DIFFUSION-CONTROLLED STRESS RELAXATION OF SWOLLEN RUBBER-LIKE NETWORKS

DIFFUSION-CONTROLLED STRESS RELAXATION OF SWOLLEN RUBBER-LIKE NETWORKS

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE TECHNISCHE WETENSCHAPPEN AAN DE TECHNISCHE HOGESCHOOL DELFT OP GEZAG VAN DE RECTOR MAGNIFICUS DR. IR. C. J. D. M. VERHAGEN, HOOGLERAAR IN DE AFDELING DER TECHNISCHE NATUURKUNDE, VOOR EEN COMMISSIE UIT DE SENAAT TE VERDEDIGEN OP WOENSDAG 12 JUNI 1968 TE 14 UUR

DOOR

DAVID ENGEL KNIBBE

CHEMISCH DOCTORANDUS

GEBOREN TE LEIDEN

1968

UNIVERSITAIRE PERS ROTTERDAM

DIT PROEFSCHRIFT IS GOEDGEKEURD DOOR DE PROMOTOR
PROF. DR. W. PRINS.

Aan allen in het Koninklijke/Shell Laboratorium Amsterdam, het Koninklijke/Shell Plastics Laboratorium Delft en de Technische Hogeschool Delft, die aan de totstandkoming van dit proefschrift hebben bijgedragen, betuig ik hierbij mijn dank en erkentelijkheid.

CONTENTS

1. INTRODUCTION

The stress-strain characteristics of cross-linked elastomer networks have been the subject of detailed thermodynamic studies. A clear picture has emerged explaining long-range elasticity in terms of the configurational entropy of network chains, modified where necessary by minor energy contributions[1]. The same theory can be used when dealing with the swelling of elastomer networks by means of a suitable diluent.

This study deals with the stress-strain equation for networks in the presence of an excess of diluent. Here and in the following chapters, the word '*network*' refers exclusively to elastomer networks.

Generally, the stress-strain equation of a network can be described by a semi-empirical equation of the type:

$$f = (\Lambda - \Lambda^{-2})(C_1 + \Lambda^{-1}C_2) \tag{1}$$

the so-called Mooney-Rivlin equation, where f is the stress per unstrained cross-section, Λ the elongation ratio and C_1 and C_2 are constants.

In the case of swollen networks, C_2 is often found to vanish, and the remaining part of equation (1) is then similar to an equation derived theoretically on the basis of molecular chain configurations of a network. This equation, applied to swollen networks in excess diluent, will be derived in Chapter 2.

The factor C_2 in equation (1) is often considered to be a non-equilibrium parameter[2,3,4]. The non-ideal conditions in the network are ascribed, for example, to the high viscosity of the assembly of cross-linked chains. Such an explanation is suggested by the zero value of C_2 in swollen gels.

Recently, however, BLOKLAND[5] as well as BOBEAR[6] have shown that the situation is more complex. Both authors note that the values of the constants C_1 and C_2 in the Mooney-Rivlin equation depend on the type of deformation. They conclude that it is incorrect to relate C_1 exclusively to the number of elastically effective chains in the network as long as $C_2 \neq 0$.

The theoretical stress-strain relation apparently does not fit the observed data when $C_2 \neq 0$, but does so when $C_2 = 0$. This constitutes the major reason for investigating an elastomer network in the *swollen* state.

While measuring the restoring force of strained networks, swollen in an excess of diluent, we observed that stretching resulted in stress relaxation, noticeable even after several hours. Prolonged testing showed that an equilibrium stress was finally obtained which could be maintained, within the limits of experimental error, for several days. This indicated that no significant chemical degradation took place.

On further analysis of this stress relaxation, it was found that for the main part it could be described by only *one* discrete relaxation time: waiting until the final equilibrium stress f_∞ was known, and plotting $\log \{f(t) - f_\infty\}$ *vs* time yielded a straight line, except for the very first part of the relaxation.

The main part of the stress relaxation could therefore be described by the following equation:

$$f(t) = f_\infty + f_r \, e^{-t/\tau} \tag{2}$$

where $f(t)$ = stress actually measured at time t
f_∞ = final equilibrium stress
f_r = relaxational part of the stress
τ = relaxation time.

By taking the difference between the stress actually measured and that given by equation (2), the remaining part of the stress relaxation was obtained. This difference is of course only significant during the early phase of stress relaxation. This difference was treated exactly as the original stress relaxation: by plotting $\log \{f(t) - f_\infty - f_r \, e^{-t/\tau}\}$ *vs* time a second relaxation time was determined, although the accuracy was less than in the first case. An example of these plots is given in Figure 1.

In Chapter 3 we examine the possibility of relating the stress relaxation to the change in swollen volume, which according to Chapter 2 may be expected on deforming a network submerged in diluent.

A description of the materials, equipment and techniques used in this study is given in Chapter 4, and the results obtained are described in Chapter 5. A discussion of these results follows in Chapter 6, in which a comparison is also made with the results of other investigations. This chapter ends with a discussion of the advantages of the method developed in this study for determining elastomer network parameters over those currently in use in rubber technology.

2. STRESS-STRAIN AND EQUILIBRIUM SWELLING EQUATIONS

The derivation of the stress-strain and swelling equations of a swollen network begins with a calculation of the difference in Gibbs free energy between a swollen network on the one side and a similar unswollen network and free diluent on the other. This is done by calculating for both cases the difference in free energy with respect to a collection of free chains, corresponding to the network chains between cross-links.

Using the derivation of FLORY *et al.*[7-11], the difference ΔG (free chains $\rightarrow$swollen network) is split up into:

ΔG_{mix} = the free energy change on mixing chains and diluent

ΔS_{cr} = the entropy change on connecting the chains (volume-dependent part only)

ΔG_{el} = the free energy change on elastic deformation of the network.

When referring to one cm³ of polymeric constituent, ΔG_{mix} is given by:

$$\Delta G_{mix} = kT\{n_1 \ln(1 - q^{-1}) - v^* \ln q + \chi n_1 q^{-1}\}, \tag{3}$$

in which:

n_1 = number of diluent molecules in the swollen gel

v^* = number of elastically effective chains in the gel

q = volume ratio of solution or of swollen gel to non-swollen (dry) polymeric constituent

χ = polymer/solvent interaction parameter.

ΔS_{cr} refers to the volume dependence of the probability of network formation from a set of free chains. According to FLORY,

$$\Delta S_{cr} = -2kv^* \frac{f-1}{f} \ln q, \tag{4}$$

where f = functionality of the cross-link; in this work always taken to be 4.

HERMANS, however, gives a different equation for ΔS_{cr}, *viz*[12]:

$$\Delta S_{cr} = -kv^* \ln q \tag{5}$$

FLORY obtains his equation for ΔS_{cr} by assuming a volume-dependent part

of the entropy change for all of the cross-linking reactions needed for network formation[10]. HERMANS argues that this does not hold for the ring closure reactions which actually form the three-dimensional network, because the chain ends are at that stage no longer free to move through the volume q. HERMANS' argument becomes less convincing when in the cross-linking reactions the *concentration* of free chain ends in an appropriate small volume element ΔV around any given chain end is taken to be the decisive factor: increasing the available volume q will move the reactive chain ends further apart and thus decrease their concentration.

Both theories are corroborated by experimental evidence, but in neither case to such an extent as to definitely support one or the other. For this reason, a generalized equation for ΔG will be used which accommodates both theories.

For the calculation of ΔG_{el}, a volume ratio q_0 is defined at which the network chains have the same mean square end-to-end distance as a corresponding set of free chains[13]. This volume, at which the network is unstretched, is often called the *normal* or *relaxed* volume, and any deformation will yield a positive value for ΔG_{el}.

In the case of a dry network, cross-linked in the absence of solvent, the free chains have a mean square end-to-end distance of $\langle r_0^2 \rangle$, and the network chains, of $\langle r_c^2 \rangle$. By the above definition,

$$q_{0c}^{2/3} = \frac{\langle r_0^2 \rangle}{\langle r_c^2 \rangle} \tag{6}$$

The volume ratio q_{0c} is not necessarily realizable; it may be no more than a network parameter, $q_{0c}^{-1/3}$ being the expansion factor of the chains due to cross-linking. In the following, it will only be used in this sense, and this expansion factor is assumed to be the same whether cross-linking occurs in the dry state or in solution.

We further assume that the chain dimensions, either free or as part of a network, are expanded by a factor α when brought into contact with a solvent, and that this factor α is constant in the range of concentrations considered. This expansion factor is introduced to take into account specific diluent effects, *i.e.* short-range interaction between polymer and solvent only.

The mean square free chain length to be used in calculating the relaxed state of a swollen network thereby becomes $\alpha_1^2 \langle r_0^2 \rangle$ with diluent 1, $\alpha_2^2 \langle r_0^2 \rangle$ with diluent 2, *etc.*

To keep the calculation of ΔG_{el} as general as possible, we assume the network has been cross-linked in diluent 1, and is afterwards swollen to equilibrium in diluent 2. In order to make the calculation of ΔG_{el} possible when swelling in any given diluent, we calculate the difference ΔG_{el} between the network swollen in diluent 2 and the isotropic unswollen network ($q = 1$).

The mean square end-to-end distance of the chains in diluent 1 is $\alpha_1^2\langle r_0^2\rangle$ before cross-linking, and $\alpha_1^2\langle r_c^2\rangle$ afterwards. On removal of the diluent the chain dimensions become $\alpha_1^2\langle r_c^2\rangle q_{cr}^{-2/3}$, where q_{cr} is the volume of the solution during cross-linking containing 1 cm³ of polymeric chains. This means that when q_{cr} is large, the chains in the diluent-free network may be highly *supercoiled*.

The reference chains of this dry network have a mean square distance of $\langle r_0^2\rangle$. The relaxed volume q_{0d} of the dry polymer is thus given by:

$$q_{0d}^{2/3} = \frac{\langle r_0^2\rangle}{\alpha_1^2\langle r_c^2\rangle q_{cr}^{-2/3}} = \alpha_1^{-2} q_{0c}^{2/3} q_{cr}^{2/3} \tag{7}$$

In the case of swollen networks, the elastic free energy has to be calculated with respect to a reference state where the chains have a mean square end-to-end distance of $\alpha_2^2\langle r_0^2\rangle$. The relaxed volume q_{02} of a network swollen in diluent 2, therefore, is:

$$q_{02}^{2/3} = \frac{\alpha_2^2\langle r_0^2\rangle}{\alpha_1^2\langle r_c^2\rangle q_{cr}^{-2/3}} = \alpha_2^2 q_{0d}^{2/3} \tag{8}$$

This result is easily recognized: q_{0d} is the relaxed state of the *dry* polymer, and expansion of the chain lengths by a factor α_2 due to specific diluent effects will increase the relaxed volume by a factor α_2^3 to $\alpha_2^3 q_{0d}$.

When now the network is swollen and deformed to the ratios λ_x, λ_y and λ_z ($\lambda_x\,\lambda_y\,\lambda_z = q$), the deformation ratios with respect to the dry and the swollen relaxed network are

$\lambda_x q_{0d}^{-1/3}$, $\lambda_y q_{0d}^{-1/3}$, $\lambda_z q_{0d}^{-1/3}$ and

$\lambda_x \alpha_2^{-1} q_{0d}^{-1/3}$, $\lambda_y \alpha_2^{-1} q_{0d}^{-1/3}$, $\lambda_z \alpha_2^{-1} q_{0d}^{-1/3}$, respectively.

For a network swollen with diluent 2, these deformation ratios yield a free energy change ΔG_{el}:

$$\frac{\Delta G_{el}\,(\text{swollen-relaxed})}{kT} =$$

$$= \tfrac{1}{2}\nu^*\{(\lambda_x^2 + \lambda_y^2 + \lambda_z^2)\,\alpha_2^{-2} q_{0d}^{-2/3} - 3\} - \nu^* \ln q q_{0d}^{-1} \alpha_2^{-3} \tag{9}$$

In the case of the dry network, where $\lambda_x = \lambda_y = \lambda_z = 1$, ΔG_{el} is given by:

$$\frac{\Delta G_{el}\,(\text{dry-relaxed})}{kT} = \tfrac{1}{2}v^*(3q_{0d}^{-2/3} - 3) - v^* \ln q_{0d}^{-1} \qquad (10)$$

The difference in free energy between a swollen and deformed network on the one hand, and a dry, isotropic network on the other, is obtained by adding equations (3), (4) and (9) and subtracting equation (10). The mixing and cross-linking terms of the dry polymer are necessarily zero. We therefore find:

$$\frac{\Delta G\,(\text{swollen-dry})}{kT} = n_1 \ln(1 - q^{-1}) - \frac{2}{f} v^* \ln q + \chi n_1 q^{-1} + \\ + \tfrac{1}{2}v^* q_{0d}^{-2/3}\{(\lambda_x^2 + \lambda_y^2 + \lambda_z^2)\alpha_2^{-2} - 3\} + v^* \ln \alpha_2^3 \qquad (11)$$

In HERMANS' theory, the term $-\frac{2}{f}v^* \ln q$ is to be replaced by $-v^* \ln q$.

