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MECHANICAL PROPERTIES AND STRUCTURE OF POLYMERS

by

A. J. STAVERMAN

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CENTRAAL LABORATORIUM TNO, P.O. BOX 217, DELFT, THE NETHERLANDS

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A. J. STAVERMAN

Central Laboratory T.N.O., Delft, The Netherlands

INTRODUCTION

Our present day understanding of the relation between mechanical properties and chemical structure of polymers may be said to have originated about 30 years ago from the fundamental papers of Mark and Guth[1] and of Kuhn[2] on the molecular origin of rubber elasticity. These papers contained the idea that elastic forces shown by rubbers on deformation are due to the fact that the molecules are very large and flexible, and that they can assume very many configurations for any given macroscopic shape of the sample in which they are contained.

Our understanding of this relation was further advanced about 12 years ago when several laboratories[3–5] began to investigate in a systematic way the time- or frequency-dependence of the elastic modulus and loss factor of a large number of polymers. This time dependent behaviour of polymers can be expressed in "mechanical spectra" which are characteristic for each polymer. The interpretation of these spectra proceeded in a heuristic way and was not based upon a theoretical conception about the molecular configuration of macromolecules.

A connection between the theory of rubber elasticity on one hand and the data on mechanical spectra on the other hand, was made by Rouse[6] in 1953, and also by Bueche[7] and Zimm[8]. These authors introduced "normal modes" to describe the numerous configurations possible for macromolecules. The total deformation of a macromolecule can be considered as the sum of normal deviations which proceed nearly independently, each with its own characteristic relaxation time.

The normal modes of deformation of macromolecules should not be confused with the normal modes of deformation crystals or of molecules as shown in optical spectra. The former are considered to arise from the balance of elastic and frictional forces with neglect of inertial forces; the latter arise from the balance between elastic and inertial forces with neglect of frictional forces. The former constitute the *relaxation* behaviour of the molecule and the latter the *vibration* behaviour. The characteristic times for these types of deformations are different and so are the normal modes to describe them. The neglect of inertial forces in the relaxation treatment becomes increasingly serious with increasing frequency, the neglect of frictional forces in the vibration treatment becomes less acceptable with increasing interaction of a molecule with its surroundings.

Notwithstanding these three important steps in the development of our understanding, our theoretical background with respect to the entire problem

is still very unsatisfactory. Some of the most unsatisfactory features of the present situation are listed here and will be treated in more detail in the following sections.

(*i*) Normal modes have been calculated (with one adaptable parameter) for simple linear molecules only. The effect of crosslinks, which every real rubber must possess, on the normal modes is profound but has been treated only by *ad hoc* and intuitive extensions of the theory for linear molecules.

(*ii*) A molecular interpretation of macroscopic behaviour should at least result in a quantitative relation between a macroscopic measurable quantity and a molecular quantity. However, various versions of the theory of rubber elasticity lead to different values of the elasticity modulus as expressed in the number of chains or of crosslinks. Experimentally, the latter number is found to be not constant or, in other words, the experiments cannot be described by a one parameter theory.

(*iii*) The characteristic relation times of different macromolecules cannot be calculated from molecular models in a straightforward way and the effect of the environment on these times and on the mechanical loss factor is not as expected.

DEGREES OF FREEDOM; NORMAL MODES

We will now consider a general network consisting of ν chains connected by n_k crosslinks of different functionality f. A small number, n_e, of the chain ends is fixed in space by the measuring apparatus, while n_1 chain ends are loose. Thus, if n_f is the number of crosslinks of functionality f we have the following relations:

$$n_k = \Sigma n_f \tag{1}$$

$$2\nu = \Sigma f n_f + n_e + n_1 \tag{2}$$

The number of chains effective in deformation is $\nu_e = \nu - n_1$. In equation (2) the second term of the left hand side is much smaller than the first. The total number of configurations of the network can be written formally[9]:

$$\Omega = \int \Pi_i \, \omega_i{}^{\nu_i{}^k} \mathrm{d}\tau_k \tag{3}$$

where index $\mathrm{d}\tau_k$ is the $3n_k$-dimensional space element indicating the positions of the crosslinks; $\nu_i{}^k$ is the number of chains with a given end-to-end distance r_i in the configuration k of the crosslinks and ω_i is the number of configurations of a chain with end-to-end distance r_i. We assume all chains to be chemically identical, so ω_i depends on r_i only.

