quence of the pure-component reduction parameters which are chosen for the SCF additive. These reduction parameters are probably very temperature sensitive. Further modeling work which accounts for the temperature sensitivity of these parameters is being performed for the mixtures investigated in this study.

Conclusion

We have presented new experimental data on the high-pressure phase behavior of various polymer solution–SCF mixtures. The results from this study indicate that adding an SCF additive to a polymer–organic solvent mixture causes the LCST curve to shift to much lower temperatures. In some cases the LCST and UCST curves merge. Hence, polymer can be recovered from solution at very moderate temperatures by introducing an SCF additive to the mixture.

The *T*(LCEP) can be correlated to the critical temperature of the solvent or SCF solvent mixture. The phase behavior data can also be qualitatively explained by using the corresponding states model of Patterson. Although Patterson's model offers physically satisfying explanations for the phase behavior observed in this study, physically unrealistic values for one of the model parameters are needed to correlate the data. The further attempts are being made to make the model suitable for engineering calculations.

Acknowledgment. We are indebted to Jaime Ayarza, Mark Kalbfleisch, and Andrew Seckner, who performed a great many of the experiments reported in this study. Acknowledgment is made for the financial and technical support of the Exxon Chemical Co.

Registry No. methane, 74-82-8; ethylene, 74-85-1; propylene, 115-07-1; carbon dioxide, 124-38-9; (ethylene)·(propylene) (copolymer), 9010-79-1.

Supplementary Material Available: Ten tables of experimental pressure–temperature data (10 pages). Ordering information is given on any current masthead page.

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Behavior of Elastomer Networks in Moderately Large Deformations. 1. Elastic Equilibrium[†]

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ABSTRACT: An elastic potential of the form $W = (G_X/2)(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) + (2G_N/m^2)(\lambda_1^m + \lambda_2^m + \lambda_3^m - 3)$ is proposed, where G_X is the modulus associated with the chemical cross-links of the network, G_N is the modulus contribution arising from the presence of topological constraints, and m can be taken as 0.34. The moduli are linked by the relation $G_X + G_N = G$, where G is the shear modulus. The constitutiveness of this potential is demonstrated on published data in general biaxial deformation of natural rubber. Some of our own data on natural and styrene–butadiene rubber cross-linked to different degrees are also discussed. The nature of G_N has been studied on published data on several different swollen networks.

Introduction

The basic laws of motion, conservation of mass, balance of momenta, conservation of energy, and principle of entropy, valid for all types of continuua, do not form a complete set of equations to describe the response of a material to a mechanical excitation. It is necessary to complement the set with constitutive equations that characterize the material response.

Though largely arbitrary in form, constitutive equations are subject to the restrictions of the constitutive theory.[1] To formulate a constitutive equation valid for all types of materials is a useless task because, due to the generality of such an equation, it would have to contain too many experimentally determined parameters. It is more expedient to group materials into various classes and find a constitutive equation for each class.

Because of their novel characteristics and easy processibility, polymeric materials are being used in increasing

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[†] This paper is dedicated to Pierre Thirion on the occasion of his retirement.

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amounts instead of conventional materials. For design purposes it is necessary to be able to predict the deformation properties of these materials under given conditions. The theories of linear elasticity and linear viscoelasticity are exact theories that describe the equilibrium and time-dependent properties of polymeric materials when they undergo infinitesimal deformations. In applications, however, the deformations are not infinitesimal, and it is therefore necessary to be able to predict their behavior in *finite deformations*.

Most cross-linked polymers in the rubbery state are capable of large deformations vastly exceeding those of other elastic materials. Elongations of 300–400% are not uncommon with rubber networks. Due to this characteristic, they have been termed *hyperelastic* materials.

To describe the equilibrium stress–strain behavior of hyperelastic materials, two paths are available for the formulation of an elastic potential valid for large deformations. Either the small-scale response of the polymer chains to a given macroscopic excitation is assumed to be known, and one then describes the material response using the methods of statistical mechanics, or one proposes a potential consistent with the axioms of constitutive theory and the available experimental data and then tries to interpret the molecular nature of the phenomenological coefficients. This is needed to understand the region of validity of the equation and to enable one, eventually, to design a material for a given application.

A potential is commonly called constitutive when it does not violate any of the principles of continuum mechanics. Many potentials which are constitutive in this sense are restricted to certain types of deformations. We call a potential constitutive in the narrower sense when it appears to describe the mechanical properties of the network with the same material parameters in any deformation. This will be discussed separately further below.