A more generalised equation, accommodating the theories not only of FLORY and HERMANS, but also those of others, has been proposed by PRINS[14] to simplify confrontation with experiment. A similar generalised equation in our notation reads:

$$\frac{\Delta G\,(\text{swollen-dry})}{kT} = n_1 \ln(1 - q^{-1}) + \chi n_1 q^{-1} + \\ + \tfrac{1}{2}Av^* q_{0d}^{-2/3}\{(\lambda_x^2 + \lambda_y^2 + \lambda_z^2)\alpha_2^{-2} - 3\} - Bv^* \ln q + Cv^* \ln \alpha_2^3 \qquad (12)$$

In this generalised equation, FLORY's theory is represented by $A = C = 1$, $B = \frac{1}{2}$, whereas according to HERMANS, $A = B = C = 1$. Proposals by DUISER and STAVERMAN[15] and CHÖMPFF and DUISER[16] to correct the theories lead to the statement that in FLORY's case, $A = C = \frac{1}{2}$, $B = \frac{1}{4}$, and in HERMANS' case, $A = B = C = \frac{1}{2}$. The theory of JAMES and GUTH[17] leaves A in principle undetermined, but definitely yields $B = C = 0$.

Equation (12) is sometimes given as[18]:

$$\frac{\Delta G}{kT} = n_1 \ln(1 - q^{-1}) + \chi n_1 q^{-1} + \tfrac{1}{2}Av^*(3q^{2/3}q_{02}^{-2/3} - 3) - \\ + Bv^* \ln q q_{02}^{-1} \qquad (13)$$

This representation is incorrect; the difference with equation (12) stems from the fact that in deriving equation (13), a mixing term is calculated with respect to the unswollen network ($q = 1$) and an elastic term with respect to the normal state ($q = q_{02}$) of the swollen network. Therefore, equation (13) may be safely used only when q_{02} is constant. However, variations in q_{02} are possible, *e.g.*, by change of temperature or diluent.

The difficulties in determining A and B by experiment stem sometimes from an uncertainty in v^*, and always from the fact that A and $q_{0d}^{-2/3}$ invariably go together. q_{0d} is likely to roughly equal the volume at cross-linking, q_{cr}, but unlikely to exactly equal it.

From the expression for ΔG, the equilibrium degree of swelling for both strained and unstrained networks, and the stress on deformation are calculated as follows:

Free swelling equilibrium

The equilibrium degree of swelling without external constraints, q_i, is a balance between the tendency of network and diluent to mix and the retractive force of the deformed chains. It is found by differentiating equation (12) with respect to the number of diluent molecules n_1. Making use of the relations:

$$q_{02} = q_{0d}\alpha_2^3,$$
$$\lambda_x = \lambda_y = \lambda_z = q_i^{1/3},$$
$$q = 1 + \frac{n_1\bar{v}_1}{N} \quad \text{and}$$
$$\frac{dq}{dn_1} = \frac{\bar{v}_1}{N}$$

where $\bar{v}_1$ is the partial molar volume of the diluent and N is Avogadro's number, and expressing the number of chains in moles ($v = \frac{v^*}{N}$), one finds

$$\frac{1}{kT}\left(\frac{\partial \Delta G}{\partial n_1}\right)_{p,T} = \ln(1 - q_i^{-1}) + q_i^{-1} + \chi q_i^{-2} + \\ + A v \bar{v}_1 q_{02}^{-2/3} q_i^{-1/3} - B v \bar{v}_1 q_i^{-1} = 0 \qquad (14)$$

The terms containing A and B are sometimes called the elastic part of the free energy change. At a degree of swelling $q = q_{02}$ these terms are then expected to cancel, from which it is concluded that A should equal B[12]. This is no valid argument against FLORY's theory, since according to this theory, B contains a contribution from ΔS_{cr} as well as from ΔG_{el}.

Swelling equilibrium at constant elongation

When λ_x is kept constant, λ_y and λ_z are given by: $\lambda_y^2 = \lambda_z^2 = q\lambda_x^{-1}$.

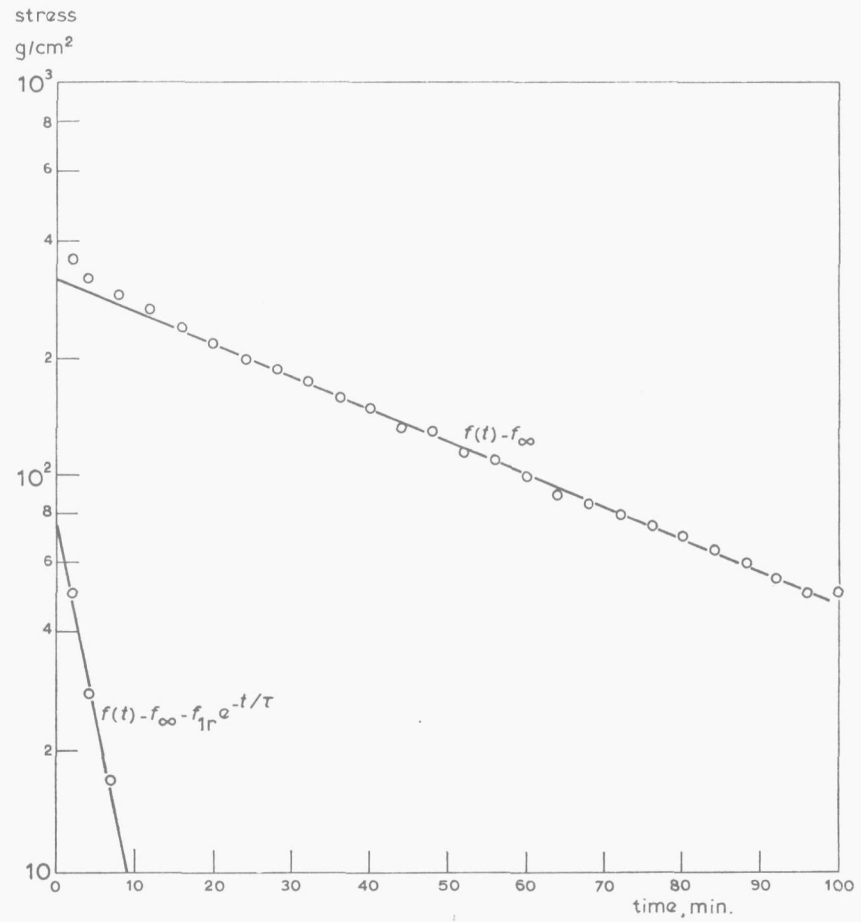

Fig. 1

Separation of $f(t)$ into f_∞ , $f_{1r}e^{-t/\tau_1}$ and $f_{2r}e^{-t/\tau_2}$

Differentiation of equation (12) with respect to n_1 now yields the degree of swelling q_λ:

$$\frac{1}{kT}\left(\frac{\partial \Delta G}{\partial n_1}\right)_{p,T,\lambda_x} = \ln(1 - q_\lambda^{-1}) + q_\lambda^{-1} + \chi q_\lambda^{-2} + A v \bar{v}_1 q_{02}^{-2/3} \lambda_x^{-1} - B v \bar{v}_1 q_\lambda^{-1} = 0 \qquad (15)$$

Equation (14) may be considered a special case of equation (15): without external stress, $q = q_1$ and $\lambda_x = q^{1/3}$, which, when substituted into (15), indeed give (14).

Equation (15) shows that the degree of equilibrium swelling q increases with increasing λ. This has been experimentally confirmed by GEE[19] and TRELOAR[20]. However, not all investigators have always been aware of this swelling upon stretching. Initially, FLORY and REHNER[9] predicted deswelling upon stretching, but in subsequent articles they made a correction for this. In a much later article[21] the same error was made by TOBOLSKY *et al.* Many authors, when calculating cross-link densities, neglect the change in volume altogether[22–24]. A few have tried to eliminate the additional swelling upon stretching by greatly diminishing the rate of diluent uptake: GUMBRELL, MULLINS and RIVLIN[25] keep their elongated samples in diluent vapour, ADAMS and JOHNSON[26] in water saturated with diluent. Comment on these techniques will be made in Chapter 6.

Stress at constant degree of swelling

When deforming the network to a ratio λ_x while keeping the volume constant, a stress results which is found by differentiating with respect to λ_x:

$$f = \left(\frac{\partial \Delta G}{\partial \lambda_x}\right)_q = ART v q_{02}^{-2/3} \left(\lambda_x - \frac{q}{\lambda_x^2}\right) \qquad (16)$$

In this, as in all following cases, f always refers to the force per cm² of *dry* polymer.

Stress while in equilibrium with diluent

As a special case of equation (16), we consider the swelling ratio q_λ. This is the equilibrium swelling ratio at an extension λ_x, in the presence of an excess of diluent, as given by equation (15). Denoting the differentiation at equilibrium degree of swelling by the subscript 'eq', one finds:

$$f = \left(\frac{\partial \Delta G}{\partial \lambda_x}\right)_{eq} = ART v q_{02}^{-2/3} \left(\lambda_x - \frac{q_\lambda}{\lambda_x^2}\right) \qquad (17)$$

3. THEORY OF DILUENT DIFFUSION AND THE RESULTING STRESS RELAXATION

3.1 DIFFUSION-CONTROLLED VOLUME CHANGE

The difference between q_l and q_λ, as discussed in the preceding chapter, warrants a discussion of the diffusion phenomena likely to be important. These phenomena have been extensively studied, and we shall therefore omit further details, which are dealt with in monographs and surveys[27-29].

3.1.1 *Plane sheet*

The equation describing the diffusion of an excess of diluent in a plane sheet is given by Fick's second law:

$$\frac{\partial c(y, t)}{\partial t} = \frac{\partial}{\partial y}\left(D \frac{\partial c}{\partial y}\right) \tag{18}$$

where $c\,(y,t)$ is the concentration of penetrant as a function of the distance y from the surface and of the time, and D is the diffusion coefficient. When the thickness of the sheet is $2l$, the boundary conditions are:

$$c = c_\infty,\ y = \pm l,\ t \geq 0$$
$$c = c_0,\ -l < y < l,\ t = 0,$$

where c_0 = initial concentration, if any

c_∞ = concentration at equilibrium (at $t = \infty$).

Assuming D to be constant, the solution may be given as a series of error functions or as a trigonometric series.

On integrating over y and dividing by $2l$, the average concentration over the thickness of the sheet as a function of time is obtained. For the error function solution this yields:

$$\frac{\bar{c}(t) - c_0}{c_\infty - c_0} = 2\sqrt{\frac{Dt}{l^2}}\left\{\pi^{-1/2} + 2\sum_{n=0}^{\infty}(-1)^n \operatorname{ierfc}\frac{nl}{\sqrt{Dt}}\right., \tag{19}$$

where $\operatorname{ierfc} z = \int_z^\infty \operatorname{erfc}\xi\, d\xi = \frac{1}{\sqrt{\pi}} e^{-z^2} - z \operatorname{erfc} z.$

The average concentration according to the trigonometric solution becomes:

$$\frac{\bar{c}(t) - c_0}{c_\infty - c_0} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-(2n+1)^2 D\pi^2 t/4l^2} \tag{20}$$

Equation (19) is especially suitable for describing the early phases of the diffusion process: up to $t = \frac{l^2}{4D}$, the term $2\pi^{-1/2} \sqrt{\frac{Dt}{l^2}}$ alone is sufficient for an accuracy of 1.2%; at longer times the necessary number of terms increases rapidly.

Conversely, equation (20) is unwieldy at short times, but at $t > \frac{4l^2}{3\pi^2 D}$, the second and higher terms of the summation are less than 1% of the first.

As will be described in Chapter 5, at short times two different relaxation mechanisms appear to be working, *viz* an *isochoric* stress relaxation (viscosity-delayed chain reorientation) and a *diffusion-controlled* increase in volume. The error function solution as given by equation (19) therefore cannot always be used. At longer times this complication is not encountered and therefore the trigonometric solution (equation (20)) is suited to our data.

