Plasticiser Transportation Studies in NR and Acrylonitrile-butadiene Rubber 1. Diffusion Coefficient and Equilibrium Uptake of TBEP in NBR Vulcanisates

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The diffusion coefficients (D) of tributoxyethylphosphate in gum, white- and black-filled vulcanisates of acrylonitrile-butadiene rubber (NBR) determined by means of mass uptake measurements were observed to decrease as crosslink density increases. As filler level increases for black-filled vulcanisates of NBR at fixed sulphur and accelerator levels, D was observed to continuously decrease. D, on the other hand, was found to increase as filler level increases in white-filled vulcanisates of NBR at fixed sulphur and accelerator levels. These observations are explained in terms of degree of rubber-filler interaction.

Key words: plasticiser; TBEP; NBR; vulcanisates; diffusion coefficient; gum; crosslink density; black-filled; white-filled; absorption

Diffusion in polymers is the mechanism by which molecules are transported from an area of higher concentration to one of lower concentration because of random molecular motions. The rate of transport of a material in a polymer is governed by its concentration gradient and by the degree of mobility in the bulk of the rubber, which is essentially its diffusion coefficient. The swelling of rubber by liquids is primarily a diffusion-controlled process and this has been extensively studied and reviewed¹⁻⁶ by many workers. The present paper reports the absorption of tributoxyethylphosphate (TBEP) plasticiser by gum, white- and black-filled vulcanisates of acrylonitrile-butadiene rubber (NBR). The paper also discusses the effects of crosslink density in gum vulcanisates and both crosslink density and filler level in white- and blackfilled vulcanisates of NBR on the diffusion coefficient, D, of TBEP in the rubber.

The filled vulcanisates considered here form the basis of a designed experiment investigating the effect of crosslink density and filler loading on partition of TBEP between vulcanisates; this work will be reported elsewhere. As a consequence, the diffusion

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data reported here are suitable for regression analysis to give equations describing the dependence of D on the two variables. A suitable form of regression analysis is identified and the observed behaviour is rationalised.

Fillers have different degrees of activity; most carbon blacks may be categorised as high and medium activity fillers, while calcium carbonate is an inactive filler. Filler activity is seen to have an important influence on both swelling and diffusion.

Crank⁷ has considered the mathematical treatment of diffusion for specimens of diverse geometries in detail. In the present work, the primary interest is with diffusion into a plane sheet, which is generally the type of test piece used, and the diffusion behaviour will be the same as that for a semi-infinite sheet. In the early stages of diffusion, a plane sheet behaves like semi-finite medium and the equation normally used in this case is:

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

where *D* is the diffusion coefficient, M_l is the mass of liquid absorbed per unit area of the sheet after immersion for time *t*, M_{∞} is the amount of liquid absorbed per unit area after infinite time, and *l* is the thickness of the sheet. The measurement of diffusion coefficient for plasticisers has been broadly classified as a steady-state method⁷. The steady-state method involves the monitoring of the amount of diffusing substances across a polymer-liquid interface with the passage of time until a state of equilibrium is achieved. This is made possible through the mass uptake method by plotting the amount of mass absorbed againts the square root of time.

MATERIALS AND METHODS

The NBR used in the present investigation was Breon N41C45[®] with 41% acrylonitrile content. The sample was supplied by Zeon Chemicals (South Wales) and the density was 1.02 g/cm³. It was employed mainly because of the required polarity and incompatibility with respect to NR. The plasticiser chosen in this work is TBEP, which is a non-volatile liquid of phosphoric acid derivative. It was supplied by SurfaChem Group PLC (Leeds, England). Low volatility is desirable to minimise losses during compounding at elevated temperatures and when performing swelling measurements.

In order to avoid any inconsistencies within and between compounds of a particular rubber, the same bales of each rubber were used throughout the investigation. Zinc oxide and stearic acid were supplied by Elementis Specialty (England). TMO (poly-2,2,4-trimethyl,2-dihydroquinoline, Flectol H[®], Flexsys) was obtained from Whitfield Chemicals (Staffordshire). Sulphur was supplied by Schill and Seilacher (Northampton). TBBS was used as the accelerator and was supplied by Flexsys of Clwyd LL (Wales). The fillers used were FEF (N550) carbon black supplied by Cabot Carbon Limited (Chesire) and Winnofil S[®], which is a surface-treated calcium carbonate, supplied by Ellis & Everard (Bradford, West Yorkshire). Classification of carbon black⁸ used in this study was made according to ASTM-D 1765 and the density was 1.86 g/cm³. The density of Winnofil S[®] was taken to be 2.71 g/cm³.