Molecular Theories of Rubber Elasticity

The isothermal stress–strain behavior in finite deformation of an elastomer in mechanical equilibrium can be formulated by modeling the elastomer as a network of freely jointed chains. The distribution of the displacement length (end-to-end distance) of a chain is normally considered to be Gaussian in the undeformed state. The chains are allowed to pass through each other without hindrance, constituting what is now commonly known as a phantom network. The stress resulting from a given elongation then is the result of a decrease in the free energy of the hypothetical network. Imperfections in the network structure, such as terminal (dangling) chain ends, loops, and entanglements, are not considered to alter the form of the elastic potential. The equilibrium stress resulting from an elongation is then given by

$$\bar{\sigma} = RTF(\lambda^2 - 1/\lambda) \qquad (1)$$

where $\bar{\sigma}$ is the Cauchy stress based on the deformed cross-sectional area, F is a structure factor, λ is the stretch ratio in the direction of the pull, R is the gas constant, and T is the absolute temperature. The derivation and the thermodynamic implications of eq 1 have been discussed in detail by Flory.[2]

The form of the structure factor results from specific assumptions made about the microscopic movement of the junction points of the network. In the theory of James and Guth[3] the displacements of the mean position of the junction points become affine in the macroscopic strain and the fluctuations about the junction points are independent of the strain. The structure factor can then be expressed as

$$F = \nu_X(1 - 2/\psi) \qquad (2)$$

where ν_X is the number of chains between cross-link points per unit volume, and ψ is the functionality of the junction points. It is also possible to consider the junction points to be firmly imbedded in the polymer matrix (see, e.g., Flory[2]). In this case they do not fluctuate and their displacements, not the mean positions of the junctions, are affine in the macroscopic strain. The structure factor is then simply given by $F = \nu_X$ and the stress resulting from a given strain in an elastomer becomes

$$\bar{\sigma} = \nu_X RT(\lambda^2 - 1/\lambda) \qquad (3)$$

This prediction appears to overestimate the stress, at least in the case of natural and styrene–butadiene rubber (see the discussion following eq 13) even in only moderately large deformations. In simple tension we consider a deformation to be moderately large if the principal stretch ratio remains below the inflection point in a plot of the nominal stress vs. the ratio. We will give a more general description further below.

More recently, Flory[4] and Flory and Erman[5] proposed a new statistical mechanical theory which is based on the idea that the fluctuations of the junction points are affected by various topological constraints but are independent of the strain. According to this theory, only the mean positions of the junction points are affine in the macroscopic strain. The stress resulting from a given strain is expressed as the sum of two additive terms. The first models the displacement of the mean positions of the junction points and has the form given by eq 3. The second term accounts for the severity of the constraints which affect the fluctuations of the junction points. The form of the complete equation is too lengthy to be reproduced here, but is is important to point out that the second term is evaluated by using statistical mechanical methods and contains one adjustable parameter which characterizes the severity of the topological constraints. We shall refer to this theory as the Flory–Erman theory.

Phenomenological Equations in Terms of the Invariants of the Deformation Tensor

One can formulate a constitutive equation phenomenologically for large equilibrium deformations of hyperelastic materials by postulating the existence of a strain energy density function (reversible work of deformation), W, from which the stress is derivable. The most general constitutive equation for equilibrium deformations of an initially isotropic, homogeneous, incompressible material has been derived by Rivlin[6] and also by Ariano.[7] It contains no assumptions other than the ones stated above. The Rivlin–Ariano equation has the form

$$\bar{\sigma}_{kl} = -P\delta_{kl} + 2\frac{\partial W}{\partial I_1}B_{kl} - 2\frac{\partial W}{\partial I_2}(B^{-1})_{kl} \qquad (4)$$

in indicial notation, where $\bar{\sigma}_{kl}$ is the Cauchy stress tensor, B_{kl} is the Finger deformation tensor, $(B^{-1})_{kl}$ is its inverse, and P is an arbitrary hydrostatic pressure required by the assumption of incompressibility. I_1 is the first and I_2 is the second invariant of the deformation tensor. Thus, if W is known, one can describe the equilibrium deformations of rubberlike materials using the Rivlin–Ariano equation. W is most commonly expressed in terms of the invariants of the deformation tensor for a material that is homogeneous, initially isotropic, and incompressible. The assumption of incompressibility requires that the third invariant be unity. If W is now expanded around the undeformed state of the material in a Taylor series, one obtains

$$W = \sum_{i,j=0}^{\infty} C_{ij}(I_1 - 3)^i(I_2 - 3)^j \quad (5)$$

where C_{ij} are the phenomenological coefficients. The two invariants of the deformation tensor are given by