Denoting $\frac{\pi^2 D}{4l^2}$ by Ψ, we can rearrange equation (20) as:

$$\frac{c_\infty - \bar{c}(t)}{c_\infty - c_0} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-(2n+1)^2 \Psi t} \tag{21}$$

According to the foregoing, all terms except the first may be neglected at $t > \frac{1}{3\Psi}$.

Equation (20) holds when the thickness of the sheet and the diffusion coefficient of the penetrant in the solid phase remain constant. In the case of increased swelling, the thickness of course *increases with time*, and the diffusion coefficient is likely to *change with concentration.*

HARTLEY and CRANK[30] have shown that the effect of the *change of thickness* with the concentration of the diluent can be eliminated by using adapted units of length in the derivation of equation (20). Instead of absolute units such as cm, units are chosen that increase in absolute size in the same ratio as the swelling rubber. Since they may be thought of as being coupled to the frame of the network, they may be called *frame units.*

In our case, we couple the grid formed by these frame units to the network as it is at $t = 0$, *i.e.* at a degree of swelling q_i, and a deformation ratio λ_x.

On further swelling (finally reaching a degree of swelling q_λ), a cube of 1 cm³ of the swollen rubber will become a rectangular parallelepiped with sides ξ, η and ζ cm in the x, y and z directions, resp. (for the general case we assume deformation in three directions, although in our specific case, $\eta = \zeta$ and $\xi = 1$ since $\lambda_x =$ constant). In frame units, these sides will have unit length. In general, to find the number y' of frame units to describe a given length y, we divide its number of cm, y, by η:

$$y' = \frac{y}{\eta}, \text{ and likewise, } x' = \frac{x}{\xi} \text{ and } z' = \frac{z}{\zeta} \tag{22}$$

The *thickness* of the sheet is $2l$ before additional swelling takes place. Expressed in frame units it is $2l' = \dfrac{2l}{\eta}$ and necessarily remains constant, whereas the number of cm to describe the thickness, $2l$, will increase with time.

The *flux* is the rate of transport of diluent through a section of unit area. If, for example, n moles of diluent per second pass through an area of 1 cm², the flux in normal units is $F = n$. Through a unit area in frame units, measuring $\xi\ \zeta$ cm² in normal units, $\xi\ \zeta\ n$ moles per second will pass, and $F' = \xi\ \zeta\ n$. The number of frame units, F', and that of standard units, F, to describe the rate of transport of a given amount of diluent through a section with a given area are thus related by:

$$F' = \xi\zeta F \tag{23}$$

Similarly, the *concentration* in frame units, c', is the number of units of diluent contained in a volume $\xi\eta\zeta = \dfrac{q}{q_i}$ cm³. In standard units, the concentration c is defined as the number of units of diluent in 1 cm³ of swollen rubber (at a degree of swelling q). The amount of diluent contained in the volume $\xi\eta\zeta$ cm³ is thus:

$$c' = \xi\eta\zeta c = \frac{q}{q_i}\, c \tag{24}$$

When c is expressed as cm³ of diluent per cm³ of swollen network, containing $\dfrac{1}{q}$ cm³ of polymer, then

$$c = 1 - \frac{1}{q} \tag{25}$$

and

$$c' = \frac{q}{q_i}\left(1 - \frac{1}{q}\right) = \frac{q-1}{q_i} \tag{26}$$

The diffusion coefficient corresponding to these frame units is called D_A^B and Fick's second law in frame units thus becomes:

$$\frac{\partial c'(y', t)}{\partial t} = \frac{\partial}{\partial y'}\left(D_A^B \frac{\partial c'}{\partial y'}\right) \tag{27}$$

with boundary conditions:

$$c' = c'_\infty,\ y' = \pm l',\ t \geq 0$$

$$c' = c'_0,\ -l' < y' > l',\ t = 0$$

The relation between the usual diffusion coefficient, D_v, and D_A^B is obtained from their definitions. Both diffusion coefficients are defined as the mass transfer per unit area per second, divided by the concentration gradient:

$$D_v = \frac{-F}{\frac{\partial c}{\partial y}} \text{ and } D_A^B = \frac{-F'}{\frac{\partial c'}{\partial y'}} \tag{28}$$

Substitution of equations (22), (23) and (24) yields:

$$D_A^B = \frac{-F'}{\frac{\partial c'}{\partial y'}} = \frac{-\xi\zeta F}{\xi\eta^2\zeta \frac{\partial c}{\partial y}} = \eta^{-2} D_v \tag{29}$$

This relation is different from that given by HARTLEY and CRANK, *viz* (in our terminology):

$$D_A^B = \frac{q_i^2}{q^2} D_v \tag{30}$$

The difference between their equation and ours stems from the fact that theirs is derived for the *one*-dimensional case only, leaving $\xi = \zeta = 1$. Only when this is the case (or rather, when $\xi\zeta = 1$) are the two relations equivalent.

The equations (18) and (27) being of the same form, the solutions given above for equation (18) also hold for equation (27) when the same units are used in the solutions as in equation (27).

Actually, from equations (22) and (29) it appears that:

$$\frac{D_A^B}{(l')^2} = \frac{D_V}{l^2} \tag{31}$$

with the result that the factor Ψ in equation (21) remains unaltered.

As regards the dependence of D_V on *concentration*, many relationships have been proposed, but usually they cover the case of low diluent concentrations only. Moreover, measurements were sometimes carried out on polymers below the glass transition point in the dry state, which were then plasticised by the diluent[31, 32, 33].

Once the polymer is fully elastomeric and occupies only a small part of the available volume, D_V might reasonably be assumed to be roughly proportional to q, the inverse volume fraction of polymer:

$$\frac{D_V(q)}{q} = \frac{D_V(q_i)}{q_i} \tag{32}$$

Furthermore, since at constant elongation of the network, $\frac{q}{q_i} = \xi\eta\zeta = \eta^2$, we use the result $D_A^B = \eta^{-2} D_V = \frac{q_i}{q} D_V = D_V(q_i)$ to find that in the case of constant elongation, D_A^B is independent of the degree of swelling. The thickness in frame units is also constant, so in equation (21), Ψ is constant.

We therefore conclude that neither the change in dimensions nor the change in value of the diffusion coefficient during swelling prevents us from using equation (21), provided the concentration is defined as cm³ of diluent per $\frac{1}{q_i}$ cm³ of dry polymer (see equation (26)). The resulting diffusion coefficient then equals the diffusion coefficient D_V describing the diffusion into a network swollen to a ratio q_i.

A final complication sometimes arises from the *inhomogeneity* of the swelling. For instance, the swelling of the outer layers of the sheet imposes a dilatational stress on the less swollen inner core; conversely, the inner core restrains the outer layer. The net effect will be that D_V at the outside will be slightly smaller, at the centre slightly larger than if these strains were absent. The effects of inhomogeneous swelling on D_V are negligibly small when the

Young's moduli at the inside and the outside are about equal and both small[34, 35]. In the present cases of highly swollen networks these requirements are fulfilled.

3.1.2 *Cylinder*

In the case of a circular cylinder where no diffusion takes place through the cross-sectional surfaces, the diffusion equation is:

$$\frac{\partial c}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD\frac{\partial c}{\partial r}\right) \tag{33}$$

For a cylinder of radius R the boundary conditions become:

$$c = c_\infty,\ r = R,\ t \geq 0$$

$$c = c_0,\ 0 < r < R,\ t = 0$$

To obtain the average concentration as a function of time, the solution analogous to equation (19) is:

$$\frac{\bar{c}(t) - c_0}{c_\infty - c_0} = 4\pi^{-1/2}\left(\frac{Dt}{R^2}\right)^{1/2} - \frac{Dt}{R^2} - \tfrac{1}{3}\pi^{-1/2}\left(\frac{Dt}{R^2}\right)^{3/2} + \ldots \tag{34}$$

The range in time for which this solution is convenient is smaller than in the case of a plane sheet.

For longer times a solution results corresponding to equation (20)[36]:

$$\frac{\bar{c}(t) - c_\infty}{c_0 - c_\infty} = 4\left(\frac{1}{5.783}e^{-5.783Dt/R^2} + \frac{1}{30.47}e^{-30.47Dt/R^2} + \right.$$
$$\left. + \frac{1}{74.89}e^{-74.89Dt/R^2} + \ldots\right) \tag{35}$$

Here, the second term of the summation is already less than 1% of the first term at $t = \dfrac{0.034\,R^2}{D}$ (which is 0.20 times the factor $\dfrac{R^2}{5.783\,D}$ introduced in the next section as the relaxation time τ_1).

By the same arguments as developed in the preceding section, solutions (34) and (35) are also applicable to the case of a swelling network, when c is again defined as $c = \dfrac{q-1}{q_i}$.

3.2.1 *Plane sheet*

As shown in Chapter 2, the stress at constant elongation is given by:

$$f = ARTvq_{02}^{-2/3}\left(\lambda - \frac{q}{\lambda^2}\right) \tag{16}$$

This relation is now assumed to hold also if the diluent is not quite evenly distributed over the polymer. This means that in equation (16), q is replaced by $\bar{q} = q_i\bar{c} + 1$, where $\bar{c}$ is given by equation (21) (omitting a small correction for diffusion through the sides of the strip). In view of the relatively small variation of c when going from c_0 to c_∞, this assumption is very reasonable. Thus, at constant elongation λ, recalling that $q = q_i c + 1$ and $q_i = q_i c_0 + 1$ when c is expressed in the frame units defined earlier, equation (16) may be used to obtain:

$$\frac{f^*(t) - f_\infty}{f_0^* - f_\infty} = \frac{\bar{q}(t) - q_\lambda}{q_i - q_\lambda} = \frac{\bar{c}(t) - c_\infty}{c_0 - c_\infty} \tag{36}$$

The asterisks on $f^*(t)$ and f_0^* imply that these stresses do not contain isochoric stress relaxation terms. That is to say, f_0^* is the hypothetical equilibrium stress at a degree of swelling q_i that would result if the network chains were not delayed by a viscosity effect in taking up their new equilibrium configuration conforming to the deformed state (or whatever mechanism may further give rise to isochoric stress relaxation). Similarly, $f^*(t)$ is the stress that corresponds to $q(t)$ in the absence of isochoric stress relaxation terms.

Now, equation (21) shows that after a certain time (of the order of $\frac{1}{3\Psi}$), within the limits of error the rate of change of $\bar{c}(t)$ is given by:

$$\frac{\bar{c}(t) - c_\infty}{c_0 - c_\infty} = \frac{8}{\pi^2} e^{-\Psi t} \tag{37}$$

On the other hand, in the experiments reported in Chapter 1, the stress relaxation after 10–15 minutes was found to satisfy equation (2):

$$f(t) - f_\infty = f_{1r} e^{-t/\tau_1} \tag{2}$$

From the remarkable fact that the stress relaxation of swollen rubbers can be described (except for the first 10–15 minutes) with the aid of one relaxation time only, *i.e.* from the similarity of equations (2) and (37), we can

conclude that after $t \approx \frac{1}{3\Psi}$, isochoric stress decay is no longer significant, *i.e.* the asterisk on $f^*(t)$ in equation (36) may be dropped. This amounts to the following equation (combining equations (2), (36) and (37)):

$$\frac{f_{1r}\, e^{-t/\tau_1}}{f_0^* - f_\infty} = \frac{8}{\pi^2} e^{-\Psi t} \tag{38}$$

from which is obtained:

$$f_0^* = f_\infty + \frac{\pi^2}{8} f_{1r} \tag{39}$$

and

$$\tau_1 = \frac{1}{\Psi} = \frac{4l^2}{\pi^2 D} \tag{40}$$

Using these two equations it is possible to determine f_0^* and τ_1 from the stress relaxation curve according to the method described in Chapter 1: a value of f_∞ is chosen such that $\ln \{f(t) - f_\infty\}$ *vs* time yields a straight line with slope τ_1^{-1} after time $= \frac{\tau_1}{3}$. Extrapolating back to $t = 0$ then yields $\ln f_{1r}$. f_{1r} is smaller than $f_0^* - f_\infty$ by the sum $f_{2r} + f_{3r} + \ldots$ Of this sum, f_{2r} is by far the largest component; the corresponding relaxation time is $\tau_2 = \frac{\tau_1}{9}$. It should be noted that in the example of Figure 1, the second relaxation time is indeed about one ninth of the first relaxation time. Any difference between $f(t)$ and $f^*(t)$ is attributable to isochoric stress relaxation.