Masterbatches were prepared to the formulations shown in *Table 1*. The gum and white-filled masterbatches were mixed in a BR Banbury internal mixer according to the mixing cycle given in *Tables 2* and *3*, respectively. The black-filled masterbatches

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Mix number	Calcium carbonate	Carbon black (N550)
7	_	_
76	20.0	_
77	32.5	_
78	45.0	_
79	57.5	_
80	70.0	_
81	_	20.0
82	_	32.5
83	_	45.0
84	_	57.5
85	_	70.0

TABLE 1. NBR MASTERBATCH FORMULATIONS^a

^aAll contain NBR 100 parts, ZnO 5 parts, Stearic acid 1 part, and TMQ 2 parts

Fill factor	0.75
Rotor speed	70 r.p.m.
Time (min)	Procedure
0	Add rubber; ram down
1	Add powders
2	Sweep powder down chute
4	Dump

TABLE 2. MIX CYCLE FOR GUM MASTERBATCH

TABLE 3. MIX CYCLE FOR WHITE-FILLED MASTERBATCHES

Fill factor	0.75
Rotor speed	50 r.p.m.
Time (min)	Procedure
0	Add rubber; ram down
1.0	Add powders and 1/3 white filler
2.0	Add 1/3 white filler
2.5	Add 1/3 white filler
3.0	Sweep powder down chute
4.0	Sweep
6.0	Dump

were mixed in a 00C Banbury internal mixer according to the mixing cycle presented in Table 4. A semi-EV vulcanisation system, which is suitable for NBR, was employed at a fixed 1:1, sulphur:accelerator ratio. The addition of curatives was carried out on a $0.3 \text{ m} \times 0.15 \text{ m}$ two-roll mill with the rolls cooled by circulating cold water so that the shear stresses produced in the rubber did not raise the temperature above 30°C. In order to achieve a wide range of crosslink densities when the rubber mixes were vulcanised, the curatives were added according to the amounts shown in Table 5. Vulcanisation was carried out by using a compression mould in a steam-heated press at 150°C to produce a flat vulcanised sheet of uniform thickness $(228 \text{ mm} \times 228 \text{ mm} \times 1 \text{ mm}).$

The compounds had marching cures with the torque continuing to rise without any sign of reaching a steady value after 60 min. In view of this observation, cure times were fixed at 60 min.

Determination of Crosslink Density

Physically effective crosslink densities, $n_{\rm phys}$, of the gum vulcanisates were determined by estimating the Mooney-Rivlin constant, C_1 , from stress-strain measurements as described in detail elsewhere9. When using such procedures for the estimation of crosslink densities of filled vulcanisates, it is necessary to first pre-cycle the test pieces (scragging) in order to minimise the effects of filler interaction on the stress-strain measurements⁹, and the crosslink densities of the filled NR vulcanisates were obtained in this manner⁹. This technique is not suitable for the NBR vulcanisates due to relaxation arising from the relative proximity of the glass transition temperature to the test temperature⁹. However, empirical relationships allowed the calculation of crosslink densities for the calcium carbonate filled NBR vulcanisates⁹, and these were in close accord with crosslink densities for the corresponding gum vulcanisates⁹.

Physical crosslink densities for the carbon black filled NBR vulcanisates were determined from equilibrium volume swelling measurements and application of the Flory-Rehner equation to volume fraction of rubber corrected for swelling restriction by the carbon black according to Kraus, as described in detail elsewhere⁹.

Crosslink densities for all of the vulcanisates are included in *Table 6*.

Plasticiser Absorption Measurements

Absorption measurements were carried out in TBEP by using the mass uptake method, which entails the following. Samples of vulcanisates were cut to the dimensions of 25.4 mm \times 25.4 mm from a 228 mm \times 228 mm \times 1 mm thick sheet. The thickness of each test piece was measured at three different locations, using a Mercer dial-gauge capable of reading ± 0.01 mm. The average value of the three readings was recorded. A small hole (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 TBEP. The initial weight of the test piece was recorded using a laboratory balance capable of reading to ±0.0001g (Sartorious model 1601MP8). The test piece was then attached to the stainless steel hook, immersed in TBEP and allowed to absorb the plasticiser in a carefully controlled environment at 23°C. At appropriate time intervals, the test piece was removed from the TBEP. The surfaces were then cleaned by dipping in petroleum ether,