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \quad (6)$$

$$I_2 = 1/\lambda_1^2 + 1/\lambda_2^2 + 1/\lambda_3^2 \quad (7)$$

in terms of the stretch ratios. The fact that W must be zero for an undeformed material imposes the restriction that $C_{00} = 0$. Once a form for W is known, the stress resulting from a given deformation characterized by the three principal stretch ratios λ_1, λ_2, and λ_3 (i.e., the positive square roots of the eigenvalues of the deformation tensor) can be obtained as

$$\bar{\sigma}_i = \lambda_i(\partial W/\partial \lambda_i) - P \qquad i = 1, 2, 3 \quad (8)$$

where $\bar{\sigma}_i$ is the Cauchy stress in the ith principal direction. The assumption of incompressibility further relates the three stretch ratios by the equation

$$\lambda_1\lambda_2\lambda_3 = 1 \quad (9)$$

Thus, only two of the three stretch ratios can be specified independently. Note that eq 8 is identical with eq 4.

If one keeps only the first term of eq 5, then eq 6–9 would yield

$$\bar{\sigma}_1 - \bar{\sigma}_2 = 2C_{10}(\lambda_1^2 - 1/\lambda_1) \quad (10)$$

for simple tension, where λ_1 is the stretch ratio in the direction of the pull, $\bar{\sigma}_1$ is the corresponding Cauchy stress, and $\bar{\sigma}_2$ is zero since the boundary normal to the direction of the pull is a free boundary. It is apparent that $2C_{10} = G$, the shear modulus, because of the requirement that the results of linear elasticity should be reproduced as $\lambda_1 \to 1$. It can be seen that eq 10 is identical with eq 1 letting $2C_{10} = RTF$.

Mooney[8] proposed an extension of eq 10 by postulating that a plot of $\bar{\sigma}/(\lambda^2 - \lambda^{-1})$ vs. $1/\lambda$ is linear in simple tension, and Hooke's law is obeyed in simple shear. Mooney's equation, which is commonly referred to as the Mooney–Rivlin equation, has the form

$$\bar{\sigma}_1 - \bar{\sigma}_2 = 2C_1(\lambda_1^2 - 1/\lambda_1) + 2C_2(\lambda_1 - 1/\lambda_1^2) \quad (11)$$

for simple tension, where C_1 and C_2 are the phenomenological coefficients. It is required that $2C_1 + 2C_2 = G$. Equation 11 can be derived with $C_1 = C_{10}$ and $C_2 = C_{01}$, by retaining the first two terms of eq 5. It shows good agreement with experimental data in simple tension, but it does not do so constitutively. In other words, if one estimates the values of C_1 and C_2 from simple tension data, and predicts the results for a different mode of deformation, the predictions do not fit the data.

Phenomenological Equations in Terms of the Stretch Ratios

Later workers in the field abandoned the idea that W is most easily formulated in terms of the invariants of the Finger deformation tensor and expressed it in terms of the stretch ratios.

Carmichael and Holdaway,[9] Mooney,[10] and Valanis and Landel[11] concluded, on the basis of certain symmetry arguments, that W should be the same function of the three stretch ratios. Thus, W should have the form

$$W = w(\lambda_1) + w(\lambda_2) + w(\lambda_3) \quad (12)$$

for a homogeneous, initially isotropic, incompressible rubber. Valanis and Landel[11] and Kawabata et al.[12] have confirmed eq 12 experimentally.

Most of the well-known nonlinear strain measures can be subsumed in a strain energy density function of the form

$$W = (2G/n^2)(\lambda_1^n + \lambda_2^n + \lambda_3^n - 3) \quad (13)$$

where n is allowed to take on any integer value between −2 and 2. With $n = 2$, eq 13 reduces to the so-called neo-Hookean potential from which eq 10 follows at once. Equation 13 with integer values was first proposed by Seth.[13] It was later generalized by allowing n to be a material parameter,[14] which can take nonintegral values. Ogden[15] used three terms of this same form to describe the behavior of rubbers in large tensile deformations, up to break. When one allows n to be a material parameter, none of the axioms of the constitutive theory are violated.[16] Hence, from the point of view of continuum mechanics, eq 13 is a valid constitutive equation. Equation 13 has been shown by Blatz, Sharda, and Tschoegl[14] to be constitutive in the narrower sense for a styrene–butadiene rubber (SBR), and for natural rubber (NR), below the upswing region. Henceforth, we shall call eq 13 the BST potential for convenience.