The stress relaxation data f_0^* and f_∞ give information about the increase in degree of swelling, Δq: from equation (16) one obtains:

$$\frac{f_0^* - f_\infty}{f_0^*} = \frac{q_\lambda - q_i}{\lambda^3 - q_i} = \frac{\Delta q}{\lambda^3 - q_i} \tag{41}$$

If the elongation with respect to the swollen dimensions is Λ, so that $\Lambda = \lambda q_i^{-1/3}$, this equation reads:

$$\frac{\Delta q}{q_i} = (\Lambda^3 - 1)\frac{f_0^* - f_\infty}{f_0^*} \tag{42}$$

3.2.2 *Cylinder*

For a compressed cylinder, essentially the same arguments hold, but the stresses now have a sign opposite to that found in stretching.

The equilibrium stress at $t = 0$ for a cylinder reads:

$$f_0^* = f_\infty + \frac{5.783}{4} f_{1r} \tag{43}$$

and the relaxation time τ_1 is given by:

$$\tau_1 = \frac{R^2}{5.783D} \tag{44}$$

Equation (42) remains unchanged; the fact that a network decreases in swelling ratio when compressed is accounted for by $(\Lambda^3 - 1)$ being negative.

4. MATERIALS AND TECHNIQUES

The stress relaxation in the presence of diluent was studied for extended as well as compressed networks. In the former case, strips of vulcanized ethylene-propylene rubber were used, in the latter case, cylinders of cross-linked poly(*p*-nitrophenyl-methacrylate). In the following sections a more detailed description of these networks and the apparatus used is given.

4.1 UNIDIRECTIONAL EXTENSION

Vulcanizates were used, which were based on an experimental terpolymer of ethylene, propylene and dicyclopentadiene of random structure (EPDM). The ethylene content is 62 mole per cent, the unsaturation, measured by ozone uptake[37], is 4.3 double bonds per 1000 C atoms, *i.e.*, about 4.9 double bonds per 1000 backbone atoms. A rather high molecular weight was chosen (Mooney viscosity = 143; viscosity-average molecular weight $250–300 \times 10^3$) to obtain a more accurate value for q_{cr} and to minimize the effect of loose chain ends.

Although loose chain ends are no serious disadvantage in the experiments, they do not contribute to the elastic network and may be considered as immobilized diluents. Since we are studying the transport of diluent in the networks, it is preferred to keep the number of loose chain ends low.

In order to vary q_{cr}, vulcanization in the presence of solvent was effected by extending the rubber with a highly paraffinic oil, *viz* 'SHELL ONDINA' 33.

Sheets of about 2 mm thickness were prepared, using a normal accelerated sulphur-type vulcanization recipe, *viz*:

Compound	A	B	C
Rubber	100	82.5	65
'SHELL ONDINA' 33	—	17.5	35
Zinc oxide	3	3	3
Stearic acid	1	1	1
Sulphur	0.5	0.6	0.6
2-Mercaptobenzothiazole	0.5	0.5	0.5
Tetramethyl thiuramdisulphide	0.6	0.6	0.6
Antioxidant	0.5	0.5	0.5
Curing time at 150 °C, min	60	60	60

Samples were extracted by leaving them in an excess of *n*-heptane for at least three days, changing the solvent several times. Prior experiments had shown this to be sufficient to remove all non-rubber constituents, except bound sulphur and unconverted zinc oxide.

The stress relaxation measurements were carried out with an Instron tensile testing machine*, provided with a glass cylindrical vessel** high enough to accommodate both grips at all elongations used in this study. Before extracting the rubber, strips with a cross-section of about 10×2 mm were cut out, marked with ink lines and extracted as described above. When immersed, readings were taken with a cathetometer; previously, by taking readings from a strip of graph paper, it had been made certain that irregularities in the transparent cylinder were absent. The accuracy achieved in measuring the elongation was better than 0.5%. The resulting stress was recorded on graph paper, and from this, readings were taken at 1 and 2 minutes and subsequently once every 4 minutes. These readings were analysed as described in Chapter 3, section 3.2.

Equilibrium swelling values were determined by the weighing technique. Swollen pieces of rubber were dried superficially to remove adhering solvent and weighed in tared bottles. The rubber content of these pieces was then determined by drying to constant weight. The reproducibility of the

* model TT/CM-M, serial no. 408.

** immersion testing equipment, model G-90-4.

results thus obtained was better than with direct measurement of the swollen dimensions.

In the calculation of q_1, the weights of the dry and swollen samples were corrected for the weight of the zinc oxide; the specific gravity of the rubber is 0.866, that of the 'SHELL ONDINA' 33 oil 0.882, that of the *n*-heptane 0.684. The molar volume of the heptane is 146.5. Corrections for the volume of the zinc oxide were so small that they were omitted.

The temperature during the swelling and stress relaxation measurements was kept at 20°C $\pm$ 0.5. To obtain information on the influence of temperature variations on the swelling equilibrium, the latter was also determined at 25°C. Table I gives the values of q_1 at both temperatures; it is seen that even a 5°C variation in temperature has a negligible influence on q_1.

For the three vulcanizates, the degree of swelling in benzene was also determined. From the stress-strain data in *n*-heptane the factor $Avq_{02}^{-2/3}$ is known; assuming q_{02} to be the same, whether swelling in *n*-heptane or in benzene, the conclusions drawn in Chapter 6 allow the values for χ (EPDM/benzene) to be calculated and compared with literature data, independently of the value of Bv.

4.2 UNIDIRECTIONAL COMPRESSION

The compression experiments were carried out with the same networks as used by VAN DE KRAATS[18]. These networks are based on poly(*p*-nitrophenyl methacrylate) (PNPMA), cross-linked with hexamethylene diamine. By cross-linking a 20% solution of PNPMA in dimethylformamide, a fairly large q_{cr} was achieved. For practical reasons, after network formation, the solvent had to be replaced by nitrobenzene.

Surprisingly, this seems to result in a substantial increase in q_{02}. Investigations by VAN DE KRAATS show this effect to be attributable to the breaking-up of molecular aggregates present in a solution of poly(*p*-nitrophenyl methacrylate) in dimethylformamide.

The value of q_{02}, therefore, is quite different from the volume at cross-linking q_{cr}. VAN DE KRAATS has tentatively suggested the following relation:

$$q_{02} \text{ (in nitrobenzene)} \approx 3^{3/2} q_{cr}$$

Exact values of q_{02}, calculated from equation (16), depend on the values assumed for A and v. Consequently, when the number of chains per unit volume, v, is known, it is possible to arrive at only the product $Aq_{02}^{-2/3}$ rather than q_{02} as such.

When also v is unknown, the ratio $\dfrac{B}{Aq_{02}^{-2/3}}$ can still be determined, as shown in Chapter 6, section 6.5.

As explained in Chapter 2, we assume q_{02} to be independent of the degree of swelling in the range of swelling ratios considered. The networks all having been formed at the same concentration in solution, their q_{02}-values will all be the same, except for small variations due to differences in degree of cross-linking. Furthermore, the specimens all have the same circular cylindrical shape with height equalling diameter, and all contain the same amount of PNPMA, *viz* 0.5688 gram. As will be discussed later, the diameter of the test pieces (ranging between 1.8 and 2.1 cm, depending on the degree of swelling) is inconveniently large for carrying out stress relaxation experiments. The dimensions of the cylinder, however, have to be so large to make regular deformations in compression possible.

The stress relaxation of compressed samples was followed by placing a swollen cylinder vertically between two horizontal flat Teflon discs. Teflon was used, since it was found to allow affine deformation of the samples on compression, that is to say, the low friction between Teflon and swollen PNPMA permitted the contact area between the two to increase in the same ratio as the cross-section of the bulk of the test sample. The lower disc was placed in a glass diluent container with two plane-parallel sides on a firm mounting. The other Teflon disc was fitted to an inductive pressure transducer*, which itself could be adjusted vertically by a micrometer screw. The height of the sample, before and after applying a compressive strain, was read with a cathetometer, and the difference between these two values was checked with the distance over which the micrometer was moved. The height of the undeformed sample was only used as a control on the value of the swelling ratio; the height of the compressed sample was divided by the height of the diluent-free cylinder (0.805 cm) to obtain λ.

The stress signal as measured by the transducer was amplified** and continuously recorded. From the recorder sheet, readings were taken at intervals of one hour, and analysed as before.

Swelling equilibrium values were again determined by weighing; in this case, however, direct measurement of height and diameter with the cathetometer was possible also during the stress relaxation measurements.

The measurements were carried out at 27.4 ± 0.1°C. At this temperature, the volume of the polymer is 0.410 cm^3, the specific gravity of nitrobenzene is 1.196, and its molar volume 102.9. Here, as in the case of EPDM/*n*-heptane, partial molar volumes are considered to be the same as molar volumes.

* type Q 1/5, Hottinger-Baldwin, Darmstadt, Germany

** carrier wave amplifier, type KWS/II-5, Hottinger-Baldwin

5. EXPERIMENTAL RESULTS

5.1 SAMPLES SUBMERGED IN DILUENT-SATURATED WATER

Before proceeding to further determination and analysis of the stress relaxation of strained networks, an independent check was carried out on the validity of our hypothesis which ascribes most of the stress relaxation to diffusion. To this end, EPDM strips, swollen to equilibrium (q_i), were stretched in a surrounding medium of water saturated with *n*-heptane. In this case the equilibrium swelling ratio q_λ of stretched samples will eventually be the same, but the rate of attainment of q_λ is far lower than when pure heptane is the medium.

Moreover, the rate of transport of diluent within the gel will also be governed by the rate of transport in the surrounding medium. As a result, the concentration of diluent at the surface of the gel, c_0, is no longer constant. Consequently, equation (21) no longer describes the increase in the swelling ratio, and the 'normal' relaxation time τ_1, mentioned in Chapter 1 and occurring in all experimental results given in this chapter, section 5.2, will be absent.

The resulting stress relaxation curves could not indeed be accurately described by an equation like equation (2), even when using three relaxation terms. It seemed that a large part of the relaxation might only be described by a continuous relaxation spectrum.

Nevertheless, the data relating to a few samples of stretched, swollen vulcanizates in saturated water were analysed (a computer programme being available to adjust the parameters f_∞, f_{1r}, f_{2r}, f_{3r}, τ_1, τ_2 and τ_3 simultaneously). This yielded the results given in Table II.

The sample submerged in water shows a relaxation term with a relaxation time of five minutes, but the normal relaxation term with $\tau_1 = 37$ minutes, occurring in the reference sample and in the results of the next section, is absent. The terms with $\tau_3 = 108$ and $\tau_4 = 126$ minutes are to be seen as attempts to characterize a relaxation spectrum with the aid of two discrete relaxation times only.

Apparently, the diffusion into the sample submerged in water takes place more slowly than in the case of the reference, and cannot be described by

equation (21). These results confirm the relation between stress relaxation and diffusion: unlike relaxation due to increased swelling by diffusion of additional diluent into the network, isochoric stress relaxation is not dependent on the surrounding medium. We therefore ascribe the term $f_{2r}e^{-t/\tau_2}$ at least partly to isochoric stress relaxation, and the term with τ_1 to diffusion.

It should be mentioned that in the preparation of this experiment it was difficult to avoid the adherence of free diluent to the test piece. In preliminary experiments where this occurred, a small relaxation term with a τ-value of 40–50 minutes was observed. Therefore, unless adhering diluent is carefully removed, false conclusions may easily be drawn from such experiments.

5.2 STRESS RELAXATION DATA OF EXTENDED EPDM SAMPLES

The stress relaxation curves obtained with stretched EPDM test pieces all conformed to the graphical representation as shown in Figure 1, and are therefore fully identified by the parameters $f_\infty, f_{1r}, f_{2r}, \tau_1$ and τ_2. The values of these parameters as determined for the various EPDM vulcanizates are given in Table III. The same table also contains the main quantities derived from the stress relaxation curves directly, *viz* f_0^*, $Avq_{02}^{-2/3}$ and q_λ. In the calculation of $Avq_{02}^{-2/3}$ and q_λ, the q_1-data reported in Table I have been used. A discussion of the other network parameters is deferred to Chapter 6.