$$\omega_i = C\, e^{-\beta^2 r_i{}^2} \tag{4}$$

where C is a proportionally constant and β^2 is connected to the mean square end-to-end distance $r_0{}^2$ by

$$\beta^2 = \frac{3}{2r_0{}^2} \tag{5}$$

In equation (3) the total number of configurations of the network is written as a product of the number of configurations of crosslinks and of

chains with fixed end points. Although this product is not very useful for a quantitative calculation because the movement of chains and the movement of crosslinks do not represent quasi-independent normal modes of movement, yet expression (3) is exact and has the correct number of dimensions. By assuming the crosslinks to be fixed in space, the number of degrees of freedom is drastically reduced but Ω remains large and does not vanish.

In the theories of Flory and Wall[10] and Hermans[11], ν_i before deformation, is supposed to be proportional to ω_i

$$\nu_i \, dx_i dy_i dz_i = \nu\beta^3\pi^{-3/2} \exp\left[- \beta^2 r_i^2\right] dx_i dy_i dz_i \tag{4}$$

being the number of chains with end-to-end vectors in the volume element $dx_i dy_i dz_i$. Now putting $\beta^2 = (3/2r_0^2)$ and $1/3\, r_0^2 = x_0^2 = y_0^2 = z_0^2$, one can consider the components of the mean square end-to-end vector x_0^2, y_0^2 and z_0^2 as moduli describing the distribution ν_i of the chains. The effect of deformation λ_x, λ_y, λ_z of a unit cube is, in these theories, supposed to consist of changing these moduli into $\lambda_x^2 x_0^2$, $\lambda_y^2 y_0^2$ and $\lambda_z^2 z_0^2$, respectively. However, if one changes the moduli, the volume element $dx_i dy_i dz_i$ of the chain ends must be changed by a factor $\lambda_x\lambda_y\lambda_z$, which gives rise to a factor $(\lambda_x\lambda_y\lambda_z)^\nu$ in Ω. Since, however, the ν chain ends cannot move independently but are connected into n_k crosslinks, clearly the correct number of degrees of freedom is employed by taking $(\lambda_x\lambda_y\lambda_z)^{n_k}$ instead of the above factor. Thus, the coefficient $n_k = (2\nu/f)$ of the term $\ln \lambda_x\lambda_y\lambda_z$ in the expression of Flory and Wall for the free energy of deformation is justified on general grounds. However, their basic assumption that the effect of deformation is to affect the modulus of the distribution (4) as stated above, appears to be unsatisfactory.

A suitable extension of the theory of Rouse to crosslinked systems should give the correct normal modes of the system and, therefore, the correct number of degrees of freedom involved not only in static deformation but also in time dependent deformation. Although it is not possible to extend Rouse's treatment to unspecified networks, some general conclusions can be drawn from applying it to a single crosslink, as is shown by Duiser[12].

In Rouse's theory the system is considered to consist of a large number N of Gaussian chains which interact in a way specified by the structure of the system and described by the interaction matrix A. If we write x_i for the x coordinate of the end-to-end vector of submolecule (chain) i, then in the simple case in which all N submolecules are connected into a free linear molecule, the rate of change of x_i can be written

$$\dot{x}_i = - B\left(- 1 \frac{\partial \mu}{\partial x_{i-1}} + 2 \frac{\partial \mu}{\partial x_i} - 1 \frac{\partial \mu}{\partial x_{i+1}} \right) \tag{5}$$

in which B is the mobility of every junction, and μ is the thermodynamic potential of the chain.