2NW Potential

Although the BST potential is a valid constitutive equation, the parameter n appears to be difficult to interpret molecularly. Tschoegl[17] proposed a related elastic potential which is based on the assumptions that (1) a cross-linked polymer can be modeled as consisting of two networks—the phantom and the constraint networks, (2) the contribution of the two networks to W is additive, and (3) the stress–strain behavior of the phantom and the constraint networks can be described by the neo-Hookean and BST potentials, respectively.

The first network characterizes the effect of the change in the mean positions of the chemically cross-linked junction points. This network is called the phantom network. The chains in the phantom network can freely pass through each other and have no physical characteristics such as volume. Junction points can fluctuate freely about their mean positions. The modulus associated with the phantom network is denoted as G_X. Its stress–strain behavior is neo-Hookean.

The second network will be called the constraint network. It models the effects of the physical nature of the polymer chains, which causes the fluctuations of the junction points to be different from their phantom counterparts. The constraint network can be modeled as if it were held together by equivalent cross-links and may be considered to have a modulus G_N associated with it.

On the basis of these assumptions the most general form for the strain energy density function W can be written as

$$W = \frac{G_X}{2}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) + \frac{2G_N}{m^2}(\lambda_1^m + \lambda_2^m + \lambda_3^m - 3) \quad (14)$$

where the λ's are the three principal stretch ratios, and m is the nonlinear strain parameter of the BST potential. We use $m = 0.34$ because it closely approximates the strain function we obtain from a molecular theory which we will discuss elsewhere.[18] This reduces the unknown parameters to two, and they occur linearly in the model. This is convenient when treating experimental data. We will name the potential represented by eq 14 the 2NW (or two-network) potential. To investigate the validity of the

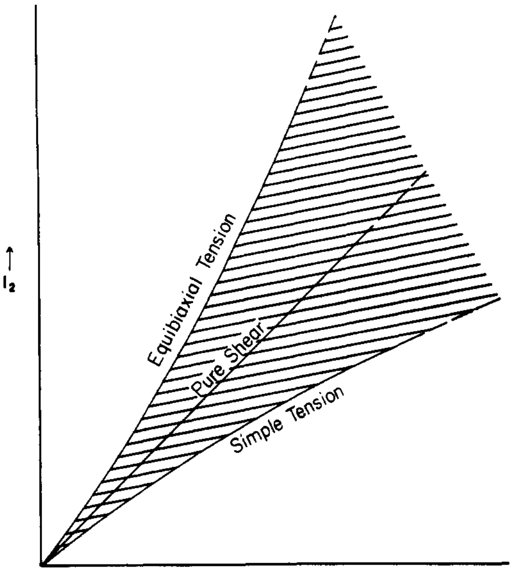

Figure 1. Region of admissible deformations for an incompressible material.

above assumptions, we will show that eq 14 predicts the stress–strain behavior of rubber networks constitutively, in the narrower sense, and is able to predict swelling behavior correctly. The problem of constitutiveness will be addressed first.

Constitutiveness in the Narrower Sense

In continuum mechanics, any equation that does not violate the axioms of constitutive theory[1] is a valid constitutive equation. In a stricter sense, a constitutive equation must represent material response to any mode of deformation with the same set of phenomenological coefficients. The Flory–Erman theory as well as the BST and 2NW potentials discussed earlier appear to meet this requirement. The 2NW potential is attractive, because it has only two linear material parameters.

It can be shown[16] that, for an initially isotropic, homogeneous, and incompressible material, all possible deformations lie in the wedge-shaped region of the I_1,I_2 plane shown in Figure 1. Uniaxial tension and equibiaxial tension form the boundaries of this region, pure shear being the straight line with unit slope. Deformations outside of this wedge-shaped region are not admissible. The whole region inside the wedge can be covered experimentally by biaxial tension experiments in which two dimensions of a rectangular piece of material are changed independently, leaving the third dimension stress-free. Therefore, it is possible to cover all deformations that an incompressible material can undergo by performing biaxial tension measurements covering the whole range from simple tension to equibiaxial tension. If a proposed equation can describe such experiments with a single set of material parameters, the equation will very likely be constitutive. We emphasize that it is not possible to prove constitutiveness in the narrower sense; it is only possible to disprove it. One can, however, gather sufficient evidence from biaxial tension measurements to support the constitutiveness of an equation in the narrower sense.

