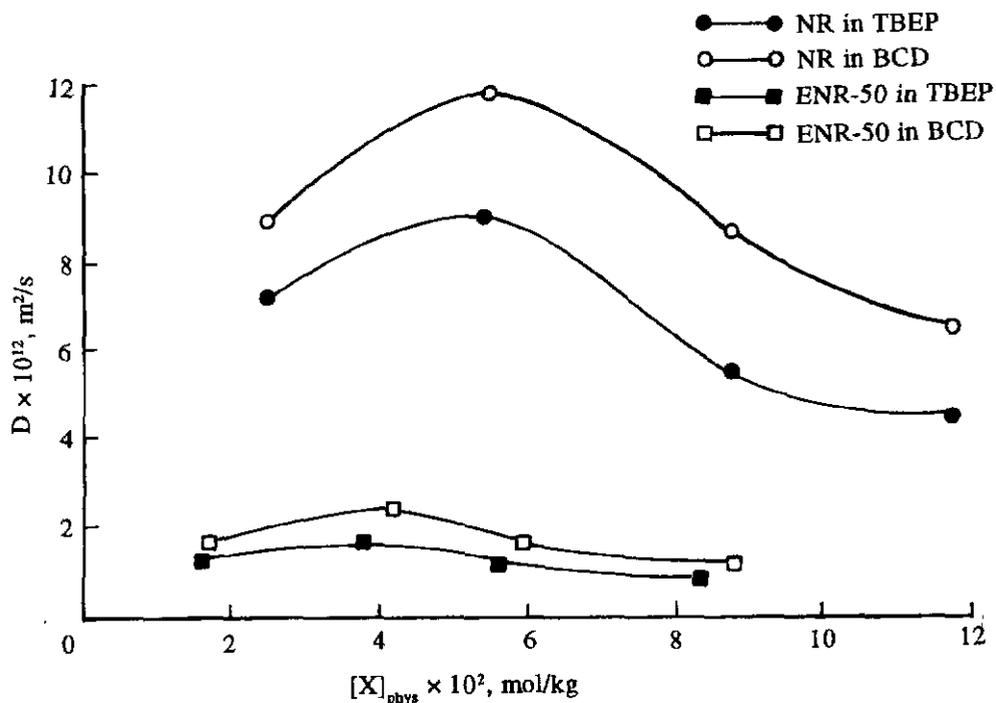


Figure 5. Dependence of diffusion coefficient on physical crosslink density.

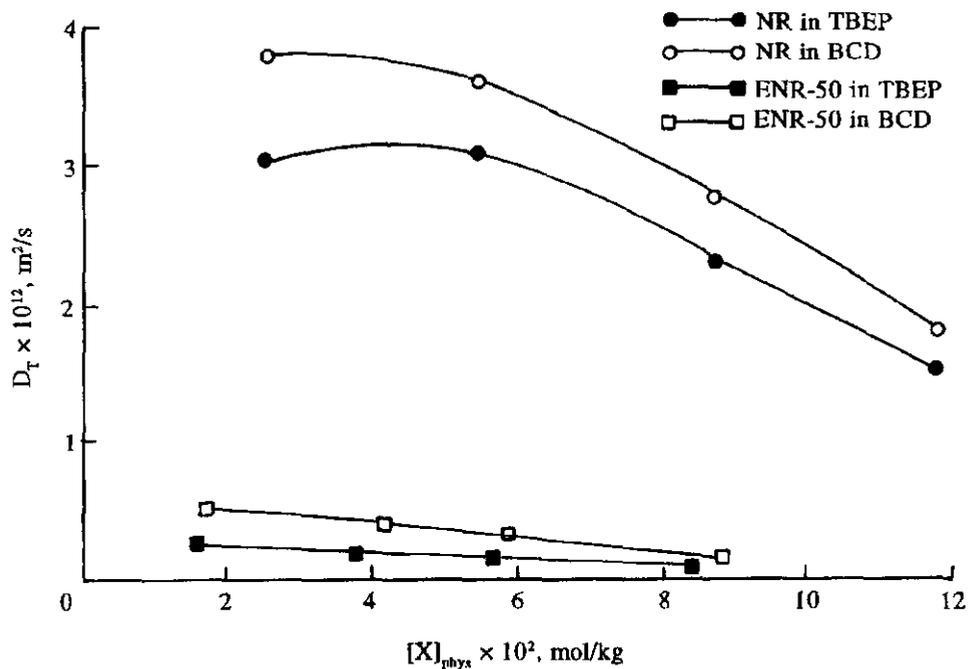


Figure 6. Dependence of thermodynamic diffusion coefficient  $D_T$ , on physical crosslink density.

elastomers. The value is higher for NR (*ca.*  $5.5 \times 10^{-2}$  mol/kg) than for ENR-50 (*ca.*  $4.0 \times 10^{-2}$  mol/kg).