In vector notation (5) reads:

$$\dot{\mathbf{x}} = - B\mathbf{A} \, \nabla_x \mu \tag{6}$$

where **A** is the connectivity matrix.

$$\mathbf{A} = \begin{vmatrix} 3 & -1 & 0 & . & . & 0 & 0 & 0 \\ -1 & 2 & -1 & . & . & 0 & 0 & 0 \\ 0 & -1 & 2 & -1 & . & . & . & . \\ . & . & . & . & . & . & . & . \\ . & . & . & . & . & . & . & . \\ 0 & 0 & 0 & . & . & -1 & 2 & 1 \\ 0 & 0 & 0 & . & . & 0 & -1 & 3 \end{vmatrix} \tag{7}$$

A consists of N rows and columns. The fact that the ends of the molecule are free has been accounted for by assigning a mobility $2B$ to the end junction leading to

$$\dot{x}_1 = -B\left\{2\frac{\partial\mu}{\partial x_1} + \left(\frac{\partial\mu}{\partial x_1} - \frac{\partial\mu}{\partial x_2}\right)\right\} = -B\left(3\frac{\partial\mu}{\partial x_1} - \frac{\partial\mu}{\partial x_2}\right)$$

which is taken into account in the matrix **A** by putting the elements (1,1) and (N,N) equal to 3.

The case of a molecule with fixed endpoints is represented by assigning a mobility zero to these points which leads to the matrix

$$\mathbf{A} = \begin{vmatrix} 1 & -1 & 0 & . & . & . \\ -1 & 2 & -1 & . & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ . & . & . & -1 & 2 & -1 \\ . & . & . & 0 & -1 & 1 \end{vmatrix} \tag{8}$$

The normal modes of the molecule are found by solving the equation

$$|A| - \lambda|E| - 0 \tag{9}$$

where the N solutions of λ are characteristic of the relaxation times of the normal modes. With

$$\mu = -kT\beta^2\Sigma x^2 \tag{10}$$

the relaxation times turn out to be

$$\tau_p = \frac{1}{2\ BkT\beta^2\lambda_p} \tag{11}$$

Now the solutions of (9) are different for a molecule with free ends (equation 7) and one with fixed endpoints (equation 8). In the first case the smallest value of λ is $\lambda_1 = (\pi^2/N^2)$ and $\lambda_p = (p^2\pi^2/N^2)$. For the molecule with fixed endpoints $\lambda_p = (p^2\pi^2/N)$ with the first solution $p = 0$ and $\lambda = 0$.

Obviously, the mode with $\lambda = 0$, $\tau = \infty$ is the only mode that contributes to equilibrium elasticity, which occurs in the molecule with fixed endpoints and not in the molecule with free ends.

If the distance in the X-direction between the fixed points is x_E in the

undeformed state, then it is $\lambda_x x_E$ in the deformed state. The free energy of deformation is[13]

$$\Delta\mu_\lambda = kT \frac{x_E^2}{2x_0^2} (\lambda_x^2 - 1) \tag{12}$$

where x_0^2 is the mean square end-to-end distance in the X-direction of the total molecule if kept free.

In the theory of rubber elasticity of networks, some assumption must be made to account for the coherence of the network. One of these assumptions is that the crosslinks are fixed in space and subject to affine deformation. This assumption is clearly too restrictive. In reality only the surface of the sample is fixed in space and the crosslinks inside are free to perform Brownian motion.

In order to find the normal modes of the network contributing to its equilibrium elasticity, the connectivity matrix **A** of the entire network should be constructed and solved. This is generally impossible. However, one can guess some of the features of the general solution by solving the problem for a single crosslink[14].

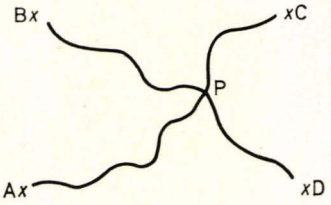

Figure 1

We consider first a system of 4 N submolecules consisting of 4 chains AP, BP, CP and DP connected by a 4-functional crosslink P (*Figure 1*). The chain ends A, B, C and D, are fixed in space, the submolecules are numerated as follows: from A to P: 1 to N; from P to B: $N + 1$ to $2N$; from C to P: $2N + 1$ to $3N$; and from P to D: $3N + 1$ to $4N$. The mobility of P is assumed lower than that of the other junctions, $B_p = (1 - \delta)B$.