Fill factor	0.75
Rotor speed	50 r.p.m.
Time (min)	Procedure
0	Add rubber; ram down
1.0	Add powders and 1/3 black filler
2.0	Add 1/3 black filler
4.5	Add 1/3 black filler
5.0	Sweep powder down chute
6.0	Sweep
9.0	Dump

TABLE 4. MIX CYCLE FOR BLACK-FILLED MASTERBATCHES

TABLE 5. FORMULATIONS OF NBR VULCANISATES^a

Vulcanisate	Masterbatch		Sulphur	TBBS
number	Number	Amount (Parts)	(Parts)	(Parts)
71	7	108	1.09	1.09
72	7	108	1.6	1.6
73	7	108	2.1	2.1
74	7	108	2.61	2.61
75	7	108	3.11	3.11
86	76	128	2.1	2.1
87	77	140.5	1.6	1.6
88	77	140.5	2.61	2.61
89	78	153	1.09	1.09
90	78	153	2.1	2.1
91	78	153	3.11	3.11
92	79	165.5	1.6	1.6
93	79	165.5	2.61	2.61
94	80	178	2.1	2.1
95	81	128	2.1	2.1
96	82	140.5	1.6	1.6
97	82	140.5	2.61	2.61
98	83	153	1.09	1.09
99	83	153	2.1	2.1
100	83	153	3.11	3.11
101	84	165.5	1.6	1.6
102	84	165.5	2.61	2.61
103	85	178	2.1	2.1

^aAll contain 100 parts NBR

TABLE 6. LEVELS OF VARIABLES FOR THE VULCANISATES							
number	Filler Design units	Filler level Design units p.h.r.		k density Mol/m ³			
71	-	0	-2	33.3			
72	_	0	-1	52.0			
73	_	0	0	71.3			
74	_	0	1	80.5			
75	_	0	2	97.0			
86	-2	20	0	71.3			
87	-1	32.5	-1	52.0			
88	-1	32.5	1	80.5			
89	0	45.0	-2	33.3			
90	0	45.0	0	71.3			
91	0	45.0	2	97.0			
92	1	57.5	-1	52.0			
93	1	57.5	1	80.5			
94	2	70.0	0	71.3			
95	-2	20.0	0	84.5			
96	-1	32.5	-1	71.0			
97	-1	32.5	1	106.3			
98	0	45.0	-2	55.0			
99	0	45.0	0	107.7			
100	0	45.0	2	141.4			
101	1	57.5	-1	94.7			
102	1	57.5	1	136.6			
103	2	70.0	0	142.8			

which was allowed to dry off, and the test piece was re-weighed and re-immersed in the TBEP. The procedure was continued until equilibrium TBEP uptake was attained.

The mass uptake per unit original surface area, M_i , was plotted against the square root of the time of immersion. The diffusion coefficient, D, was calculated from the slope of the linear part of the plot and the equilibrium amount of plasticiser absorbed by using the following equation⁷:

$$D = \left[\frac{(M_{t} l \pi^{1/2})}{(4M_{\infty} t^{1/2})}\right]^{2} \qquad \dots 2$$

where M_t is the mass of liquid absorbed per unit area of the sheet after immersion for time t, M_{∞} is the amount of liquid absorbed per unit area after infinite time and l is the thickness of the sheet.

RESULTS AND DISCUSSION

The experimentally determined diffusion coefficients, D_{exp} , of TBEP in the NBR vulcanisates were calculated by using *Equation 2*. For each vulcanisate, M_t was plotted against the square root of time of immersion. Typical experimental absorption curves are illustrated

in Figures 1 and 2 for gum and filled NBR vulcanisates respectively, all vulcanised with a sulphur level of 2.10 p.p.h.r. It can be seen that all of the curves are sigmoid in shape. Absorption curves of this shape have been reported in the literature^{1,10-12} and Southern¹¹ has attributed the anomalous behaviour to the boundary conditions used to solve the diffusion equation not being correctly fulfilled. During the swelling the surface layer of swollen rubber is subjected to a two dimensional compressive stress by the unswollen dry rubber. As the swelling proceeds this stress gradually becomes less and is zero when final equilibrium is reached. Since the equilibrium swelling of rubber is dependent on stress¹ and the surface of the rubber is at all times in equilibrium with the diffusing liquid, it is clear that the surface concentration of liquid is not constant throughout the experiment as assumed in the solution of the diffusion equation, but gradually increases as the swelling proceeds. Also the surface area of the sheet increases, and these two effects can be expected to cause a gradual increase in the rate of absorption.