The following comments on the data collected in Table III can be made:

a. To speed up the experiments, the strain was sometimes varied without first letting the sample deswell to the original degree of swelling q_1. Application of a further strain then again gave rise to diffusion according to equation (20), but here the initial degree of swelling was calculated from the foregoing stress relaxation measurements using equation (16): the last reading of a stress before switching to another elongation was called f_{tr}, and this value was used to calculate the degree of swelling at the moment of transition, q_{tr}. The value of Δq determined from the second stress relaxation measurement has thus to be added to q_{tr} to obtain the value for q_λ corresponding to the new strain.

b. Sample B1 was not fully swollen before being stretched to an extension $\lambda = 1.88$. As a result, a much larger increase in swelling ratio occurred during stress relaxation than corresponds to the transition $q_1 \rightarrow q_\lambda$. This manifested itself in too high a relaxation term f_{1r}, and hence too high values for $Avq_{02}^{-2/3}$ and q_λ. The final stress agreed very well with that of

the two other specimens. To enable the data of sample B1 to be used at $\lambda = 2.14$, it was first assigned the average swelling ratio q_λ of the two other samples with $\lambda = 1.88$. From the difference between f_{tr} and f_∞, the difference between q_λ ($\lambda = 1.88$) and q_{tr} was calculated following the procedure explained in comment *a*. The value for q_{tr} thus obtained was used as the initial swelling ratio in the stress relaxation measurement at $\lambda = 2.14$.

c. Assuming an accuracy of 0.5% in λ, the uncertainty in $\lambda - \frac{q}{\lambda^2}$ is about 6% at the most. In the determination of Δq according to equation (42), as far as λ is concerned, Δq is known with an accuracy of about 7%.

d. The standard deviation of the fit of the experimental data was very small: for the individual values of f_∞ it was always less than $1‰$, and for those of f_{1r} it was about $1‰$. However, a slow drift or variation of the recorder was noted (the recorder chart was read with greater accuracy than is recommended by the manufacturer). This may cause a variation of 15–20 g/cm² in the values for f_∞ and f_{1r}. The deviations largely compensate each other, and the variation in f_0^* is therefore less than 10 g/cm². Consequently, f_∞ and f_0^* are known with an accuracy of about 1%. As follows from equation (41), Δq is proportional to f_{1r}, in which the variations, expressed in per cent, may range from 10 to 20%. This yields a variation in Δq of 0.04–0.07. Concomitant with a variation in f_{1r} is a variation in τ_1, which explains the scatter in τ_1-values.

e. Combining the statements *c* and *d* above, the accuracy of $A v q_{02}^{-2/3}$ may be about 7% and that of Δq, 20–25% in unfavourable cases.

f. In all cases given in Table III, the inequality $f_{2r} > \frac{1}{9} f_{1r}$ holds. Apparently the relaxation term $f_{2r} e^{-t/\tau_2}$ consists partly of a diffusion-controlled contribution and partly of other, isochoric, contributions with about the same relaxation time. This observation justifies the distinction drawn between f_0^* and $f(0)$ in Chapter 3, section 3.2.

g. Permanent set was found to be absent from all samples tested.

The equilibrium swelling ratios in benzene are given and discussed in Chapter 6, section 6.4, where χ (EPDM/benzene) as calculated from these data is compared with the values determined by other investigators.

5.3 STRESS RELAXATION DATA OF COMPRESSED PNPMA SAMPLES

The stress relaxation data of strained samples of PNPMA are shown in Table IV. The collection of these data was severely hampered by the very long relaxation times; experience shows that one stress relaxation measurement should last at least as long as one relaxation time to yield reliable information. In this case, therefore, experiments lasted about a week, which required careful control of the test conditions. Moreover, reconditioning of the samples in nitrobenzene to obtain the equilibrium degree of swelling q_1 again for a new experiment took not less than three weeks. This difficulty was observed while determining q_1 by the weighing method.

These long relaxation times are a direct consequence of the large diameters of the test pieces, which according to equation (44) enter the expression for τ_1 squared. The diameter of samples in compression experiments must, however, necessarily be large.

On the other hand, these data very clearly illustrate an advantage of the method developed in this study: it would be even far more time-consuming to wait until the equilibrium degree of swelling of a deformed sample has actually been reached.

Concerning the data shown in Table IV, the following comments can be made:

a. Here too, λ was determined with an accuracy of *ca* 0.5%, resulting in an accuracy in $\lambda - \frac{q}{\lambda^2}$ of *ca* 4%.

b. Adjustment of the parameters f_{1r} and f_∞ was again the main source of error. The accuracy in f_{1r}, *ca* 15%, does not greatly influence the value of f_0^*, but in combination with remark *a* above, it leads to a possible error in Δq of *ca* 20%.

c. No significant isochoric stress relaxation was noted. Experiments on non-fully swollen samples showed it to take place in less than 15 minutes.

d. The inaccuracy in the values of f_{1r} was seen to originate mainly from temperature variations. Instead of a straight line in a plot as shown in Figure 1, a slightly undulating line was obtained, the deviations in which corresponded to oscillations in temperature. This shows that a very close control of the temperature is required to carry out fully effective stress relaxation measurements. When the change in temperature is slow

compared with the time needed for the stress relaxation determination (as was the case with the extended EPDM strips), the requirement of constant temperature is less stringent.

6. NETWORK CHARACTERIZATION THROUGH STRESS RELAXATION MEASUREMENTS AND COMPARISON WITH OTHER INVESTIGATIONS

The results mentioned in the preceding chapter allow the determination of further parameters pertaining to swollen networks, apart from those already reported. In the following sections, the various parameters will be dealt with, and the results compared with those of other workers.

6.1 THE ELASTIC PARAMETER COMBINATION, $Avq_{02}^{-2/3}$

When information about the cross-link density of a network is required, swollen stress-strain measurements are frequently carried out. Usually, the change in swelling ratio is neglected, but the stress is nevertheless allowed to relax until it is 'sufficiently' constant. In the case of the EPDM rubbers described earlier, which case is typical of many practical rubber vulcanizates, this results in values for $Avq_{02}^{-2/3}$ which are 15–20% too low. The stress relaxation of the PNPMA networks is so slow that after, for example, one hour of stress relaxation, the correction would amount to not more than 2%.

The values of $Avq_{02}^{-2/3}$ measured for the PNPMA networks are in very good agreement with those reported by VAN DE KRAATS[18], *viz* (mole/cm^3 $\times$ 10^6):

sample	this study	VAN DE KRAATS
D	2.2	2.3
E	4.0	4.0
F	7.0	—

6.2 THE CHANGE IN SWELLING RATIO ON STRAINING, Δq

As regards the change in degree of swelling with straining, direct measurements on rubbers have been reported by TRELOAR[20] as well as others. TRELOAR's data on natural rubber vulcanizates are fully comparable to our own results obtained with EPDM swollen in *n*-heptane, as the degree of swelling and the χ-values do not differ greatly (χ for natural rubber/benzene is reported as 0.42–0.44; χ for natural rubber/*n*-heptane as 0.43–0.50. In section 6.4 below, it is shown that χ for EPDM/*n*-heptane is 0.425).

Our results, plotted together with those of TRELOAR in Figure 2, clearly demonstrate that the increase in swelling, calculated from stress relaxation data, closely resembles the corresponding increases measured directly.

The data of other investigations are not so well suited to comparison with either the EPDM or PNPMA networks used in this study, because of fairly large differences in q_i, q_{cr} and/or χ-values.

Direct measurement of the dimensions of the PNPMA gels with a cathetometer confirmed the Δq-values calculated from the stress relaxation data. However, unless measured regularly as a function of time to permit extrapolation to $t = \infty$, they give no information on the equilibrium degree of swelling q_λ of the strained sample.

Moreover, unless the samples are so large that the relaxation times become impractically long, optical measurements are less reliable than stress measurements (which are in any case required to determine $A v q_{02}^{-2/3}$), except when very sophisticated apparatus is used.

Finally, optical measurements do not lend themselves to continuous recording.

As mentioned in Chapter 2, several authors[25,26] have tried to circumvent the complications of additional swelling on stretching by straining in diluent vapour, or in diluent-saturated water. Such methods retard the rate of increase of swelling, but cannot stop it. Since in testing one has to wait for isochoric stress relaxation anyway, one works neither with the initial degree of swelling q_i, nor with the equilibrium swelling q_λ, but with an unknown degree of swelling between these two. Moreover, the better this retardation of additional swelling (*i.e.*, the better the technique), the greater becomes the difficulty in ascertaining that in the isotropic state just prior to stretching, equilibrium in swelling has been obtained without excess of diluent adhering to the test piece, or without the sample losing some diluent by evaporation. The precautions necessary when determining the degree of swelling by the weighing technique illustrate this objection. Only when the rate of evaporation is extremely low are valid stress-strain data at constant degree of swelling easily obtainable. In the great majority of cases found in the literature, however, rather volatile swelling agents are used, such as benzene, toluene, *n*-heptane, cyclohexane and acetone.

6.3 THE DIFFUSION COEFFICIENT, D

Experience gained in this study shows that the value of the relaxation time

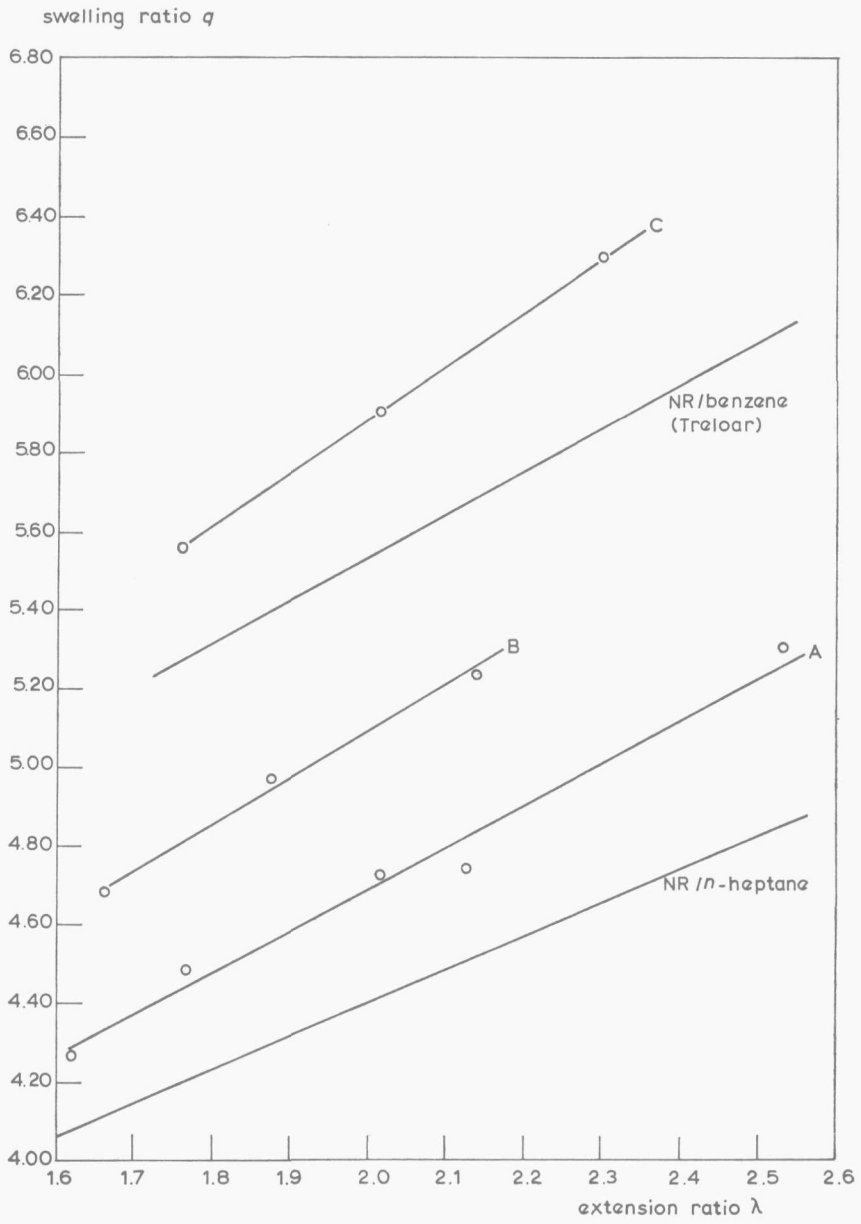

Fig. 2

Equilibrium swelling ratio as a function of extension.

τ_1, and accordingly the value of the diffusion coefficient of the diluent in the swollen network, are likely to scatter more than those of f_{1r} or f_∞. A dependence of D on concentration cannot therefore be determined, although the results obtained suggest that the dependence is small.