When eq 14 is used in the Rivlin–Ariano equation, one obtains the true normal stress difference as

$$\bar{\sigma}_\alpha - \bar{\sigma}_\beta = G_X(\lambda_\alpha^2 - \lambda_\beta^2) + \frac{2G_N}{m}(\lambda_\alpha^m - \lambda_\beta^m) \quad (15)$$

Kawabata et al. have performed[19] general biaxial tension measurements on natural rubber cross-linked with dicumyl peroxide. Their data are plotted in Figure 2. The axes were chosen so that the theoretical predictions, as indicated by eq 15, would lie on the straight line with unit slope. The two moduli, G_X and G_N, were obtained from simple tension data. As can be seen from the figure, agreement between experiment and theory is excellent. Some of the general biaxial tension data were left out of the figure for clarity, but the agreement for those is just as good.

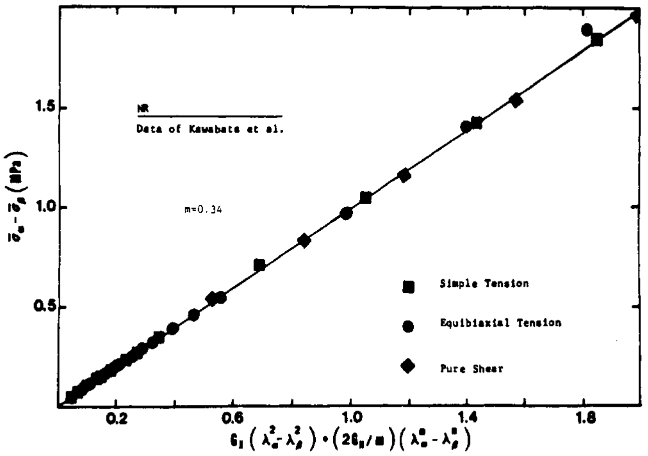

Figure 2. Data on NR compared with the predictions of the 2NW potential.

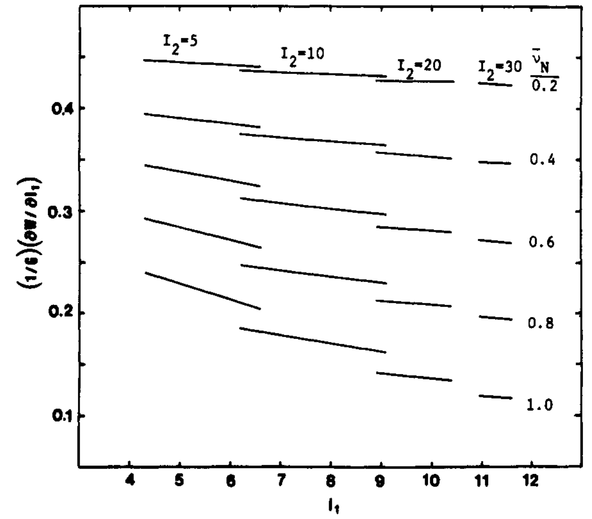

Figure 3. Predicted behavior of the derivative of the strain energy density function, *W*.

Using eq 14 and 4, one obtains

$$2\frac{\partial W}{\partial I_1} = \frac{1}{\lambda_\alpha^2 - \lambda_\gamma^2}\left[\frac{\lambda_\alpha^2(\bar{\sigma}_\alpha - \bar{\sigma}_\beta)}{\lambda_\alpha^2 - \lambda_\beta^2} - \frac{\lambda_\gamma^2(\bar{\sigma}_\gamma - \bar{\sigma}_\beta)}{\lambda_\gamma^2 - \lambda_\beta^2}\right] \qquad \alpha, \beta, \gamma = 1, 2, 3 \quad (16)$$

$$2\frac{\partial W}{\partial I_2} = \frac{1}{\lambda_\gamma^2 - \lambda_\alpha^2}\left[\frac{\bar{\sigma}_\alpha - \bar{\sigma}_\beta}{\lambda_\alpha^2 - \lambda_\beta^2} - \frac{\bar{\sigma}_\gamma - \bar{\sigma}_\beta}{\lambda_\gamma^2 - \lambda_\beta^2}\right] \qquad \alpha, \beta, \gamma = 1, 2, 3 \quad (17)$$

where the stress differences are given by eq 15. Figures 3–6 show the contour plots of $\partial W/\partial I_1$, and $\partial W/\partial I_2$ vs. I_1 and I_2. The general shapes of the curves at large I_1 and I_2 are in agreement with those shown by Kawabata[20] et al. They observe rather complex behavior for these contours at infinitesimal deformations which are not reproduced by our theory. We would like to point out that $\partial W/\partial I_1$ and $\partial W/\partial I_2$ have meaning only in large deformation theory.

