Diffusion in network polymers: model development and evaluation*

M. G. Kulkarni and R. A. Mashelkar
Department of Chemical Engineering, National Chemical Laboratory, Poona 411 008, *India*

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In spite of the importance of diffusion in network polymers, there exist no theoretical models with predictive ability. A two-phase concept has been used to develop a modified Maxwell model to establish diffusivity–structure correlation in network polymers for the first time. The physical significance of the model parameters has been elaborated and existing data examined to substantiate the model. Pragmatic implications of the model are discussed.

INTRODUCTION

Study of transport properties of multicomponent polymer systems is pragmatically important. For example, effectiveness of plasticizers in PVC formulations is governed by diffusion of plasticizer to the surface; oxidative degradation of rubber is controlled by the diffusion of oxygen in rubber and weatherability of rubbers depends on the choice of antioxidant systems which can provide both short and long term protection. For example, the kinetics of oxidation of rubber is governed by the relative magnitudes of diffusion coefficient of oxygen and the antioxidant. Kuzminskii[1] observed that in organic liquids the coefficient of diffusion of oxygen and phenyl-2-napthylamine are of the same order. In polybutadiene, however, diffusion coefficient of phenyl-2-napthylamine (2×10^{-8} cm^2 s^{-1}) is two orders of magnitude lower than that of oxygen (1.5×10^{-6} cm^2 s^{-1}). The lower activity of the antioxidant was thus attributed to lower diffusion coefficient. A judicious choice of vulcanizing agents and accelerators is an essential prerequisite to ensure uniform cure of rubber blends. Knowledge of the role of polymer morphology in determining the transport properties of the polymer is essential for systematic development of polymers, for barrier properties and membranes for separation processes.

In 1831, Mitchell[2] discovered that a rubber membrane is permeable to gases and that the rate of permeation is different for different gases. In dyeing of animal hair it was observed that an increase in number of disulphide crosslinks led to a decrease in the rate of dyeing of Acid Orange 2G[3,4]. Similarly, treatment of cellulosic textiles with formaldehyde derivatives was observed to decrease the dyeability. However, no systematic efforts were made to study the influence of crosslinking. Barrer and coworkers[5,6] studied diffusion of gases in crosslinked polymers and concluded that the influence of crosslinking on diffusivity is more drastic for gases which are larger in diameter. In the case of polymers crosslinked by organic peroxides, sulphur or irradiation[7–9], both the energy of activation for diffusion and the pre-exponential factor, D_0, increased with increasing crosslinking and increasing molecular diameters of gas. Crosslinking by sulphur leads to sulphur bridges in the network structure, which is not the case with the other two crosslinking agents. Stannett[10] showed that changes in cohesive energy of polymer due to sulphur crosslinking is quite small and use of sulphur is a valid way to introduce crosslinks in rubber without altering the chemical nature of the polymer appreciably. The decrease in diffusivity was related to decreased mobility of polymer chains due to crosslinking. No simple relationship exists between the sulphur content of crosslinked rubber and the permeability or diffusivity.

There has been no previous effort to develop a theoretical framework on which analysis of transport properties of network polymers could be based. This contrasts with a number of correlations which have been developed to correlate transport properties of semicrystalline polymers. Development of such a basis would lead to a better understanding of the influence of polymer morphology on transport properties. The present paper provides a framework which is a first approximation to the complex process of diffusion in network polymers.

THEORY

A number of transport properties such as thermal conductivity[11], molecular diffusivity[12] and electrical conductivity have been successfully correlated. Maxwell[13] studied the problem of electrical conduction in dilute dispersion of spheres of uniform size in a continuous phase. The resulting equation correlates conductivity K of the dispersion with the corresponding values of conductivity K_1 and K_2 for the continuous and dispersed phase respectively. Thus:

$$K = K_1\left[\frac{K_2+2K_1-2x_2(K_1-K_2)}{K_2+2K_1+x_2(K_1-K_2)}\right] \qquad (1)$$

where x_2 denotes the volume fraction of dispersed phase. The equation is strictly valid for dilute suspensions comprising uniform spherical particles so that flux around a particle is not affected by that of the other.