The diffusion coefficient is calculated from the linear region after the initial curvature and before the plot becomes increasingly concave to the abscissa at longer times before finally approaching an equilibrium value, as shown in *Figures 1* and 2. The slope of this linear region $(M_t/t^{1/2})$ and the equilibrium swelling in the form of volume fraction of rubber in the swollen vulcanisate, v_t , are presented in *Table 7*.

The diffusion coefficient, *D*, of TBEP in gum NBR vulcanisates decreases as crosslink density increases (*Figure 3*). Whilst there is a good fit to a second order equation:

$$D = 0.0017n_{\text{phys}}^2 - 0.338n_{\text{phys}} + 18.99$$

r² = 0.9923 ... 3

the fit to an exponential relationship is slightly better and avoids the occurrence of a minimum in calculated diffusion coefficient at a crosslink density of about 100 mol/m³:

$$D = e^{(3.297 - 0.03335n_{\text{phys}} + 0.0000735n^2_{\text{phys}})} \dots 4$$

r² = 0.9968

The effect of crosslinking is to restrict the movement of the rubber molecules so the observed continuous decrease in D is expected. Southern¹¹ and Aris *et al.*¹² on the other hand, have observed that D increases at first and then decreases continuously as the degree of crosslinking in NR gum vulcanisates increases. Aris et al.12 have also observed a similar effect in their work on ENR gum vulcanisates. Southern¹¹ proposed that this surprising behaviour was primarily due to the nonideality of the system. The driving force for diffusion in the case of non-ideal mixtures is the gradient of the chemical potential rather than the concentration gradient^{13–18}. The diffusion coefficient defined in terms of chemical potential is called thermodynamic diffusion coefficient (D_{τ}) . When Southern¹¹ plotted D_{τ} values for n-decane as a function of the degree of crosslinking in NR gum vulcanisates, he observed that the maximum almost disappeared. Aris et al.12 observed a similar trend when D_T values of TBEP and Reomol BCD[®] in NR and ENR 50, respectively were plotted againts increasing sulphur levels.

Since in the present study D is observed to decrease continuously over a wide range of crosslink densities, it may be inferred that TBEP and NBR vulcanisates exhibited a case of ideal mixtures. Therefore no attempt was made to consider D_T here.

The polymer-solvent interaction parameter, χ , was also calculated for TBEP in NBR gum vulcanisates over the range crosslink densities



Figure 1. Mass uptake per unit area as a function of root time for a gum NBR vulcanisate.



Figure 2. Mass uptake per unit area as a function of root time for a white-filled (■) *and a black-filled* (▲) *NBR vulcanisate.*

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Figure 3. Diffusion coefficient as a function of crosslink density for TBEP in gum NBR vulcanisates.

considered here by using the Flory-Rehner relationship¹⁹:

$$n_{phys} = \frac{-\left[1n(1-v_r) + v_r + \chi v_r^2\right]}{2V_o v_r^{1/3}} \qquad \dots 5$$

and a value of 3.899×10^{-4} m³/mol for the molar volume, V_o , of TBEP, and the results are included in *Table 7*. The values of χ were found to increase steadily with increasing crosslink density, and hence increasing v_r , and are sufficiently low to indicate good interaction between TBEP and NBR. They are, however, somewhat higher than were observed by Aris *et al.*²⁰ for TBEP with ENR gum vulcanisates (0.51 to 0.53).

It has already been noted that the filled vulcanisates will form the basis of a statistically designed (centre rotatable composite) experiment investigating the effects of crosslink density and filler loading on the partition of plasticiser between NR and NBR vulcanisates. The values used for the variables are not as would be required for this type of designed experiment for a two variable experiment²¹ the effect of crosslink density and filler loading on diffusion of plasticiser in NBR. Furthermore, no attempt has been made here to perform replicate experiments at the centre point, precluding rigorous analysis of the design as non-orthogonal. Nonetheless, it is possible to perform a second order regression analysis and obtain a multivariate fit. The significance of the coefficients obtained can be assessed from statistical t-tests and the fit as a whole may be judged from r².