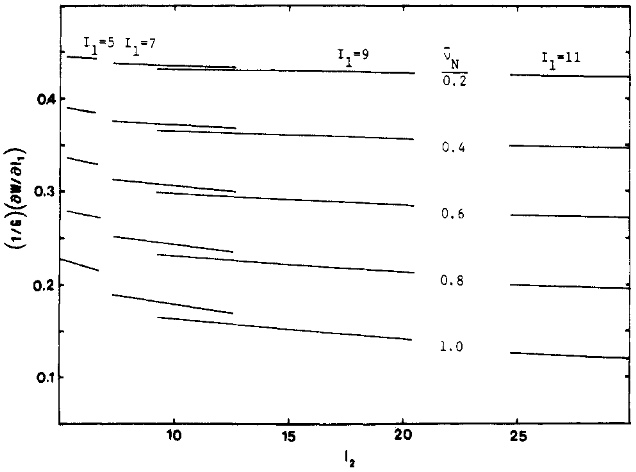

Figure 4. Predicted behavior of the derivative of the strain energy density function, *W*.

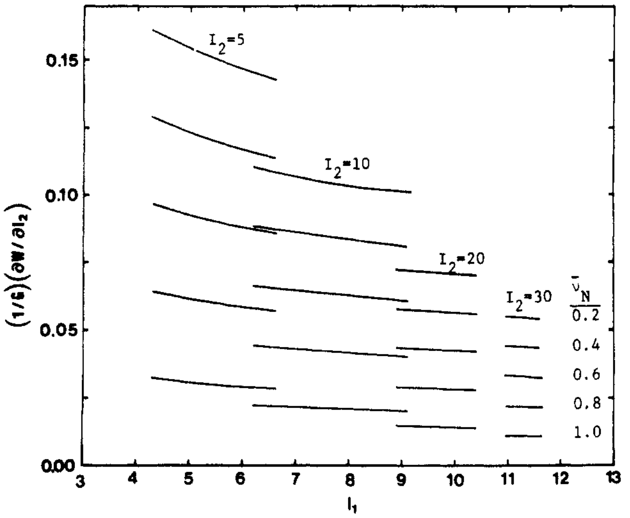

Figure 5. Predicted behavior of the derivative of the strain energy density function, *W*.

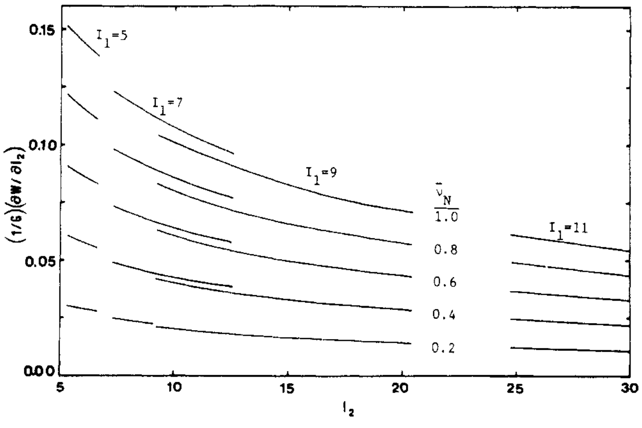

Figure 6. Predicted behavior of the derivative of the strain energy density function, *W*.

Values corresponding to infinitesimal deformations must be obtained from extrapolation of large deformation data and are critically dependent on experimental accuracy in small extensions. Unfortunately, data in that region are subject to the largest experimental error. Therefore, the discrepancy between the contours given by our theory and Kawabata's experimental contours is not critical.

Figure 3 shows plots of $\partial W/\partial I_1$ vs. I_1 for various constant values of I_2 for representative values of $\bar{\nu}_N$. Here $\bar{\nu}_N$ is the ratio G_N/G. The various values of this parameter represent different materials, $\bar{\nu}_N = 0$ corresponding to a material whose stress–strain behavior is neo-Hookean, and $\bar{\nu}_N = 1$ corresponding to an un-cross-linked rubber. In most phenomenological theories, it is assumed that $\partial W/\partial I_1$ is constant with I_1 independent of I_2. As can be seen from the figure, $\partial W/\partial I_1$ as given by the 2NW potential varies linearly with I_1 but it is not independent of I_2. The variation with I_2 is small but it is nonzero for $\bar{\nu}_N = 0$. The dependence of $\partial W/\partial I_1$ on I_2 is shown in Figure 4.