The equation has been used successfully in the past to correlate other transport properties such as permeability and thermal conductivity of composite systems. An advantage of using these equations is that their use does

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not necessitate a detailed knowledge of microstructure of each phase. Thus permeability P of a composite system is given by:

$$P=P_1\left[\frac{P_2+2P_1-2x_2(P_1-P_2)}{P_2+2P_1+x_2(P_1-P_2)}\right] \qquad (2)$$

This equation will eventually form the framework within which one could analyse the diffusion phenomena in structured polymers. We shall consider two cases of interest.

Firstly, consider diffusion in a semicrystalline polymer. This can be considered as a two phase system comprising a crystalline discrete phase dispersed in a continuous amorphous matrix. In such a case, it is assumed that permeability in the crystalline phase (P_2) is negligible compared to that in the amorphous phase (P_1). For the limiting condition $P_2 \ll P_1$, we have:

$$P=P_1\left[\frac{1-x_2}{1+\frac{x_2}{2}}\right] \qquad (3)$$

or

$$SD=S_1D_1\left[\frac{1-x_2}{1+\frac{x_2}{2}}\right] \qquad (4)$$

where S and S_1 denote solubility in the semicrystalline and purely amorphous polymer; D and D_1 denote diffusivity in semicrystalline and amorphous polymer, respectively.

It is also known that solubility is proportional to volume fraction of amorphous phase. So that:

$$S=S_1(1-x_2) \qquad (5)$$

and hence

$$D=D_1\left[\frac{1}{1+\frac{x_2}{2}}\right] \qquad (6)$$

This equation is valid for the highly idealized case. It is reasonable again to assume that real systems will show deviations from equation 6. Therefore a modified equation is proposed:

$$D=D^*\left[\frac{1}{1+\frac{x_2}{2}}\right]+D_0 \qquad (7)$$

where D^* and D_0 would be characteristic of the polymer–penetrant system under investigation.

Correlations of the form proposed in equation (7) have, to a certain extent, been used to correlate diffusivities in two phase polymer systems[12]. However, no such effort has been made to correlate diffusion in crosslinked polymers. This paper aims to present such a correlation technique.

The choice of an appropriate parameter to correlate the data for crosslinked polymer is not straightforward. This is because crosslinked polymers exhibit more complex structure and therefore their characterization is more difficult. Techniques of characterization of network polymers have been summarized by Nielsen[14].

In semicrystalline polymers, diffusivity decreases with increasing crystallinity. This decrease is attributed to two factors[15]. Firstly, the crystalline regions are impermeable. The geometric impedence to diffusion is a function of crystalline fraction alone and is independent of the nature of the diffusing molecule. Secondly, as a consequence of the fact that the polymer chains pass through both crystalline and amorphous regions, the mobility of chains in amorphous regions is hindered. However, the crystallinity remaining the same, the degree of chain immobilization experienced by a penetrating molecule will increase with increasing molecular size of the penetrant.

In the case of crosslinked polymers, the volume fraction of junction points would be extremely small. As a result, the decrease in diffusivity is due to chain immobilization alone. The degree of immobilization is normally expressed as the moles of effective network strands per unit volume (ν) and is estimated either from swelling measurements using Flory–Rehner equation [16] or from elastic moduli measurements[17].

The parameter (ν) gives a qualitative idea of the degree of crosslinking. It cannot, however, be used to correlate the data since the limiting values of this parameter are not known. The moles of effective strands per unit volume (ν) is related to molecular weight between crosslinks (M_c), by the relation

$$\nu=\frac{N\rho}{M_c} \qquad (8)$$

where N and ρ denote Avogadro number and specific gravity of the polymer, respectively.