From the τ_1-values in Table III, we calculate that the diffusion coefficient of *n*-heptane in swollen EPDM has an average value of about 3×10^{-6} cm²/s, that of nitrobenzene in PNPMA, 0.4×10^{-6} cm²/s. These values agree very well with those calculated from comparable literature data, *e.g.*:

10^{-6}–10^{-7} cm²/s for various solvents and polymers at different degrees of swelling[38],

10^{-5}–10^{-6} cm²/s for cyclohexanone/acetone in butyl rubber[39],

ca 3.5×10^{-6} cm²/s for benzene in swollen natural rubber[40],

ca 2×10^{-6} cm²/s for various solvents in highly swollen polystyrene[32].

6.4 THE POLYMER/SOLVENT INTERACTION PARAMETER, χ

For the determination of χ, equation (14) is normally used after the determination of $Avq_{02}^{-2/3}$ with the aid of equation (16). Neglect of the change in degree of swelling was mentioned as resulting in values for $Avq_{02}^{-2/3}$ of the EPDM samples which are 15–20% too low. This is reflected in values for χ which are 4–5% too high, irrespective whether $B = 0$, $\frac{1}{2}$ or 1 is used.

It is this uncertainty in B, however, which is the cause of still more ambiguity in reports of χ-values. Usually, $B = \frac{1}{2}$ is assumed, but some authors use $B = 0$[41] or $B = 1$[42]. This directly influences the value of χ: from the results in Table III, one finds $\chi = 0.41$–0.42 when $B = \frac{1}{2}$, but $\chi = 0.45$–0.46 when $B = 1$ (assuming $A = 1$ and $q_{02} = q_{cr}$).

To determine χ *independently* of B, variation of q is necessary. This permits the calculation of both χ and Bv. Variation of q may be brought about by various techniques, such as changing the activity of the diluent or varying the volume of the swollen gel by external strain.

The activity of the diluent can be varied by swelling in diluent vapour of varying partial pressure[43] or by deswelling in solutions of polymer in diluent[44].

Variations in q by means of external strain may be effected by omnilateral ('isotropic') compression and determination of the resulting equilibrium pressure[18], or by uni- or bilateral strain and subsequent determination of the equilibrium swelling ratio. RIJKE and TAYLOR[42] determined q_λ of strained strips, swollen to equilibrium, by photographic means; the stress relaxation method outlined in this study offers another, fairly simple and rapid, example of the latter category.

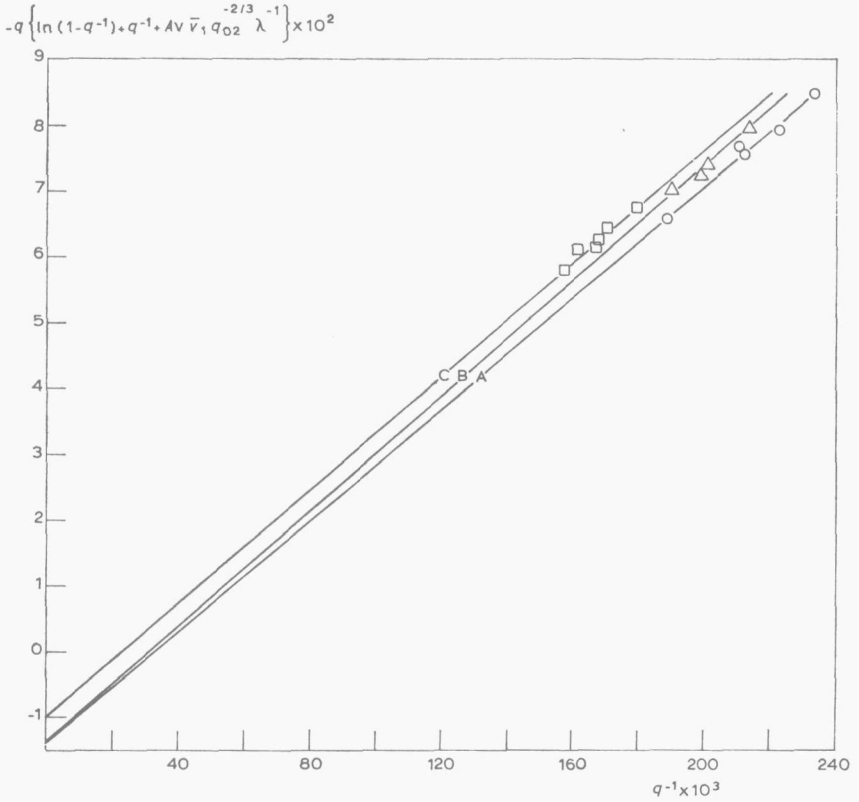

Fig. 3

Calculation of χ and Bv from strain-induced changes in swelling ratio (EPDM)

For its application, equation (15) is multiplied by q_λ, yielding:

$$q_\lambda \ln (1 - q_\lambda^{-1}) + 1 + A v \bar{v}_1 q_{02}^{-2/3} q_\lambda \lambda^{-1} = -\chi q_\lambda^{-1} + B v \bar{v}_1 \qquad (45)$$

in which the case of free swelling is represented by $q_\lambda = q_i$ and $\lambda = q_i^{1/3}$. When plotting the left-hand side of equation (45) versus q_λ^{-1}, a straight line results having a slope of $-\chi$ and an intercept, after linear extrapolation, equalling $Bv\bar{v}_1$.

Application of this technique to the EPDM-data of Table III yields the plot shown in Figure 3. The slopes as drawn here provide the following values of χ (EPDM/*n*-heptane):

sample	χ
A	0.42 ± 0.01
B	0.43 ± 0.01
C	0.43 ± 0.01

We conclude, therefore, that for this type of network in this range of swelling ratios, χ (EPDM/*n*-heptane) $= 0.42^5 \pm 0.01$.

A discussion of Bv will be given in the next section.

Once χ (EPDM/*n*-heptane) is known, χ (EPDM/benzene) can be calculated from the equilibrium swelling ratios in benzene. One may, for instance, multiply equation (14) by $q_i \bar{v}_1^{-1}$ and substitute first q_i and $\bar{v}_1$ (in heptane) and then q_i and $\bar{v}_1$ (in benzene), assuming q_{02} to be the same in *n*-heptane and benzene. Subtraction of the two resulting equations yields χ (EPDM/benzene) irrespective of the value assumed for B, since the term Bv is eliminated.

A more rapid method is substitution of Bv as found from the plot in Figure 3, and the value of q_i (benzene) in equation (14). Application of this method yields the results given in Table V. In this table, the equilibrium swelling ratios in benzene are given first, next the χ-values determined as described above, and finally a comparison with literature data by DUDEK and BUECHE[23] (applying their equation: χ (EPDM/benzene) $= 0.49 + 0.33\, q^{-1}$).

A direct comparison with the data of CRESPI and BRUZZONE[22] is not possible due to the fact that their equation (*viz*, $\chi = 0.48 + 0.29\, q^{-1}$) was determined for a saturated type of ethylene-propylene rubber (EPM) that has to be vulcanized with a peroxide.

DUDEK and BUECHE further report that χ(EPDM/*n*-heptane) $= 0.44$. Here, as in the case of χ(EPDM/benzene), they applied equation (14), assuming $A = 1$, $B = \frac{1}{2}$ and $q_{02} = q_{cr}$, and neglecting the change in q resulting from extension.

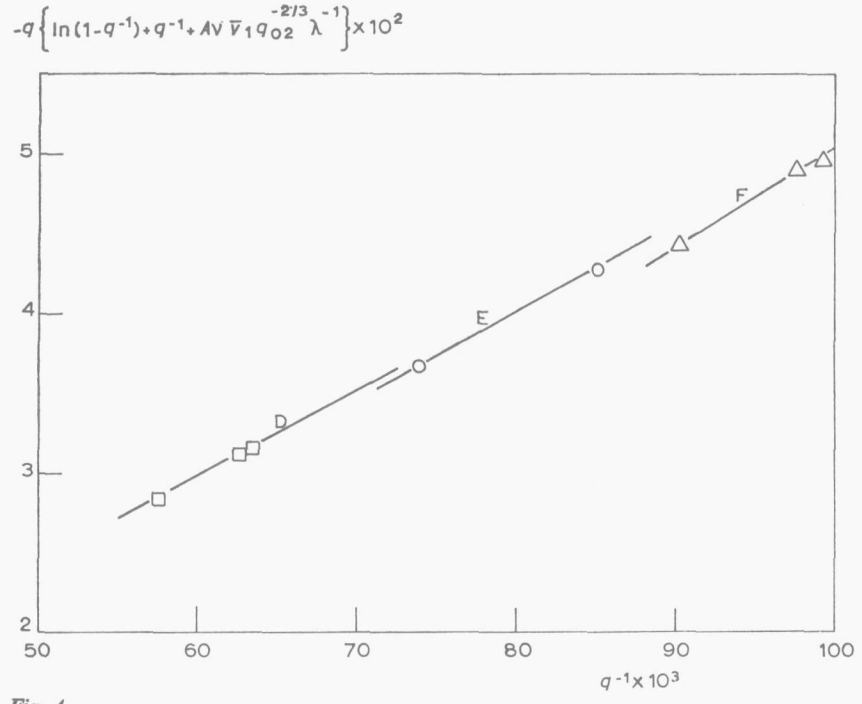

Fig. 4.

Calculations of χ and Bv from strain-induced changes in swelling ratio (PNPMA).

On the same assumptions, but accounting for Δq, our data yield χ(EPDM/*n* heptane) = 0.42 and χ(EPDM/benzene) as given in Table V. It is seen that their values for χ are on the average 4% higher than our comparable values (the better agreement with our *B*-independent data, which are *not* comparable with theirs, is fortuitous). This is exactly what might be expected when neglecting the increase in swelling, Δq; after accounting for Δq, therefore, the agreement between the data of DUDEK and BUECHE and our data is very good.

A plot to determine χ(PNPMA/nitrobenzene) independently of B is given in Figure 4. From the limited number of points we find:

sample	this study	VAN DE KRAATS
D	0.53	0.526
E	0.55	0.543
F	0.57	—

The latter values are the results obtained on the same samples by VAN DE KRAATS with a swelling pressure osmometer. The correspondence is seen to be good; the dependence of χ on chain density is also apparent. In view of the small values of Δq compared with those achieved by VAN DE KRAATS, the accuracy of our values is estimated to be somewhat less.

6.5 THE CONSTANTS A AND B IN THE SWELLING EQUATION

The theoretically most interesting parameters are the constants A and B. For their determination, prior knowledge of v, χ and q_{02} is required.

The chain density v can only rarely be determined by independent methods. Cross-linking with accelerated sulphur systems or with peroxides does not lead to values for v which can be determined from the stoichiometry of the reactants[45-47]. Physical cross-links (entanglements) and wasted cross-links (closed loop formation) may constitute another source of uncertainty.

Experiments by HASA and JANACEK[48] and by MEISSNER, KLIER and FRANTA[49] confirm the opinion that the effect of entanglements decreases with increasing dilution prior to cross-linking, or rather with increasing q_{02}. On the other hand, increasing q_{cr} promotes the occurrence of wasted cross-links through loop formation.

The PNPMA networks offer a case where the chemical chain density may closely approach the physical chain density: q_{cr} is less than 8, which means that the wasted cross-links may be few, but due to the solvent switch (see Chapter 4, section 4.2), q_{02} is much larger than q_{cr}, and also larger than the

swelling ratio of any of the samples tested. The chains are thus *supercoiled*, and this may strongly reduce the effect of entanglements.

The number of chemical cross-links in some of the PNPMA samples is known with sufficient accuracy, and on the basis of the above, substitution of this value in equations (14) and (15) seems justified in order to obtain B from Bv.

On the other hand, q_{02} of these samples is only inaccurately known, so that the value of A cannot be estimated from the experiments with PNPMA.

In many practical cases, v is calculated from stress-strain measurements by assuming $A = 1$, $q_{02} = q_{cr}$. The latter assumption is suggested by HOEVE and O'BRIEN[50] in the case of weak short-range interaction between polymer segments mutually and between polymer and diluent, and may be applied in the case of EPDM/*n*-heptane. When significant interaction is likely to occur, q_{02} may be dependent on the diluent, as appears to be the case in the experiments by RIJKE and TAYLOR[42].