The effect of the crosslinking is to restrict the mobility of the rubber molecules so it would be expected that increasing the degree of crosslinking would reduce the diffusion coefficient. The initial increase in  $D$  cannot be due to the way in which the diffusion coefficient is measured since all the results were compared at the same changing concentration of penetrant during the diffusion and would therefore be affected in the same way. An explanation of this behaviour has been proposed by other workers<sup>11</sup> who studied the diffusion of n-decane in natural rubber as a function of degree of crosslinking. A similar explanation is used here. The driving force for diffusion in the case of non-ideal mixtures is the gradient of the chemical potential rather than the concentration gradient. The diffusion coefficient defined in terms of the chemical potential gradient is called the thermodynamic diffusion coefficient ( $D_T$ ).

$D_T$  is related to  $D$  by:

$$D_T = D \frac{\partial(\ln c)}{\partial(\ln a)} \quad \dots 5$$

The activity,  $a$ , of the plasticiser in vulcanised rubber is given by the Flory-Rehner<sup>16</sup> relationship:

$$\ln a = \ln(1 - V_r) + V_r + \chi V_r^2 + \left( \frac{\rho V_o}{M_c V_r} \right) \quad \dots 6$$

and it may be shown<sup>18</sup> then that:

$$D_T = D \left\{ \left[ \frac{1}{(1 - V_r)} + 1 + 2\chi V_r - \left( \frac{\rho V_o}{M_c V_r^2} \right) (V_r - 1) \right] \right\}^{-1} \quad \dots 7$$

which reduces to  $D_T = D$  when  $V_r = 1$ .

Polymer-solvent interaction parameters were estimated for TBEP and *Reomol BCD* (Table 6) in order to apply Equation 6.

TABLE 6. NETWORK CHARACTERISTICS OF NR AND ENR-50 GUM VULCANISATES SWOLLEN IN TBEP AND *REOMOL BCD*

Mix number	B2	B4	B5	B6	B8	B10	B11	B12
	NR in TBEP				ENR in TBEP			
$V_r$	0.845	0.873	0.876	0.880	0.255	0.353	0.398	0.437
Swollen $C_1$ , MN/sq m	0.057	0.124	0.200	0.270	0.027	0.071	0.11	0.168
$[X]_{\text{phys}} \times 10^2$ , mol/kg	2.53	5.41	8.71	11.7	1.60	3.79	5.63	8.36
$\chi$	1.41	1.52	1.52	1.52	0.51	0.53	0.53	0.52
	NR in <i>Reomol BCD</i>				ENR in <i>Reomol BCD</i>			
$V_r$	0.85	0.874	0.878	0.882	0.261	0.357	0.402	0.451
Swollen $C_1$ , MN/sq m	0.058	0.126	0.201	0.271	0.029	0.078	0.116	0.179
$[X]_{\text{phys}} \times 10^2$ , mol/kg	2.57	5.49	8.76	11.8	1.70	4.15	5.92	8.80
$\chi$	1.43	1.53	1.53	1.53	0.51	0.52	0.52	0.52

The behaviour of the thermodynamic diffusion coefficients is shown in *Figure 6*, where it can be seen that  $D_T$  decreases with increasing degree of crosslinking and that the maximum has almost disappeared. It appears therefore that the non-ideality of the system accounts for most, if not all, of the observed maximum in the dependence of diffusion coefficients on crosslink density.

Over the range of crosslink densities used in the rubbers, the diffusion coefficient changes by a factor as high as about two for TBEP and BCD diffusing in ENR-50 and NR, respectively as shown in *Figure 6*.

Another observation that can be made from the measurements is that most of the plasticisers, with the exceptions of DOS, DOP, DiDA, DiDP and *Reomol MD*, exhibit significantly higher equilibrium uptake in the ENR-50 vulcanisates. For DOS, DOP, DiDA and DiDP it was not surprising that the equilibrium uptake in the ENR-50 was lower because the solubility parameters of these plasticisers are closer to that of NR,  $\delta = 16.8$  (MPa)<sup>1/2</sup>, than that of ENR-50,  $\delta = 18.2$  (MPa)<sup>1/2</sup>, and the explanation is probably the same for *Reomol MD*, although no value for  $\delta$  is available for this plasticiser.

#### CONCLUSION

The equilibrium swelling measurements of the plasticisers in NR and ENR-50 showed that there is a good correlation between diffusion coefficient and (i) liquid viscosity of the plasticiser, (ii) glass transition temperatures of the elastomer and (iii) crosslink density of the rubber. Diffusion coefficient showed an interesting dependence on crosslink density in that, as the degree of crosslinking in the rubber is increased, the diffusion coefficient increases at first and then decreases continuously. An explanation for this was proposed by using the

chemical potential gradient, which leads to the thermodynamic diffusion coefficient. This term decreases with increasing crosslink density, as expected, given the increasing restriction of mobility of the rubber molecules, this may indicate some limitations of using a simple concentration gradient.

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