The simplest case occurs with $\delta = \frac{1}{2}$. In that case **A** has the values given in (*Figure 2*).

$$\mathbf{A} = \begin{pmatrix}
1 & -1 & . & . & . & . & . & . & . & . & . & . & . & . & . & . \\
-1 & 2 & -1 & . & . & . & . & . & . & . & . & . & . & . & . & . \\
. & . & . & . & . & . & . & . & . & . & . & . & . & . & . & . \\
. & . & . & \frac{3}{2} & -\frac{1}{2} & . & . & . & . & . & . & \frac{1}{2} & -\frac{1}{2} & . & . & . \\
. & . & . & -\frac{1}{2} & \frac{3}{2} & . & . & . & . & . & . & -\frac{1}{2} & \frac{1}{2} & . & . & . \\
. & . & . & . & . & . & . & . & . & . & . & . & . & . & . & . \\
. & . & . & . & . & -1 & 2 & -1 & 0 & 0 & 0 & . & . & . & . & . \\
. & . & . & . & . & 0 & -1 & 1 & 0 & 0 & 0 & . & . & . & . & . \\
. & . & . & . & . & 0 & 0 & 0 & 1 & -1 & 0 & . & . & . & . & . \\
. & . & . & . & . & 0 & 0 & 0 & -1 & 2 & -1 & . & . & . & . & . \\
. & . & . & . & . & . & . & . & . & . & . & . & . & . & . & . \\
. & . & . & \frac{1}{2} & -\frac{1}{2} & . & . & . & . & . & . & \frac{3}{2} & -\frac{1}{2} & . & . & . \\
. & . & . & -\frac{1}{2} & \frac{1}{2} & . & . & . & . & . & . & -\frac{1}{2} & \frac{3}{2} & . & . & . \\
. & . & . & . & . & . & . & . & . & . & . & . & . & . & . & . \\
. & . & . & . & . & . & . & . & . & . & . & . & . & -1 & 2 & -1 \\
. & . & . & . & . & . & . & . & . & . & . & . & . & 0 & -1 & 1
\end{pmatrix}$$

(*Figure 2*)

The corresponding determinant can be solved by first adding the reversed upper half to the lower half and then subtracting the reversed left half from the right half. Thus, the determinant is split into 3 subdeterminants of type (8), one 2 N-dimensional and two N-dimensional. Thus, the system has 3 normal modes with $\lambda = 0$ ($\tau = \infty$) and not 4 as follows from the assumption of fixed crosslinks.

In less simple cases, the determinants are generally untractable. In the case of *Figure 2* with $\delta \neq \frac{1}{2}$ solution is again straightforward, the 2 N-dimensional subdeterminant is disturbed but the 3 normal modes with $\lambda = 0$ remain. Also, the case of three chains with one 3-functional crosslink and 3 fixed ends can be solved. One finds 2 normal modes with $\lambda = 0$, in contrast with 3 resulting from the assumption of fixed crosslinks.

The obvious generalization to be made from the observations is that the number of normal modes contributing to the free energy of deformation in equilibrium is not ν_e but $\nu_e - n_k$. Consequently, the elasticity modulus divided by kT becomes

$$\frac{G}{kT} = \left\langle \frac{x_E^2}{x_o^2} \right\rangle (\nu_e - n_k) \tag{13}$$

instead of ν_e or $\nu_e \langle (x_E^2/x_o^2) \rangle$ as has been supposed thus far. In passing we note that the factor

$$\left\langle \frac{x_E^2}{x_o^2} \right\rangle$$

is more correct than $\bar{x}_E^2/\bar{x}_o^2$ which was used formerly[15].

Our result is at present of rather academic interest. It means that in a correct theory of rubber elasticity the number of degrees of freedom involved should be taken as $\nu_e - n_k$ instead of ν_e. A quantitative experimental check of the theory is impossible since $\langle x_E^2/x_o^2 \rangle$ cannot be measured independently. The importance of this factor and the arguments against the assumption that it should equal unity have been well revised recently by Guth[16].