Diffusion in polymers is governed by the mobility of chain segments. It is thus rational to assume that molecular mobility will increase with increasing molecular weight between crosslinks. As a threshold value is reached, further increase in molecular weight will have no influence on segmental mobility. Thus the ratio $\frac{M_c}{M_\infty}$, where M_∞ denotes the molecular weight corresponding to diffusivity in uncrosslinked polymer, will denote the fractional mobility of the network structure with molecular weight between crosslinks, M_c. Correspondingly

$$f_c=1-\frac{M_c}{M_\infty} \qquad (9)$$

would denote the degree of immobilization when the molecular weight between crosslinks is M_c. We define the parameter f_c as a crosslink fraction and propose the use of the equation:

$$D=\frac{D_1}{1+\frac{f_c}{2}} \qquad (10)$$

where D_1 denotes the diffusivity in uncrosslinked polymer. Following the same logic as used in deriving equation (7):

$$D=\frac{D^*}{(1+f_c/2)}+D_0 \qquad (11)$$

The reasons for substituting f_c for x_2 in equation (7) have been discussed earlier. Equations (7) and (11) indicate that it is possible to establish a linear correlation by plotting D vs. $(1+x_2/2)^{-1}$ for semicrystalline polymers or by plotting D vs. $(1+f_c/2)^{-1}$ for crosslinked polymers. D^* and D_0 have certain physical significance. Thus for $f_c=0$, we have $D=D^*+D_0$, which denotes the diffusivity of the penetrant molecule in uncrosslinked polymers.

D^* denotes the slope of the linear plot of D vs. $(1+\frac{f_c}{2})^{-1}$.

f_c is a measure of extent of crosslinking in the polymer, i.e. loss of mobility of the polymer chain, an essential prerequisite for the diffusional jump to occur. The hindrance to the transport of a diffusant molecule, resulting from decrease in chain mobility, is expected to be a function of the effective cross-sectional area of the diffusant molecule. (D^*) is a measure of the effect of decreased chain mobility, resulting from crosslinking, on the diffusivity of the penetrant. Following arguments in the literature[15], $[D^*]^{-1}$ may be related to the probability of hinderance to segmental mobility due to the presence of crosslinks. Also, the polymer morphology remaining the same, the probability of hindrance to a diffusing molecule is expected to be proportional to the reduced cross-sectional area of the molecule. Consequently, a linear relationship between log $[D^*]^{-1}$ and the square of the reduced molecular diameter is to be expected.

The reduced molecular diameter of the diffusant is defined as $\left[d-\frac{\varphi^{1/2}}{2}\right]$, where d is the nominal diameter of the gas molecule and $\frac{\varphi^{1/2}}{2}$ is the mean unoccupied distance between the chain segments. The details of procedure for evaluation of reduced molecular diameter have been described by Michaels and Bixler[15].

RESULTS AND DISCUSSION

In the section on Theory, we have shown the development of a simple equation, relating the diffusive phenomena with the morphological features in the case of semicrystalline polymer. The validity of equation (7) for semicrystalline polymers will be examined before the validity of equation (11) for network polymers. Summary of all the systems investigated in this work appears in *Table 1*.

Seimcrystalline polymers

Diffusion and permeability coefficients of a wide range of penetrants in semicrystalline polymers have been reported in the literature. These can be analysed in the light of equation (7) presented earlier. A detailed discussion of the influence of polymer morphology on transport properties can be found elsewhere[18]. Illustrative plots which confirm the utility of this equation in correlating the data are shown in *Figures 1, 2* and *3*. Equation (7) can be used to correlate diffusivities in a wide range of semicrystalline polymers, in which one phase is impermeable. A plot of this kind for diffusion of gases in semicrystalline polymers would yield a family of straight lines with slopes increasing with the molecular diameter of the gas. Michaels and Bixler[15] studied diffusion of a wide range of gases in a family of hydrocarbon polymers, viz. LDPE, HDPE, polybutadiene and natural rubber. The data in this case do not obey a strictly linear relation because the structure of the polymer was changed as well as the crystallinity. However, the data confirm that the dependence of diffusivity on crystallinity increases with increasing molecular diameter of the penetrant (*Table 2*).