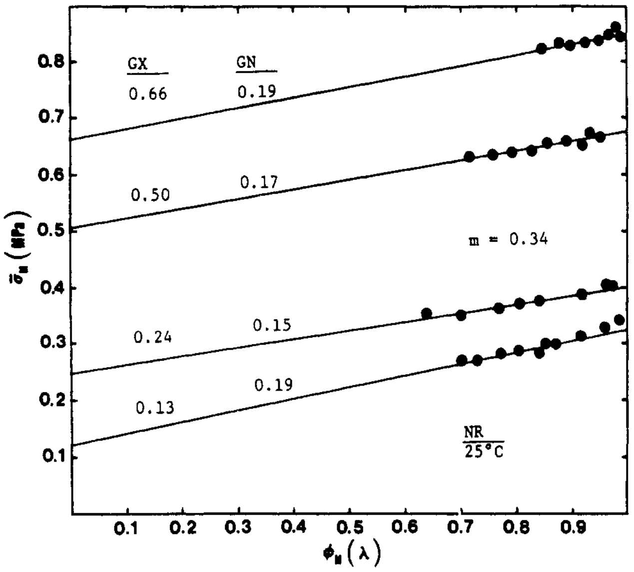

Figure 7. Equilibrium data on NR networks with varying cross-link densities compared with the predictions of the 2NW potential.

Figure 5 shows the variation of $\partial W/\partial I_2$ with I_1 for various constant values of I_2. It is usually assumed that this quantity is independent of I_1 and is constant with I_2. It is apparent from the figure that the predicted behavior of $\partial W/\partial I_2$ is very complex with respect to the invariants. Clearly, if the 2NW potential describes observed behavior, the Mooney–Rivlin equation cannot be a valid constitutive equation. Figure 6 shows the variation of $\partial W/\partial I_2$ with I_2 for various constant values of I_1.

Cross-Link Density

Figure 2 strongly supports the constitutiveness, in the narrower sense, of the 2NW potential. We now proceed to probe the nature of the phenomenological parameters. For that purpose natural rubber networks were prepared by cross-linking them to various degrees with dicumyl peroxide. The cross-linking conditions were chosen on the basis of the work of Lorenz and Parks.[21] The networks were tested in simple tension by using a floor model instron tensile tester. The specimens prepared from the networks were end-bonded to copper U-tabs to minimize problems with clamping. A large aspect ratio was used to minimize end effects.

Applied to simple tension, eq 15 yields

$$\sigma_M = G_X + G_N\varphi_m(\lambda) \tag{18}$$

where σ_N is the Mooney stress given by

$$\sigma_M = \frac{\bar{\sigma}}{\lambda^2 - \lambda^{-1}} \tag{19}$$

and $\varphi_m(\lambda)$ is given by

$$\varphi_m(\lambda) = 2(\lambda^m - \lambda^{m/2})/m(\lambda^2 - \lambda^{-2}) \tag{20}$$

These equations follow from eq 15 with $\bar{\sigma}_2 = 0$, $\lambda_1 = \lambda$, and $\lambda_2 = \lambda_3 = \lambda^{-1/2}$. Figure 7 shows the experimental data

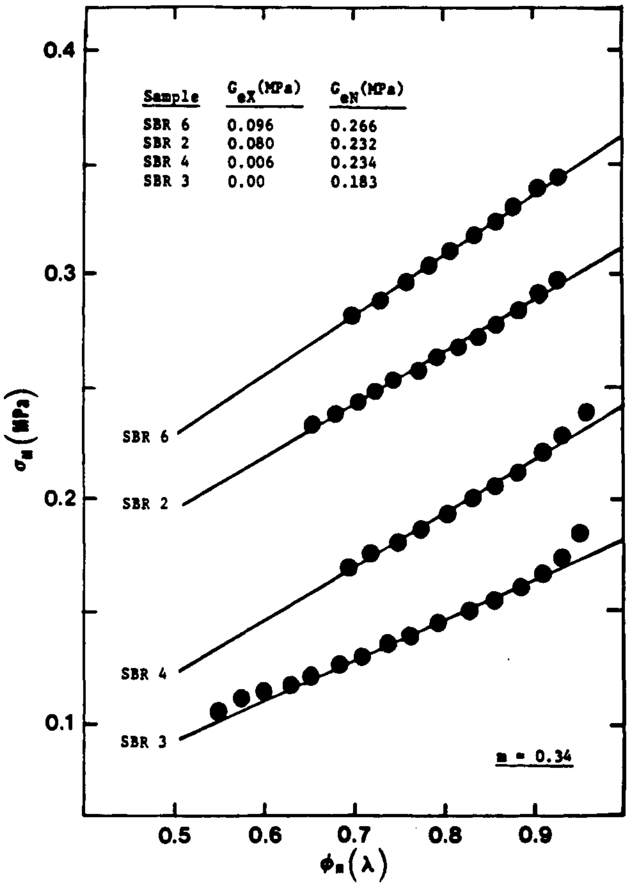

Figure 8. Equilibrium data on SBR networks with varying cross-link densities compared with the predictions of the 2NW potential.

plotted according to eq 18. The straight lines are the lines of best fit. A value of $m = 0.34$ was used as mentioned earlier. The lines for these samples are almost parallel to each other, indicating that G_N is nearly the same for these networks.