EXPERIMENTAL ON NETWORK ELASTICITY

An excellent survey concerned with experiments on network structure and properties has been compiled by Funke[17]. One of his conclusions is that the number of crosslinks as found from chemical analysis differs from that number as calculated from the elasticity modulus in an inpredictable manner.

However, the absence of quantitative agreement between these two quantities is not the only and certainly not the worst of the unsatisfactory features of the experimental situation.

Swelling measurements on carefully crosslinked cellulose acetate networks[18, 19] have shown that none of the existing network theories describes the results. Clearly the theory of swelling is complicated by the fact that change of the swelling ratio involves changes in the environment of the chains. This means that generally the environment of the chains is not a "θ-environment" in which the excluded volume of the chain segments for each other vanishes.

However, it is not clear how the concepts of the excluded volume theory[20] for solutions could be incorporated in the network theory whereas the excluded volume will presumably affect the chain statistics profoundly. The excluded volume theory introduces as an important variable the quantity z (or ψ or x) which represents a number of segments times a segment density. Whereas the segment density in networks (swollen or not) can be assigned a clear meaning, the number of segments effective in enlarging the end-to-end distance is not easily defined. One can, completely arbitrarily, take the number of segments in a chain "between crosslinks" since it is the end-to-end distance of these chains that counts in elasticity theory. Doing this, however, one does not account for an essential feature of the excluded volume theory, namely that the end-to-end distance of a part of a chain depends not only on the number of segments of that part but on the number of all the segments to which it is connected. In networks, this latter number is however, infinite, which precludes a straightforward application of excluded volume theory to networks.

A less ambitious effort to account for excluded volume effects consists in trying to describe these effects by an adaptable parameter with or without a clear physical meaning. Such a procedure has been proposed by Mukherji and Prins[22] who account for the fact that volume exclusion of segments will favour long elongations and disfavour short elongations by introducing a factor $(x_i y_i z_i)^n$ into ω_i, the number of configurations of the chain. Assuming further fixed crosslinks they find values for n which vary from 1 to 1/7 and depend on the network and on the swelling agent.

A sensitive test of network theories is given by measurements of the temperature dependence of the elastic force. In these measurements the network is always the same and the environment will not change strongly. In the classical case with $(\partial U/\partial L)_{T,V} = 0$, one expects that the interaction energy of a chain with its surroundings does not change with elongation or with temperature (if extrapolated to zero volume change), so if there is any change at all it should originate from steric factors.

In the general case with $(\partial U/\partial L)_{T,V} \neq 0$, the intramolecular forces in the chain depend on temperature and elongation so one expects that also the intermolecular forces will change. Generally, this is accounted for by supposing that r_0^2 in (13) depends on the temperature.

However, Opschoor and Prins[23] demonstrate in their contribution to this symposium, that this assumption is insufficient to describe the experimental facts. They find that dr_0^2/dT thus calculated depends both on the elongation and on the degree of crosslinking for polyethylene and a polyethylene-propylene copolymer.

The present status of the theory scarcely permits to explain these findings. Formally, one can assume that both crosslinking and elongation affects the environment of the chain in such a way that

$$dr_0^2/dT$$

changes. That this effect is so strong, even in the case of a polar hydrocarbon polymer, is certainly surprising.

Summarizing, we can only say that, since the days of Mark, Guth and

Kuhn, very little progress has been made with regard to a quantitative theory to describe experiments about rubber elasticity of polymers.

TIME DEPENDENT ELASTICITY

With respect to time dependent elasticity, progress has been made in two ways. The theory of Rouse for uncrosslinked polymers in dilute solution is well supported by experimental data[24]. This is surprising in view of the fact that in this theory internal friction is ignored and that it is expected to be sensitive to the molecular weight distribution.

Some insight into time dependent elasticity of polymers has also resulted from the large amount of data modulus and damping as functions of time *v.* frequency for very many polymers in the glassy, rubbery and transition state. These data have been summarized on various occasions[25]. Here we will only show some of the problems that have yet to be solved.