Diffusion coefficients for the filled vulcanisates are given in *Table 8* and the coefficients in the 2nd order multivariate fit are presented in *Table 9* together with the t-statistics and r^2 . The regression analyses were performed using both the design unit values for the variables and the actual values. The two fits for the white-filled vulcanisates have rather similar values for r^2 and give very similar response surfaces (*Figures 4a* and 4b), suggesting that the experimental values for crosslink density are well-founded. Diffusion coefficient decreases

Vulcanisate number	$M_i/t^{1/2}$ g/mm ² s ^{1/2}	V _r	χ
71	1.71×10^{-3}	0.387	0.572
72	$1.30 imes 10^{-3}$	0.462	0.589
73	$8.20 imes 10^{-4}$	0.499	0.597
74	$5.49 imes 10^{-4}$	0.524	0.600
75	$4.44 imes 10^{-4}$	0.544	0.602

TABLE 7. TBEP UPTAKE BY GUM NBR VULCANISATES

TABLE 8. DIFFUSION COEFFICIENTS FOR FILLED NBR VULCANISATES

Calcium ca	urbonate filler	Carbon black filler		
Vulcanisate	D 12	Vulcanisate	D 12	
number	$(m^2/s \times 10^{-13})$	number	$(m^2/s \times 10^{-15})$	
86	4.66	95	1.81	
87	7.53	96	1.97	
88	3.70	97	1.24	
89	10.00	98	5.52	
90	5.52	99	1.13	
91	4.05	100	0.44	
92	10.48	101	1.49	
93	5.41	102	0.65	
94	10.60	103	0.89	

TABLE 9. COEFFICIENTS FOR 2ND ORDER FIT OF THE DIFFUSION COEFFICIENTS TO CROSSLINK DENSITY (X) AND FILLER LOADING (F) $D = C_0 + C_1 X + C_2 X^2 + C_3 XF + C_4 F + C_5 F^2$

Fitting	Calcium carbonate filler				Carbon black filler			
for	Design units	t-statistics	Actual values	t-statistics	Design units	t-statistics	Actual values	t-statistics
C_0	5.837	9.715	14.42	1.364	0.854	1.330	15.70	1.966
C_1	-1.733	-7.449	-0.151	-0.829	-0.978	-3.929	-0.307	-2.235
C_2	0.317	1.407	0.0007	0.682	0.514	2.135	0.0019	2.380
C_3	-0.310	-0.769	-0.0012	-0.461	-0.0275	-0.0638	-0.0001	-0.0485
C_4	1.378	5.924	-0.0984	-0.411	-0.243	-0.975	-0.0938	-0.518
C_5	0.468	2.078	0.0033	1.921	0.107	0.443	0.0009	0.704
r ²	0.970		0.955		0.880		0.912	



Figure 4a. Diffusion coefficient for TBEP as a function of crosslink density (n_{phys}) and calcium carbonate loading as given by the 2^{nd} order fit using design units for the variables.



Figure 4b. Diffusion coefficient for TBEP as a function of crosslink density (n_{phys}) and calcium carbonate loading as given by the 2^{nd} order fit using actual values for the variables.

with increasing crosslink density, as expected, but increases with increasing filler loading. This behaviour is evident in the observed diffusion coefficients, as can be seen from Figure 5. At first sight, the increase in diffusion coefficient with increasing filler loading is against expectations, since the presence of filler particles would be expected to act as a barrier to the penetrant and increase the diffusion path. However, there is little interaction between calcium carbonate and NBR, so it is expected that there will be interfacial failure on swelling and the filler particles will become surrounded by liquid filled regions²². This is confirmed by the observation of decreasing v_r with increasing calcium carbonate loading (Figure 6). The diffusion path will then be effectively reduced because the liquid filled regions will act as 'shortcuts'.

For the black-filled vulcanisates, the 2ndorder fit using design units for the variables is not good, r^2 is <0.9, but the fit using actual values for the variables is better, r^2 is 0.912. Furthermore, the response surface generated from the multivariate fit using design units shows that it predicts negative values for the diffusion coefficient at high filler loadings and moderate crosslink densities (Figure 7a). No such problem is seen for the response surface when actual values are used for the variables (Figure 7b). However, both fits predict increasing diffusion coefficients at the higher crosslink densities, which is difficult to account for and is not borne out by the observed data; for example, at 45 p.h.r. carbon black, the diffusion coefficient is observed to decrease from 1.13×10^{-13} to 0.44×10^{-13} m²/s when the crosslink density increases from 107.7 to 141.4 mol/ m^3 . When considering diffusion in the gum vulcanisates, it was observed that an exponential relationship was more appropriate for describing the dependence on crosslink density and gave a

good fit to the data. The observation of a minimum in the diffusion coefficient predicted with a 2^{nd} order fit to the data for black-filled vulcanisates is at odds with the observed behaviour (*Figure 5*) and indicates that a similar approach should be investigated for the filled vulcanisates.