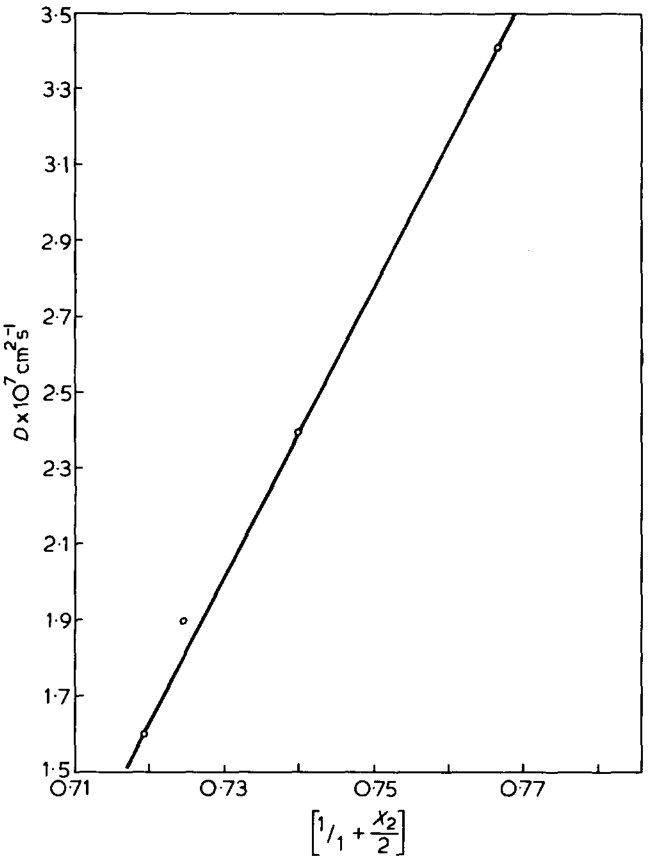

Figure 1 Effect of crystallinity on diffusion of oxygen in polyethylene (Data ref 19)

Table 1 Summary of systems investigated

Polymer	Immobilizing attribute	Penetrants studied	Method of investigation	Reference
Ethylacrylate	Copolymerization with TEGDM	Noble gases, CO_2, H_2, N_2, O_2	Time lag	22
Natural rubber	Crosslinking with sulphur	N_2, CH_4, C_2H_6	Time lag	6
Cellophane	Crosslinking with DMEU and BHES	Chrysophenine G, Chlorazol Sky Blue FF	Dye absorption	24, 25
Polyethylene	Crystallinity	O_2	Sorption expt.	19
Polyester	Crystallinity	CI Disperse red 15	Dye absorption	20
Gutta Percha	Crystallinity	Benzene	Sorption expt.	21

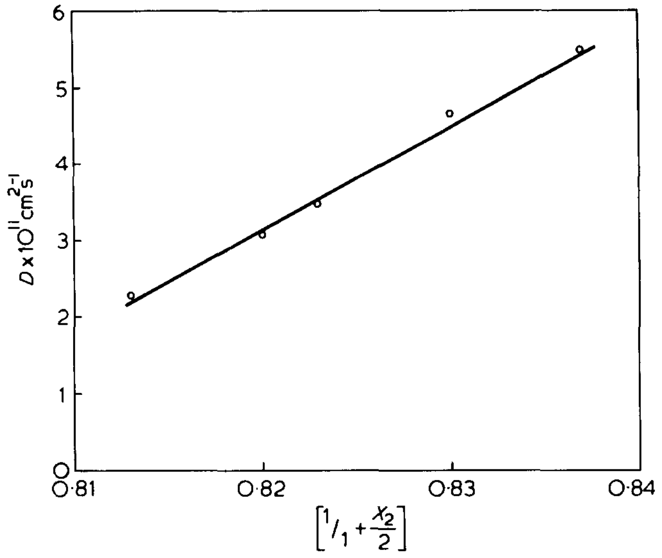

Figure 2 Effect of crystallinity on diffusion of CI disperse red 15 in polyethylene terephthalate (Data ref 20)