In the short-time region movements of small parts of molecules show up. Their characteristic times of relaxation do not depend on molecular weight and not, or only slightly, on the environment. The relaxation time and amount of energy dissipated per molecule depends only on the internal structure of the molecule. Good examples of such intramolecular movements are the movements of rings of various sizes such as those studied by Heijboer[26] and reported on in this symposium. In these systems, the particular movement under consideration can be treated as a normal mode of the molecule, unaffected by other movements. They retain their identity even in systems without macromolecules.

In longer-time regions one finds movements of larger parts of polymer molecules which are more likely to interact with the molecule as a whole and with the environment. The effect of the environment is not always easily understandable even qualitatively. For instance, addition of a plasticizer is, in the first place, supposed to alter the viscosity of the medium. For a given intramolecular movement, one expects that this will result in a reduced relaxation time without much effect on the total energy dissipated in the movement.

However, Heijboer's experiments indicate that addition of plasticizer to poly(methyl methacrylate) has an unexpected effect. The relaxation time of the β-peak is not affected at all and the dissipated energy is *increased* (*Figure 3*). In order to understand such a phenomenon, we have to consider three quantities determining the position and shape of a loss peak in the relaxation spectrum: the number of molecular groups involved, the free energy change involved in the movement of each group and the friction coefficient, B, determining the relaxation time. If, on addition of plasticizer, the relaxation time does not change, one must assume that, contrary to expectation, B is not affected by this change of environment. The fact that the loss maximum increases means either that the number of molecular groups partaking in the deformation increases or that the amount of free energy released per group on deformation increases. In equation (13), this latter quantity is represented by

$$kT\left\langle \frac{x_E^2}{x_o^2} \right\rangle$$

and the former quantity by ν.

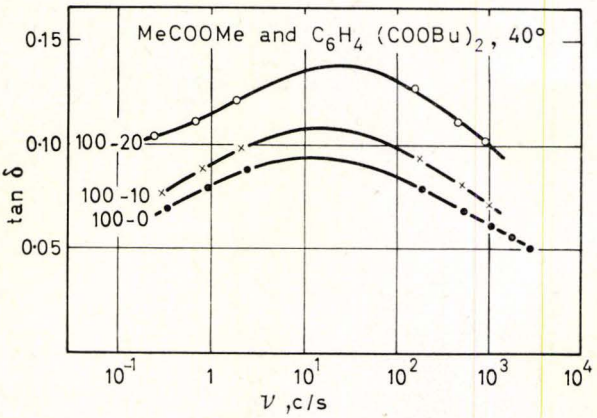

Figure 3

In this connection, two points should be stressed. The first is that the β-peak corresponds to a change of configuration of a part of the chain and not, as in the case of the cyclic systems, with the motion of a side chain. The second point is that the plasticizer does affect the transition temperature or, in other words, the relaxation time of the entire chain, very much. Thus, the mechanism producing the β-peak and the mechanism producing the glass-transition must be expected to interact strongly. Again, a really satisfactory description of these movements would be in terms of quasi-independent normal modes which need not preserve their identity if the environment is changed appreciably. Yet it remains surprising that the characteristic relaxation times of certain molecular motions are often not very sensitive to change in the environment.

The last effect to be treated in this survey is the effect of a network with non-permanent crosslinks on the elasticity of a polymer. The temporary crosslinks may be due to chemical reactions or to entanglements. Such networks have been treated with a variety of more-or-less intuitive extensions of the classical theory of rubber elasticity[27, 28] or of Rouse's theory[29]. In view of the intricacies and uncertainties of the motion of the crosslinks in deformation, it would seem desirable to review these theories by trying to describe them in terms of normal modes of deformation of such networks on the lines indicated in the beginning of this lecture[30].

Summarizing, we can say that our knowledge of the subject treated in this conference is largely heuristic and intuitive. Much information has been collected systematically in this way. The time has come for a really fundamental theory of mechanical properties as a function of chemical structure.

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