Accordingly, the multivariate fit was performed for:

$$D = e^{(C_0 + C_1 X + C_2 X^2 + C_3 X F + C_4 F + C_5 F^2)} \dots 6$$

where X is crosslink density and F is filler loading and C_0 , C_1 etc. are coefficients. In practice, the relationship fitted was:

$$\ln D = C_0 + C_1 X + C_2 X^2 + C_3 XF + C_4 F + C_5 F^2 \qquad \dots 7$$

Fits were performed using both design units and actual values for the variables. Although the fit using actual values had a slightly higher correlation coefficient, t-statistics indicated that none of the coefficients for the variables were significant and the response surface showed an exaggerated increase in diffusion coefficient at low crosslink densities and high filler contents. Only the fit using design units will be considered further. The coefficients are presented in Table 10 and the response surface is illustrated in Figure 8. The latter shows decreasing diffusion coefficient with increasing crosslink density and increasing filler level, except at low crosslink densities when an increase is predicted at the highest filler levels.

This predicted increase in diffusion coefficient cannot be explained and is most likely an artefact of the fit. The generally decreasing diffusion coefficient with increasing filler content is expected, the filler particles acting as a barrier thereby increasing the diffusion path, as noted above. This fit to an exponential



Figure 5. Observed diffusion coefficient for TBEP as a function of crosslink density for gum, white-filled and black-filled NBR vulcanisates.



Figure 6. Volume swelling, as given by v_r, as a function of crosslink density for different calcium carbonate loadings.



Figure 7a. Diffusion coefficient for TBEP as a function of crosslink density (n_{phys}) and carbon black loading as given by the 2^{nd} order fit using design units for the variables.



Figure 7b. Diffusion coefficient for TBEP as a function of crosslink density (n_{phys}) and carbon black loading as given by the 2^{nd} order fit using actual values for the variables.

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Figure 8. Diffusion coefficient for TBEP as a function of crosslink density (n_{phys}) and carbon black loading as given by the exponential fit using design units for the variables.

TABLE 10. COEFFICIENTS FOR EXPONENTIAL FIT OF THE DIFFUSION COEFFICIENTS TO
CROSSLINK DENSITY (X) AND FILLER LOADING (F)
$\ln D = C_0 + C_1 X + C_2 X^2 + C_3 XF + C_4 F + C_5 F^2$

Fitting	Calcium carbonate filler			Carbon black filler				
for	Design units	t-statistic	Actual values	t-statistic	Design units	t-statistic	Actual values	t-statistic
C_0	1.741	19.99	3.48	2.277	0.108	0.4878	3.66	2.256
C_1	-0.265	-7.853	-0.0266	-1.010	-0.529	-6.190	-0.0385	-1.462
C_2	0.0294	0.9005	3.96×10^{-5}	0.2601	0.0831	1.003	1.3×10^{-4}	0.8820
C_3	0.0123	0.2111	9.8×10^{-5}	0.2574	-0.0917	-0.6189	-2.87×10^{-4}	-0.4905
C_4	0.196	5.815	-0.0268	-0.7727	-0.195	-2.285	-0.0264	-0.7773
C_5	0.0542	1.660	3.96×10^{-4}	1.616	0.0318	0.3838	7.54×10^{-4}	0.9680
r ²	0.9704		0.9568		0.9375		0.9528	

relationship is better than the 2nd order fit, both in respect of the lack of a minimum in diffusion coefficient with increasing crosslink density and the significantly higher correlation coefficient. Although the 2^{nd} order fit to the data for the white-filled vulcanisates was good, it is logical to consider a fit to an exponential relationship. The outcome is included in *Table 10*; the correlation coefficients are comparable to

Vulconicato		2 nd order fit			Exponential fit	
number	D_{calc} $(\text{m}^2/\text{s} \times 10^{-13})$	$D_{\text{calc}} - D$ $(\text{m}^2/\text{s} \times 10^{-13})$	Difference %	D_{calc} $(\text{m}^2/\text{s} \times 10^{-13})$	$D_{calc} - D$ (m ² /s × 10 ⁻¹³)	Difference %
	(11/5/(10))	(11757110)	70	(11/5/(10))	(11757(10))	/0
86	4.95	0.29	6.28	4.79	0.13	2.71
87	6.67	-0.86	11.5	6.73	-0.80	10.7
88	3.82	0.12	3.24	3.86	0.16	4.40
89	10.57	0.57	5.71	10.9	0.90	9.00
90	5.84	0.32	5.74	5.70	0.18	3.33
91	3.64	-0.41	10.2	3.78	-0.27	6.74
92	10.04	-0.44	4.17	9.71	-0.77	7.30
93	5.96	0.55	10.1	5.86	0.45	8.34
94	10.47	-0.13	1.27	10.5	-0.11	1.03
		Average	6.46		Average	5.95