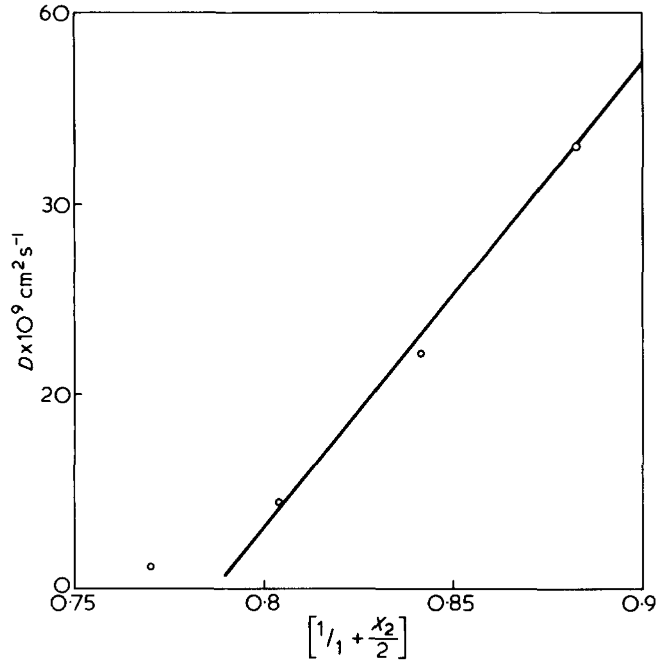

Figure 3 Effect of crystallinity on diffusion of benzene in Gutta Percha (Data ref 21)

Crosslinked polymers

Ethylacrylate–tetraethyleneglycol dimethacrylate copolymers. Barrer *et al.*[22] studied diffusion of various noble gases and of carbon dioxide, hydrogen, nitrogen and oxygen in copolymers of ethylacrylate and tetraethyleneglycol dimethacrylate. For this system M_∞ was calculated by plotting M_c *versus* composition and extrapolating the plot to the point corresponding to ethylacrylate homopolymer. The plots of D vs. $\left(1+\frac{f_c}{2}\right)^{-1}$ for various gases are shown in *Figure 4*. The plots are linear as predicted by equation (11).

Two features of this plot deserve consideration. Firstly, the linear dependence predicted is not observed in the case of hydrogen and helium (not shown in the Figure) and secondly, the point corresponding to homopolymer of tetraethyleneglycol dimethacrylate does not lie on the straight line. Diffusion of helium and hydrogen exhibits characteristics different from those of others because of their very small molecular diameters. In fact, Barrer's[3] earlier studies on diffusion of helium in lightly vulcanized rubbers led to the conclusion that crosslinking has no influence on transport of gases through rubbers. The decrease in chain mobility resulting from light crosslinking (2phr sulphur) does not affect diffusion of helium through the membrane.

In the case of tetraethyleneglycol dimethacrylate homopolymer, the calculated value of M_c is much less than the value obtained experimentally. This indicates that the anticipated degree of crosslinking is not reached in the homopolymer. The chain mobility is greater than in the case of completely crosslinked material and hence the diffusivity is greater than that predicted.

Table 2 Diffusivities of gases in semicrystalline polymers relative to diffusivities in natural rubber [Michaels and Bixler (15)]

Gas	$\left(d-\frac{\phi}{2}\right)^{1/2}$ A°	HDPE	LDPE	Poly-butadiene
He	1.3	0.142	0.315	0.699
Ar	2.7	0.085	0.265	0.706
N_2	2.8	0.079	0.274	0.633
CH_4	3.2	0.064	0.217	0.607
C_2H_6	4.3	0.036	0.170	0.600
C_3H_8	4.9	0.023	0.153	0.571
SF_6	5.5	0.014	0.117	0.487