Although difficult to realize, the most promising experiment to determine A would consequently have to be carried out with an apolar polymer, cross-linked at a moderate dilution with a cross-linking system that allows an accurate determination of the number of chemical cross-links introduced, combined with an apolar solvent that does not swell the network much, so as to minimize an elastic contribution from entanglements.

The factor B can in principle be read from the plots in Figures 3 and 4 when v is known. In the case of our data on the PNPMA networks, the extrapolation needed to discriminate between $B = 0$, $\frac{1}{2}$ or 1 cannot be carried out with sufficient accuracy (VAN DE KRAATS, with a wider range of q-values, finds $B = 0.5 \pm 0.1$, assuming q_{02} to be independent of q).

For the EPDM networks, the values of $Bv\bar{v}_1$ are seen to be $1.0 - 1.3 \times 10^{-2}$. For the calculation of B, we obviously need a value for v, which, however, is unknown for the EPDM rubbers. Assuming in this case that $q_{02} = q_{cr}$, the product Av is known from the stress-strain experiments, but v itself is not known. Consequently, it is only possible to determine the ratio $\frac{B}{A}$. For the three EPDM networks, this ratio is:

sample	$\frac{B}{A}$
A	0.65
B	0.72
C	0.66

The accuracy in these data is estimated to be about 20%, and no definite conclusion from these experiments can be drawn about the ratio $\frac{B}{A}$. $B = 0$ appears to be very improbable; the results tend to favour the ratio $\frac{B}{A} = \frac{1}{2}$ somewhat more than $\frac{B}{A} = 1$. If this conclusion may be combined with VAN DE KRAATS' conclusion that $B = \frac{1}{2}$, A would be 1 and FLORY's theory would fit the experimental data better than the other theories mentioned in Chapter 2. However, the speculative elements in this conclusion should be stressed.

6.6 ISOCHORIC STRESS RELAXATION

Data on isochoric stress relaxation other than chemical stress relaxation seem to be scarce. Some results have been reported by COTTON and BOONSTRA[51] for *cis*-polybutadiene rubber (BR) vulcanizates, swollen in decalin and kept at a constant degree of swelling. According to these authors the relaxation can be described by the equation:

$$f(t) = f_{1.0}t^{-n}, \tag{46}$$

where $f(t)$ is the stress in kg/cm^2 as a function of time t (in minutes) and $f_{1.0}$ is the stress after 1 minute.

$f_{1.0}$ was used because it could be more accurately measured than $f(t = 0)$: an experience not unlike ours. For gum vulcanizates, swollen to $q = 4$ and extended by 75%, they found $n = 0.007$. The range of time studied was not given, but was certainly not large enough to find that $f(t)$ should have a finite lower limit, instead of tending to zero as predicted by equation (46).

Calculating the values of $f(t)$ between 4 and 20 minutes, using COTTON and BOONSTRA's data, yielded a stress relaxation curve which could equally well be represented by equation (2). The resulting relaxation time was 6–9 minutes; although it must be coincidental that this is also what was derived for isochoric stress relaxation in the foregoing chapters, it is in excellent agreement with our conclusions and interpretations.

Isochoric stress relaxation should also be taken into account when interpreting the experiments of KUHN, MUELLER, KUHN and EISENBERG[52]. In these experiments, the Young's modulus of a natural rubber strip, submerged in benzene, was determined. Working with constant stress, KUHN *et al.* noticed a time dependence in the elongations of their test samples and ascribed this to diffusion of diluent into the sample. This time dependence could be described with a retardation time of *ca* 8 minutes, yielding, as KUHN[53] noted, a diffusion coefficient of the right order of magnitude.

It is indeed very likely that uptake of additional solvent caused strain retardation. However, isochoric strain retardation was not eliminated or taken into account. The degrees of swelling being about the same as those of our EPDM samples or of COTTON and BOONSTRA's BR samples, we are of the opinion that the retardation time of 8 minutes originates partly from diffusion-controlled and partly from isochoric strain retardation.

6.7 CONCLUSION

In stress-strain measurements on swollen elastomer networks, stress relaxation is usually considered a source of delay and inaccuracy. With proper analysis, however, it can be used to advantage, since it makes the determination of accurate stress-strain relations possible without neglecting, as is often done, the strain-dependent change in degree of swelling.

Secondly, it permits the determination of the polymer/solvent interaction parameter χ independently of the factor Bv in the swelling equation (14). At the same time, Bv is also obtained. From this, the factor B may be obtained if the chain density v is known, but this will only very rarely be the case. Neither will the factor A be obtainable, but with proper precautions, the ratio $\frac{B}{Aq_{02}^{-2/3}}$ can be deduced from the experiments.

The stress relaxation method has the following advantages:

a. The above-mentioned information can be obtained with standard equipment in a few hours.

b. It is applicable to extended as well as to compressed samples, although in the latter case it is rather time-consuming (a week or more).

c. It is not necessary to wait until the swelling equilibrium in a strained sample has been reached, since its value is obtainable by extrapolation.

TABLES

TABLE I. EQUILIBRIUM SWELLING DATA OF EPDM IN *n*-HEPTANE

Sample	Temperature, °C	Weight before extraction, mg	Weight after extraction, mg	Swollen weight, mg	q_{cr}	q_i
A	20	671.0	648.0	2271.5	1.04	4.27
		640.5	619.0	2173.9	1.04	4.27
	25	825.7	796.0	2787.0	1.04	4.26
		757.3	730.4	2557.2	1.04	4.26
B	20	853.5	695.5	2647.4	1.23	4.67
		867.3	707.4	2684.5	1.23	4.66
	25	940.2	765.7	2897.6	1.23	4.66
		986.1	803.7	3027.0	1.23	4.64
C	20	672.6	441.1	1946.9	1.54	5.54
		724.0	474.1	2112.4	1.54	5.57
	25	747.3	490.0	2163.7	1.54	5.54
		726.7	476.4	2100.9	1.54	5.53

TABLE II. STRESS RELAXATION OF SWOLLEN EPDM IN WATER SATURATED WITH *n*-HEPTANE

Unswollen cross-section of strips: 1 × 10 mm

Medium	Extension ratio λ	Duration of test, min	f_∞, g/cm²	f_{1r}, g/cm²	τ_1, min	f_{2r}, g/cm²	τ_2, min	f_{3r}, g/cm²	τ_3, min	f_{4r}, g/cm²	τ_4, min
water/heptane	2.57	360	9460	—	—	241	5	171	108	23	126
heptane	2.00	100	3760	372	37	105	9	—	—	—	—

TABLE III. EPDM SWOLLEN IN *n*-HEPTANE; ANALYSIS OF STRESS RELAXATION DATA

Sample	Test piece	Extension ratio λ	f_∞, g/cm^2	f_{1r}, g/cm^2	f_{2r}, g/cm^2	f_0^*, g/cm^2	f_{tr}, g/cm^2	τ_1, min	τ_2, min	q_{cr}	q_i	q_λ	q_{tr}	$A\nu q_{02}^{-2/3}\times10^4$, mole/cm^3
A	1	1.77	1150	187	33	1380		67	11	1.04	4.27	4.48		1.36
							1160						4.47	
		2.02	2860	167	93	3070		91	6			4.72		1.35
							2930						4.63	
		2.53	6010	300	85	6380		46	5			5.30		1.41
	2	2.13	4060	310	120	4440		100	9			4.73		1.50
B	1	1.88	1360	613		2115				1.23	4.67	(4.97)		
							1435						4.88	
		2.14	2805	175	97	3020		111	20			5.23		1.10
	2	1.88	1265	211	28	1525		53	4			5.01		1.10
	3	1.88	1355	172	27	1565		62	6			4.94		1.13
C	1	2.02	1050	151		1235		54		1.54	5.56	5.95		0.76
							1060						5.93	
		2.31	2155	120	23	2300		50	7			6.34		0.78
	2	2.02	1100	136	31	1265		62	3			5.91		0.76
		2.31	2175	220	50	2445		53	5			6.31		0.77
	3	2.02	1090	106	19	1220		71	10			5.85		0.74
							1110						5.81	
		2.31	2180	108	29	2315		50	5			6.19		0.76

TABLE IV. PNPMA SWOLLEN IN NITROBENZENE; ANALYSIS OF STRESS RELAXATION DATA

Sample	q_i	q_{tr}	λ	f_∞, g/cm^2	f_{1r}, g/cm^2	f_0^*, g/cm^2	τ_1, h	$Avq_{02}^{-2/3} \times 10^6$, mole/cm^3	Δq	q_λ
D	17.4		2.24	49	10	64	130	2.1	1.4	16.0
			2.26	45	13	64	110	2.2	1.7	15.7
E	13.5	13.2	2.04	86	25	122	140	4.0	1.5	11.7
F	11.1		2.03	67	29	108	100	6.7	1.0	10.1
		10.9	2.05	74	21	104	80	7.3	0.7	10.2

TABLE V. POLYMER/SOLVENT INTERACTION PARAMETERS FOR EPDM/BENZENE

	A	B	C
Swelling ratio in benzene	3.08	3.33	3.72
χ, calculated independently of Bv	0.59	0.58	0.58
χ, calculated with $B = \frac{1}{2}$	0.58	0.57	0.57
χ, according to DUDEK and BUECHE ($B = \frac{1}{2}$)	0.60	0.59	0.58

SUMMARY

Cross-linked elastomers are often characterized in the swollen state, because the thermodynamic behaviour of a network can be more adequately described by the current theories of Gaussian coiling chains when swollen, rather than when in the dry state.

During stress-strain measurements on swollen networks in an excess of diluent, a significant stress relaxation occurs, which in practice is considered to be a source of delay and inaccuracy. Analysis of the stress relaxation, however, shows that a major and recognizable part of it is due to diffusion of diluent into or out of the network.

This diffusion, which is derived for the case of changing dimensions of the network, is related to the alteration in swollen volume dictated by the imposed strain. Stress relaxation measurements therefore allow the calculation of

a. The equilibrium stress in a strained network before any diluent has migrated.

b. The equilibrium stress, when the network has reached its new equilibrium degree of swelling conforming to the imposed strain. By applying a reliable extrapolation procedure, this equilibrium stress is determined without actually reaching equilibrium.

c. The equilibrium degree of swelling after straining, provided that the unstrained swelling ratio is known.

From these data, the polymer/solvent interaction parameter can be obtained without making a choice between the various – somewhat controversial – network theories. The number of elastically effective chains, however, can only be determined by making such a choice. Having done so, the ratio of the strained to the unstrained chain dimensions can also be calculated.

An equation for the free energy of a strained, swollen network is given in a generalized form; it shows that the ratio of the strained chain dimensions in the network to the free chain dimensions, used as a reference, may depend on:

a. The cross-linking process.

b. The short-range interaction between polymer and diluent.

c. The degree of dilution during cross-linking.

The stress relaxation method is applied to a series of stretched ethylene-propylene rubbers, and to a series of poly(*p*-nitrophenyl methacrylate) networks under unilateral compression.

The results are in very good agreement with those reported in the literature. The techniques used by other workers, however, require more specialized equipment than does our method, while not yielding any more information about the network parameters.

The experiments, although not corroborating any specific network theory, nevertheless exclude some current theories.

SAMENVATTING

Parameters van rubberachtige netwerken worden vaak bij voorkeur niet aan ongezwollen, maar aan gezwollen monsters bepaald. Het thermodynamisch gedrag van een netwerk is dan namelijk meer in overeenstemming met de gebruikelijke theorieën betreffende gekronkelde ketens met een Gaussverdeling van de dimensies.

Bij de bepaling van de spanning als functie van de deformatie van een gezwollen netwerk in een overmaat van zwelvloeistof treedt meestal een aanzienlijke spanningsrelaxatie op. Deze wordt doorgaans ervaren als een oorzaak van onnauwkeurigheid en tijdverlies. Analyse van de spanningsrelaxatie toont echter aan dat een aanzienlijk, als zodanig te onderkennen, deel toegeschreven moet worden aan diffusie van zwelvloeistof in of uit het netwerk.

Voor deze diffusie is een vergelijking opgesteld voor het geval dat de dimensies van het monster toe- of afnemen tijdens het diffusieproces. Deze vergelijking beschrijft daarbij de volumeverandering van het netwerk, die uit de toegepaste deformatie moet volgen. Zodoende kan men uit de analyse van de spanningsrelaxatie de volgende grootheden berekenen:

a. de evenwichtsspanning van een gedeformeerd netwerk, voordat transport van zwelvloeistof heeft plaatsgevonden,
b. de evenwichtsspanning van een gedeformeerd netwerk, nadat de volumeverandering volledig heeft plaatsgevonden,
c. de evenwichtszwelgraad *na* deformatie, mits de evenwichtszwelgraad *voor* deformatie bekend is.