TABLE 11. CALCULATED DIFFUSION COEFFICIENTS FOR WHITE-FILLED VULCANISATES

TABLE 12. CALCULATED DIFFUSION COEFFICIENTS FOR BLACK-FILLED VULCANISATES

Vulcanisate	2 nd order fit			Exponential fit			
number	$D_{\rm calc}$	$D_{\rm calc} - D$	Difference	D_{calc}	$D_{\rm calc} - D$	Difference	
number	$(m^2/s \times 10^{-13})$	$(m^2/s \times 10^{-13})$	%	$(m^2/s \times 10^{-13})$	$(m^2/s \times 10^{-13})$	%	
95	1.77	-0.044	2.42	1.87	0.059	3.28	
96	2.67	0.70	35.4	2.35	0.38	19.4	
97	0.768	-0.47	38.1	0.981	-0.26	20.9	
98	4.87	-0.65	11.8	4.48	-1.04	18.9	
99	0.854	-0.28	24.4	1.11	-0.016	1.44	
100	0.956	0.52	117	0.539	0.099	22.4	
101	2.24	0.75	50.2	1.91	0.42	28.3	
102	0.228	-0.42	65.0	0.552	-0.098	15.0	
103	0.796	-0.094	10.5	0.856	-0.034	3.87	
		Average	39.5		Average	14.9	

those for the 2^{nd} order fits (*Table 9*). Although the difference between r^2 for the two exponential fits is small, the fit using design units has more significant coefficients. It is also pertinent to consider the residuals of the fits, that is the difference between the observed diffusion coefficients and those calculated from the fits at the experimental points.

This comparison shows that both fits are good (*Table 11*), with the average percentage difference being about 6%, and that the exponential fit is slightly better overall. The same comparison for the black-filled vulcanisates provides a further demonstration of the better fit provided by the exponential relationship (*Table 12*).

One stern test for the fits is to consider the predictions for zero filler level and compare them with the actual values observed for the gum vulcanisates. This comparison is made in Figure 9. Apart from the increase in calculated diffusion coefficient at high crosslink densities, the agreement between the values calculated from the exponential fit for black-filled vulcanisates, using actual values for the variables, and the observed diffusion coefficients for gum vulcanisates is good. This indicates not only that the exponential fit has some utility, but also that the estimates of crosslink density are also good⁹. The agreement between the observed diffusion coefficients for gum vulcanisates and those calculated from the multivariate fit for the white-filled vulcanisates is less good, the latter being consistently high. Again a comparison of the differences between the observed diffusion coefficients and the values calculated from the various relationships is instructive (*Table 13*). The fit to the exponential relationship is clearly better in this respect for both white- and black-filled vulcanisates.

CONCLUSIONS

For TBEP diffusing in gum NBR vulcanisates, D decreased monotonically with increasing crosslink density, as expected for an ideal mixture. This behaviour differed from that observed previously for some other elastomer/penetrant mixtures, for which it was necessary to invoke the thermodynamic diffusion coefficient in order to observe the expected decrease with increasing crosslink density. The relationship between D and crosslink density was fitted better by a second order exponential relationship than by a second order power series.



Figure 9. Comparison of the observed diffusion coefficient for TBEP in gum NBR vulcanisate as a function of crosslink density with diffusion coefficients calculated from the multivariate fits for white- and black-filled vulcanisates.

	Calaium aar	aanata fillar	Carbon blook filler		
Vulcanisate number	Second order fit: Difference (%)	Exponential fit: Difference (%)	Second order fit: Difference (%)	Exponential fit: Difference (%)	
71	3.4	21.5	18.8	27.8	
72	40.5	42.2	7.1	19.7	
73	81.2	48.4	1.0	11.3	
74	129.0	48.2	24.5	4.3	
75	229.0	62.5	92.9	50.0	
Average	96.6	44.6	28.9	22.6	

TABLE 13. DIFFERENCE BETWEEN OBSERVED DIFFUSION COEFFICIENTS FOR GUM VULCANISATES AND VALUES CALCULATED FROM THE VARIOUS MULTIVARIATE FITS

A second order exponential relationship was also found to be better for fitting the dependence of D on crosslink density and filler loading for both calcium carbonate and N550 carbon black filled vulcanisates. With carbon black as filler, D decreased with both increasing crosslink density and increasing filler loading, as expected. However, with calcium carbonate as filler, the expected decrease in D with crosslink density was observed, but D increased with increasing filler loading. The latter observation runs counter to expectations based on filler particles acting to increase the diffusion path, but can be explained in terms of interfacial failure (de-bonding) between the rubber and the inactive calcium carbonate filler under the stresses arising from swelling of the rubber matrix. The resulting void was filled with liquid, thereby providing a short-cut to diffusion of the penetrant.