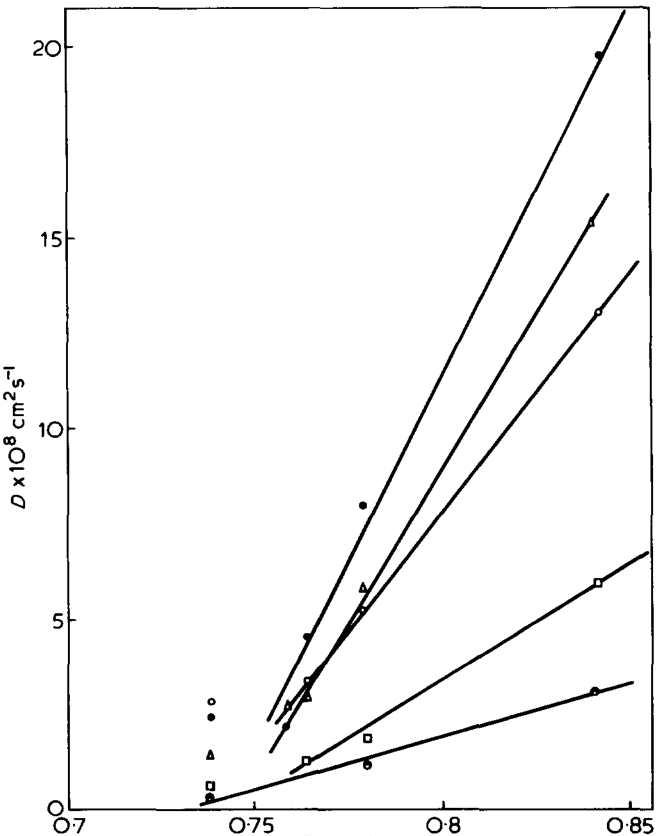

Figure 4 Effect of degree of crosslinking on diffusivity of argon (●), nitrogen (△), neon (○), krypton (□) and carbon dioxide (○) in tetraethyleneglycol dimethacrylate–ethylacrylate copolymer (Data ref 22)

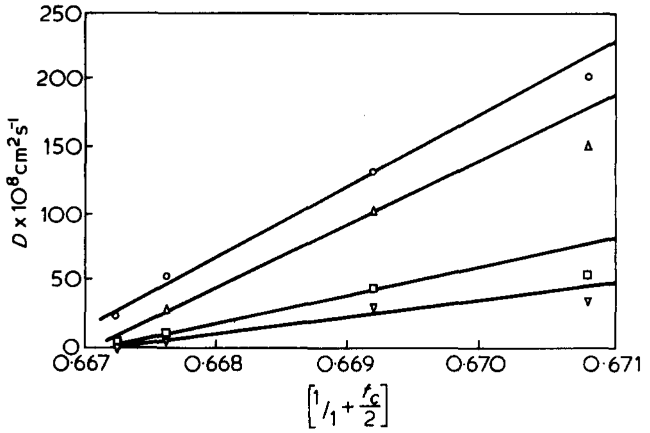

Figure 5 Effect of degree of crosslinking on diffusion of various gases at 40°C in sulphur crosslinked natural rubber, ○ nitrogen, △ methane, □ ethane, △ propane (Data ref 6)

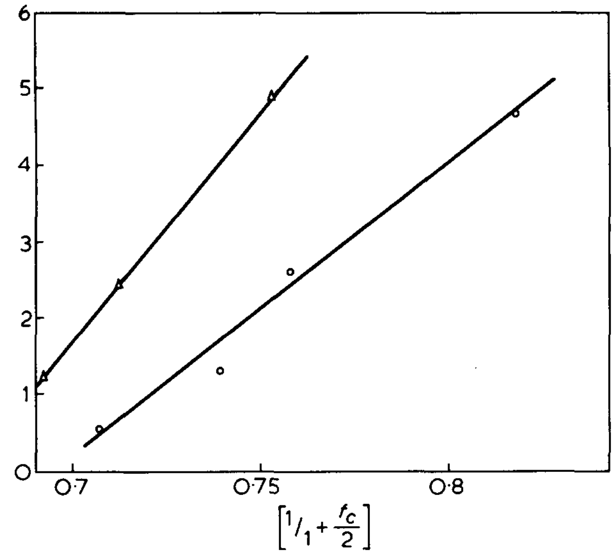

Figure 6 Effect of degree of crosslinking on diffusion of chrysophenine G at 70°C in cellophane crosslinked with dimethylol ethylene urea (○), and bishydroxyethyl sulphone (△), (Data ref 24)

Sulphur crosslinked natural rubber. Barrer and Skirrow[6] studied the diffusion of nitrogen and hydrocarbon gases in rubbers vulcanized at different loadings of sulphur. In this case, no swelling studies were made and crosslink density could not be calculated directly as in the case of ethylacrylate–tetraethyleneglycol dimethacrylate copolymer system. Crosslink density was calculated by knowing the quantity of sulphur used in vulcanization. As a first approximation, it was assumed that the crosslinks contained a single sulphur bridge. *Figure 5* shows diffusivities of various gases in rubbers vulcanized at different loadings of sulphur. In this case too, data lie on a straight line except that there is a consistent deviation observed for lowest sulphur content, indicating diffusivity values higher than suggested by the correlation. Such high diffusivity values can be explained on the basis of considerations of Flory *et al.*[23], who showed that the structure–property relationship at low levels of crosslinking are likely to be complicated by chain scission process. The observation that the same correlation holds good for crosslinked polymers and sulphur vulcanizates also supports Stannett's views, that change in cohesive energy of rubber due to sulphur crosslinking is quite small[10].