Een geschikte extrapolatiemethode wordt beschreven, waarmee deze informatie verkregen wordt in een fractie van de tijd, nodig om het nieuwe zwellingsevenwicht werkelijk te bereiken.

Uit deze gegevens kan men de z.g. polymeer/solvent interactieparameter berekenen zonder gedwongen te zijn een keuze te maken uit de verschillende,

niet geheel gelijkluidende, netwerktheorieën. Het aantal elastisch werkzame ketens kan echter alleen berekend worden wanneer men zulk een keuze maakt. In dat geval vindt men ook de dimensieverhouding tussen gedeformeerde en ongedeformeerde (vrije) ketens, welke laatste als referentie dienen bij de berekening van de vrije energie van het netwerk.

Voor de vrije energie van een gedeformeerd, gezwollen netwerk wordt een algemene formule gegeven, die laat zien hoe de dimensieverhouding van gedeformeerde netwerkketens en vrije ketens kan afhangen van:

a. het proces van de netwerkvorming,

b. de korte-afstand-wisselwerking tussen polymeer en zwelvloeistof,

c. de verdunningsgraad tijdens de netwerkvorming.

Toepassing van de analyse van spanningsrelaxatie wordt beschreven voor een reeks etheen-propeen rubbers bij rek, en voor een reeks gelen van poly-(*p*-nitrophenylmethacrylaat) bij eenzijdige compressie. De resultaten stemmen zeer goed overeen met de bestaande literatuurgegevens. In tegenstelling tot de hierboven beschreven spanningsrelaxatiemethode, vereisen de tot dusver gebruikte technieken speciale apparatuur, zonder echter meer informatie te verschaffen.

De experimentele resultaten geven niet aan, welke netwerktheorie de juiste is, maar sluiten wel enkele uit.

REFERENCES

1. P. J. Flory, '*Principles of Polymer Chemistry*', New York, Cornell University Press, 1953
2. A. Ciferri and J. J. Hermans, *J. Polymer Sci., B (polymer letters)* **2** (1964) 1089
3. G. Crespi, G. Natta and U. Flisi, *Chim. Ind. Milan* **46** (1964) 746
4. G. M. Bristow, *J. Appl. Polymer Sci.* **9** (1965) 1571
5. R. Blokland, '*Elasticity and structure of polyurethane networks*', Rotterdam, Universitaire Pers Rotterdam, 1968
6. W. J. Bobear, *Rubber Chem. Tech.* **40** (1967) 1560
7. F. T. Wall, *J. Chem. Phys.* **11** (1943) 527
8. F. T. Wall and P. J. Flory, *J. Chem. Phys.* **19** (1951) 1435
9. P. J. Flory and J. Rehner, Jr., *J. Chem. Phys.* **11** (1943) 512 and 521
10. P. J. Flory, *J. Chem. Phys.* **18** (1950) 108
11. M. L. Huggins, *J. Phys. Chem.* **46** (1942) 151
12. J. J. Hermans, *J. Polymer Sci.* **59** (1962) 191
13. A. V. Tobolsky, '*Properties of Polymers*', New York-London, John Wiley & Sons Inc., 1960
14. W. Prins, in J. A. Prins, *ed.*, '*Physics of non-crystalline solids*', Amsterdam, North-Holland Publishing Co., 1965, p. 360
15. J. A. Duiser and A. J. Staverman, *ibidem*, p. 376
16. A. J. Chömpff and J. A. Duiser, *J. Chem. Phys.* **45** (1966) 1505
17. H. M. James and E. Guth, *J. Chem. Phys.* **21** (1953) 1039
18. E. J. van de Kraats, *Thesis Delft*, 1967
19. G. Gee, *Trans. Faraday Soc.* **42**^{B} (1946) 33
20. L. R. G. Treloar, *Trans. Faraday Soc.* **46** (1950) 783
21. A. V. Tobolsky, D. W. Carlson and N. Indictor, *J. Polymer Sci.* **54** (1961) 175
22. G. Crespi and M. Bruzzone, *Chim. Ind. Milan* **41** (1959) 741
23. T. J. Dudek and F. Bueche, *J. Polymer Sci., A* **2** (1964) 811
24. B. Meissner and J. Janáček, *Collection Czechoslov. Chem. Communs.* **26** (1961) 3101
25. S. M. Gumbrell, L. Mullins and R. S. Rivlin, *Trans Faraday Soc.* **49** (1953) 1495

26. H. E. Adams and B. L. Johnson, *Ind. Eng. Chem.* **45** (1953) 1539
27. J. Crank, '*The mathematics of diffusion*', Oxford, Clarendon Press, 1956
28. W. Jost, '*Diffusion in Solids, Liquids, Gases*', New York, Academic Press, 1952
29. G. J. van Amerongen, *Rubber Chem. Tech.* **37** (1964) 1065
30. G. S. Hartley and J. Crank, *Trans. Faraday Soc.* **45** (1949) 801
31. J. Crank and G. S. Park, *Trans. Faraday Soc.* **45** (1949) 240
32. G. Rehage, *Kunststoffe* **53** (1963) 605
33. R. M. Vasenin, A. E. Chalykh and V. I. Korobko, *Vysokomolekul. Soedin. (English translation: Polymer Sci. USSR)* **7** (1965) 593
34. J. Crank, *J. Polymer Sci.* **11** (1953) 151
35. E. Southern and A. G. Thomas, *J. Polymer Sci., A* **3** (1965) 641
36. D. H. Andrews and J. Johnston, *J. Am. Chem. Soc.* **46** (1924) 640
37. H. Boer and E. C. Kooyman, *Anal. Chim. Acta* **5** (1951) 550
38. V. K. Gromov, A. E. Chalykh, R. M. Vasenin and S. S. Voyutskii, *Vysokomolekul. Soedin. (English translation: Polymer Sci. USSR)* **7** (1965) 802
39. D. J. Buckley and M. Berger, *Proc. Intern. Rubber Conf.*, Washington, D. C., 1959
40. P. Ször, *Plaste Kautschuk* **12** (1965) 402 and 604
41. *e.g.*, reference 4 and G. M. Bristow and M. Porter, *J. Appl. Polymer Sci.* **11** (1967) 2215
42. *e.g.*, A. M. Rijke and G. L. Taylor, *J. Polymer Sci., A*-1 **5** (1967) 1433
43. *e.g.*, G. Gee, J. B. M. Herberts and R. C. Roberts, *Polymer* **6** (1965) 541
44. *e.g.*, A. M. Rijke and W. Prins, *J. Polymer Sci.* **59** (1962) 171;
A. M. Rijke, *J. Polymer Sci., A* **3** (1965) 3523;
K. Dušek, *Collection Czechoslov. Chem. Communs.* **32** (1967)1554
45. C. G. Moore and W. F. Watson, *J. Polymer Sci.* **19** (1956) 237
46. B. M. E. van de Hoff, *Ind. Eng. Chem. (product res. and dev.)* **2** (1963) 273
47. L. D. Loan, *J. Appl. Polymer Sci.* **7** (1963) 2259
48. J. Hasa and J. Janáček, *J. Polymer Sci., C* **16** (1967) 317
49. B. Meissner, I. Klier and I. Franta, *Intern. Rubber Conf.*, Brighton, 1967
50. C. A. J. Hoeve and M. K. O'Brien, *J. Polymer Sci., A* **1** (1963) 1917
51. G. R. Cotton and B. B. Boonstra, *J. Appl. Polymer Sci.* **9** (1965) 3395
52. W. Kuhn, S. Müller, H. J. Kuhn and A. Eisenberg, *Makromol. Chem.* **62** (1963) 40
53. H. J. Kuhn, *J. Polymer Sci., C* **16** (1967) 859

STELLINGEN

I

De versterkende werking van kristallisatie in natuurrubber vulcanisaten vindt zijn oorsprong voor een belangrijk deel in de grensvlakken tussen kristallijne en amorfe rubber.

II

De experimenten van LAL en SCOTT geven geen antwoord op de vraag of de treksterkte van gevulcaniseerde rubber afhangt van de stabiliteit van de knooppunten.

J. Lal en K. W. Scott, *J. Polymer Sci., C* **9** (1965) 113

III

Het ontbreken van rubbereigenschappen bij polymethyleen wordt door LE BRAS, PAUTRAT en PINAZZI ten onrechte aan de verzadigdheid van de ketens toegeschreven.

J. Le Bras, R. Pautrat en C. P. Pinazzi, '*Chemical Reactions of Polymers*', '*High Polymers XIX*', *ed.* E. M. Fettes, Interscience Publishers, New York, 1964, p 194

IV

Voor de relatie tussen de gasdoorlaatbaarheid en de glasovergangstemperatuur T_g van rubbers verdient het aanbeveling T_g te definiëren als de temperatuur waarbij de eerste merkbare afwijking van het rubber-elastisch gedrag optreedt, in plaats van die waarbij de rubber volledig of nagenoeg volledig in de glastoestand is gekomen.

G. J. van Amerongen, *Rubber Chem. Tech.* **37** (1964) 1065

V

De hogere vulcanisatiesnelheid van polymere ('onoplosbare') zwavel in vergelijking met die van S_8 moleculen is toe te schrijven aan de metastabiliteit van polymere zwavel bij de gebruikelijke vulcanisatietemperaturen.

VI

Het is niet waarschijnlijk dat de door een sulfeenamide versnelde vulcanisatie van rubbers met zwavel een radicaalreactie is.

A. Y. Coran, *Rubber Chem. Tech.* **37** (1964) 668, 689

VII

BRISTOWS resultaten pleiten niet voor het weglaten van de term $Bv^* \ln q$ in de vergelijking van de vrije energie van een gezwollen, gedeformeerd netwerk.

G. M. Bristow, *J. Appl. Polymer Sci.* **9** (1965) 1571

Dit proefschrift, hoofdstukken 2 en 6

VIII

De conclusie in het proefschrift van VAN DE KRAATS, dat in de door hem bestudeerde gelen alle in zijn model gebruikte netwerkparameters constant zijn, is onvoldoende gefundeerd.

E. J. van de Kraats, *Proefschrift Delft*, 1967, p. 40

IX

De door RIJKE en TAYLOR toegepaste verwaarlozing in de berekening van de polymeer/solvent interactieparameter is ongeoorloofd.

A. M. Rijke en G. L. Taylor, *J. Polymer Sci., A-1* **5** (1967) 1433

X

Het opvallende verschil tussen q_{cr} en q_0 (in benzeen) in de resultaten van RIJKE wekt twijfel omtrent de door hem gebruikte vooronderstellingen, met name wat betreft χ.

A. M. Rijke, *J. Polymer Sci., A* **3** (1965) 3523

XI

De door CRANK aangegeven betrekking tussen de diffusie-coëfficiënten D_V en D_A^B wordt door hem ten onrechte op een zwellend rubbervel toegepast.

J. Crank, '*The mathematics of diffusion*', Oxford, Clarendon Press, 1956, p. 240
Dit proefschrift, hoofdstuk 3

XII

Het verdient aanbeveling de configuratie —CH_2—CH_2— die thans meestal *gauche* genoemd wordt, met *pravo* te betitelen (pravus, *lat.* = krom, verdraaid, misvormd).

XIII

'Links voorrang' past niet logisch in een verkeersreglement dat uitgaat van rechtshoudend verkeer.

Brochures stichting 'Links voorrang'

Op verzoek van de Senaat volgen hier enkele persoonlijke gegevens:

David Engel Knibbe werd in 1928 te Leiden geboren. Na in 1945 het staatsexamen-α en in 1946 het eindexamen gymnasium-ß behaald te hebben, werd hij in de gelegenheid gesteld een jaar aan het Central College te Pella, Iowa (U.S.A.) te studeren. Vanaf 1947 studeerde hij scheikunde aan de Vrije Universiteit te Amsterdam, waar hij in 1956 slaagde voor het doctoraal examen, met als hoofdrichting fysische chemie.

Van 1956 tot 1958 vervulde hij zijn militaire dienstplicht, laatstelijk als luitenant der veldartillerie. Van 1958 tot 1965 was hij werkzaam in het Koninklijke/Shell Laboratorium Amsterdam; sindsdien is hij in het Koninklijke/Shell Plastics Laboratorium Delft, aan de rubberafdeling verbonden.