The fitted relationships appeared to have good predictive power, even provided a reasonable estimate of D for gum vulcanisates.

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REFERENCES

- CRANK, J. AND PARK, G.S. (eds.) (1968) Diffusion in Polymers. London: Academic Press Inc.
- VAN AMERONGEN, G.J. (1964) Diffusion in Elastomers. *Rubb. Chem. Technol.*, 37, 1065–1148.
- ROGERS, C.E. AND MACHIM, D. (1972) CRC Critical Reviews in Macromolecular Science., 1, 245–313.
- 4. KUMINS, C.A. (ed.) (1973) Transport Phenomena through Polymer Films. J. Polym. Sci., C41. New York: Interscience.
- 5. BARRER, R.M. (1941) *Diffusion in and through Solids*. London: Cambridge University Press.
- FUJITA, H. (1961) Diffusion in Polymer-Diluent Systems. Fortschr Hockpolymn Forsch., 3, 1–47.
- 7. CRANK, J. (1956) *The Mathematics of Diffusion*. London: Oxford Press.
- 8. ASTM D-1756-99b (2000) Carbon Blacks Determination. Annual Book of ASTM Standards, **09.01**.

Faridah H.A.H. et al.: Plasticiser Transportation Studies in NR and Acrylonitrile-butadiene Rubber

- H.A.H., FARIDAH, TINKER, A.J. AND FARID, A.S. (2004) Determination of Crosslink Densities of Filled Rubbers by Cyclic Prestraining. J. Rubb. Res., 7(4), 248–264.
- CRANK, J. AND PARK, G.S. (1951) Diffusion in High Polymers: Some Anomalies and Their Significance. *Trans. Faraday Soc.*, 47, 1072–1084.
- 11. SOUTHERN, E. (1969) The Diffusion of Liquids in Rubber. Ph.D. Thesis, University of London.
- ARIS AHMAD, TINKER, A.J. AND AUBREY, D.W. (1995) Absorption of Ester Type Plasticisers by Natural Rubber and Epoxidised Natural Rubber–Diffusion Coefficients and Equilibrium Uptake. J. nat. Rubb. Res., 9, 1–12.
- HARTLEY, G.S. AND CRANK, J. (1949) Some Fundamental Definitions and Concepts in Diffusion Processes. *Trans. Faraday Soc.*, 45, 801–818.
- GLASSTONE, S., LAIDLER, K.J. AND EYRING, H. (1941) Theory of Rate Processes. New York: McGraw Hill.
- HARTLEY, G.S. (1946) Diffusion and Swelling of High Polymers I. The Swelling and Solution of a High Polymer Solid Considered as a Diffusion Process. *Trans. Faraday. Soc.*, **42B**, 6–23.

- BARRER, R.M. (1946) Interpretation of the Distribution of Sorbed Dye and Other Molecules in Proteins and Plastics. Soc. Dyers. Col. Sump. on Fibrous Proteins, 108–121.
- ONSAGER, L. AND FUOSS, R.M. (1932) Irreversible Processes in Electrolytes. Diffusion, Conductance, and Viscous Flow in Arbitrary Mixtures of Strong Electrolytes. J. Phys. Chem., 36, 2689–2778.
- PARK, G.S. (1950) The Diffusion of Some Halo-Methanes in Polystyrene. *Trans. Faraday Soc.*, **51**, 684–697.
- FLORY, P. AND REHNER, J. (1943) Statistical Mechanics of Cross-Linked Polymer Networks 1. Rubberlike Elasticity. J. Chem. Phys., 11, 512–520.
- ARIS AHMAD, TINKER, A.J. AND AUBREY, D.W. (1995) Distribution of Ester Plasticisers between Two Rubber Phases – Estimation of Partition Coefficients and Comparison with Theory. J. nat. Rubb. Res., 10, 1–13.
- 21. FREAKLEY, P.K. (1985) Rubber Processing and Product Organisation. New York: Plenum Press.
- KRAUS, G. (1963) Swelling of Filler-Reinforced Vulcanisates. J. appl. Polym. Sci., 7, 861–871.