DMEU and BHES crosslinked cellophane. Cellulosic fabrics have been treated with multifunctional reagents to improve dimensional stability as well as wrinkle recovery. The decrease in dyeability of such fabrics with increased crosslinking could be attributed to either (a) lack of affinity of the dye to the fibre, (b) decrease in diffusion coefficient of dye, or (c) inaccessibility of the fibre to the dye. Ibe and Valko[24,25] studied equilibrium dye uptake and the rate of dyeing of two direct dyes, Chrysophenine G and Chlorazol Sky Blue FF in cellophane, crosslinked with dimethylolethylene urea (DMEU) and bis(hydroxyethyl) sulfone (BHES). It was observed that under limiting conditions, the equilibrium dye uptake decreased by 40% whereas the rate of dyeing decreased by ~90%. Decrease in rate of dyeing of crosslinked cellulosics is thus due to the decrease in diffusion coefficient of the dye.

Typical plots for this system are shown in *Figure 6*. The relationship predicted by equation (11) is again valid. In the case of cellophane crosslinked with DMEU, the decrease in diffusion coefficient is more drastic than in the case of the polymer crosslinked with BHES (see *Table 3*). Crosslinking with DMEU leads to a more compact network compared to that formed with BHES, (evident from the molecular structure of the two compounds) which explains the diffusion behaviour in the two systems.

Diffusivity of direct dyes in cellulosic substrates is governed by the molecular size of the dye as well as affinity considerations. The role of affinity between the dye and the fibre is well established[26–28]. Standard affinity is a measure of the tendency of the dye to move from its standard state in the dye bath, on to the fibre. The number of sites available for polar interaction with the dye molecule, as well as the free volume for dye diffusion, decrease with increasing crosslink density. It is expected, therefore, that diffusivity of Chlorazol Sky Blue FF is more sensitive to crosslink density than that of Chrysophenine G (*Table 3*).

Irradiated polyethylene. Crosslinking can be introduced in polymers by irradiation. Available data[7–9] are not sufficient to test the validity of the equation in the case of radiation crosslinked polymers. The data are, however, in qualitative agreement with the anticipated behaviour, e.g. Sobolov *et al.*[7] reported no change in permeabilities of polyethylene irradiated to 10^7 roentgens whereas the same reduced by 50% when irradiated to 10^8 roentgens. The data also support our interpretation of diffusivities in crosslinked polymers. Irradiation to 10^7 roentgens corresponds to one crosslink per 600 monomer units, while in the latter case, one crosslink results for every 60

Table 3 Effect of crosslinking on diffusivity of direct dyes in cellophane crosslinked with DMEU (*Ibe and Valko*[25])

	$X_c =$	$f_c =$	$\frac{D}{D\ \text{uncrosslinked}}$ for	
M_c	$1-\frac{M_c}{M_\infty}$	$\frac{1}{1+X_c/2}$	Chrysophenine G	Chlorazole Sky Blue FF
5300	0.8262	0.7076	0.2279	0.1848
2400	0.9213	0.6846	0.1348	0.1076
950	0.9688	0.6736	0.0104	0.0078

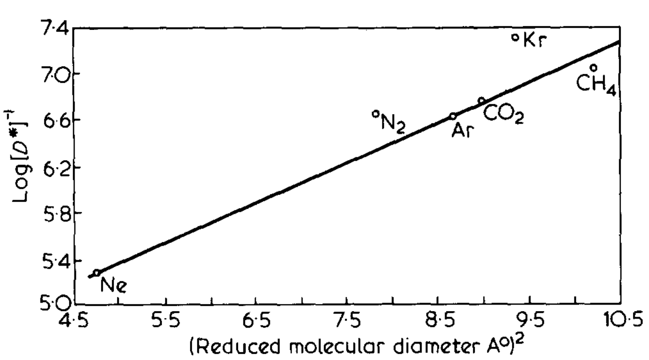

Figure 7 Correlation of D^* with reduced molecular diameter of diffusants (Data ref 22)

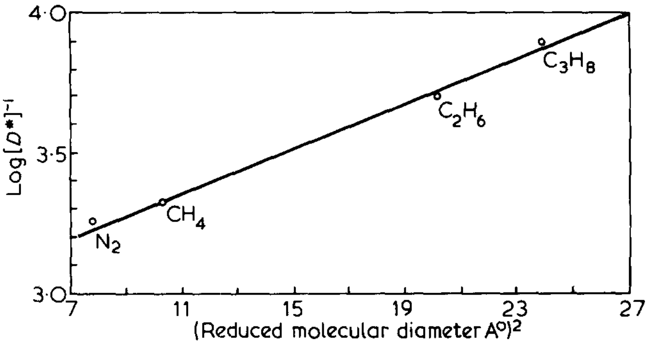

Figure 8 Correlation of D^* with reduced molecular diameter of diffusants (Data ref 6)

monomer units. The loss in chain mobility, therefore, is not realized by the gas molecules at this stage. In the latter case too the decrease in permeability is more drastic for molecules which are larger in diameter.

Significance and correlation of D*

We now examine the influence of decreased chain mobility on the diffusion process. Extensive data are not available to examine this in all the systems investigated in earlier sections.

The slopes, D^* of the linear plots shown in *Figures 4* and *5* were evaluated. These were then plotted vs. the square of the reduced molecular diameter of the diffusing gases. Here φ denotes the free volume per unit chain length of a $-CH_2-$ group and $\frac{\varphi^{1/2}}{2}$ represents mean unoccupied distance between two chain segments. Details of calculation of φ can be found in the literature[15]. There was some uncertainty in the calculation of $\frac{\varphi^{1/2}}{2}$ and approximations had to be made, which could cause large errors particularly when d and $\frac{\varphi^{1/2}}{2}$ are nearly equal. For the data examined, d was reasonably large in relation to $\varphi^{1/2}$, and therefore the approximations would not cause significant errors. The results are shown in *Figures 7* and *8*. The results are in fairly good agreement with the proposition made earlier.

On examination of *Figures 7* and *8* a relationship emerges which is similar to that proposed by Michaels and Bixler[15], between the chain immobilization factor β and the reduced molecular diameter. However, in this case, the results are likely to be falsified to a certain extent due to the contribution of geometric factors to β. In the present case, no such contribution is expected to affect the results since the volume fraction of junction points is negligible. Extension of these concepts would indicate if such a contribution exists in the case of semicrystalline polymers. Results of such an analysis will be discussed elsewhere[18].

Scientific and technological implications

The framework developed above indicates that a pseudo two phase analysis of diffusion phenomena in network polymers is possible. The curves such as the ones in *Figures 4–6* are useful in many ways. Some of the possible ways of utilization of such plots are indicated below.

It has been recognized for a long time[29] that the decrease in diffusivity with increase in crosslink density is more drastic for molecules of larger size than that for smaller size as would be clear from *Figures 4*, *7* and *8*. A mixture of gases permeating through an appropriately crosslinked membrane would be richer in gas of smaller size. Using the relationship developed in this work it would be possible to choose a membrane of the required degree of crosslinking to effect gas separation.

It is known that the antioxidants are less efficient in rubbers than in liquids because of their decreased diffusivities in the former. The decrease in diffusivity would further be more drastic for antioxidant than for oxygen with increasing degree of vulcanization. From the knowledge of diffusivity of antioxidants predicted from the relation developed above, it is possible to modify compounding formulation such that adequate concentration of antioxidant is maintained throughout the surface and in the matrix.

Network polymers are being increasingly used[30,31] to form complexes with complexes of Nickel, Rhodium, Ruthenium and Platinum. The reaction rates in polymer bound catalytic reactions are diffusion controlled and hence decrease with increased level of crosslinking in the polymer matrix[31]. The polymer bound catalyst, thus, preferentially hydrogenates a smaller olefin in the presence of larger ones. On the basis of the relationships proposed, useful guidelines could be formulated to control the extent of crosslinking to obtain desired diffusional characteristics and reactivities.

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