Similar results are shown in Figure 8 for SBR networks cross-linked to various extents with dicumyl peroxide. Once again the lines of best fit to the data, for the three-cross-linked samples, are parallel to each other, indicating that G_N is again the same for all of the networks. This point will be discussed in detail later.

We have produced evidence in support of the constitutiveness of the 2NW potential in the narrower sense. It is capable of explaining the data on networks cross-linked to various extents. The second term of the potential appears to be independent of the degree of cross-linking. This supports the assumption of additivity of the moduli as a plausible one.

Swelling of Elastomeric Networks

Swelling has been used for a long time to study the structure of polymeric networks. The stress–strain behavior of swollen networks in a uniaxial deformation is frequently analyzed by using the Mooney–Rivlin equation. The most important observation then concerns the Mooney constant, $2C_2$. This decreases with increasing swelling ratio, eventually becoming zero. Therefore, it has commonly been held that the values of the phantom modulus, $2C_1$, obtained from extrapolation of swollen stress–strain data are closer to the modulus calculated from the chemical constitution of these networks than $2C_1$ obtained on the dry networks.

In this section we interpret the stress–strain behavior of swollen networks using the 2NW potential. We discuss in detail the importance of the study of swollen networks, and their topological environment. We demonstrate that the parameters of the 2NW potential required to describe the behavior of dry networks serve equally to describe the behavior of swollen networks. This implies that the effect of an inert solvent is merely a dilution effect and that the nature of the topological constraints is not altered in swelling. In conclusion, we discuss these implications.

The strain energy density function, W, for unit volume of unswollen rubber is given by eq 14. Equation 14 applies to swollen networks as well as dry networks. However, to describe the stress–strain behavior of swollen networks, one needs to alter the reference state from the unswollen, undeformed state to the swollen, undeformed state. To that end, let v_2 denote the volume fraction of the polymer in the swollen state, and W_{sw} denote the strain energy density function per unit volume of swollen rubber. Then

$$W_{sw} = v_2 W \tag{21}$$

and

$$\alpha_i = v_2^{1/3}\lambda_i \qquad i = 1, 2, 3 \tag{22}$$

Equation 14 then becomes

$$\begin{aligned} W_{sw} = {} & \frac{G_X}{2} v_2^{1/3}(\alpha_1^2 + \alpha_2^2 + \alpha_3^2 - 3) + \\ & \frac{2G_N}{m^2} v_2^{-(m-3)/3}(\alpha_1^m + \alpha_2^m + \alpha_3^m - 3) \end{aligned} \tag{23}$$

the α's being the stretch ratios referred to the swollen, undeformed lengths. Using the Rivlin–Ariano equation, and the condition of incompressibility, one obtains

$$\bar{\sigma} = G_X v_2^{1/3}(\alpha_1^2 - \alpha_1^{-1}) + \frac{2G_N}{m} v_2^{-(m-3)/3}(\alpha_1^m - \alpha_1^{-m/2}) \tag{24}$$

for the true stress $\bar{\sigma}$ in simple tension. The symbol $\bar{\sigma}$ has been used to denote the quantity $\bar{\sigma}_1 - \bar{\sigma}_2$, since in simple tension, $\bar{\sigma}_2$ is zero. It is customary to report the nominal Mooney stress f^* when relating the results of stress–strain measurements. One can obtain the appropriate expression for f^* from eq 5 by converting the swollen to the unswollen area and dividing by the factor $\alpha^2 - \alpha^{-1}$. Thus

$$f^* = \frac{(f/A)v_2^{1/3}}{\alpha - \alpha^{-2}} = G_X + G_N v_2^{(-m+2)/3} \varphi_m(\alpha) \tag{25}$$

where A is the unswollen, undeformed cross-sectional area, and f is the force acting on it. Both eq 24 and 25 describe the behavior of swollen networks in a uniaxial deformation, if the solvent is inert; i.e., it does not interact with the polymer chains to change their configuration, but acts merely as a diluent.

Figure 9 shows the data of Allen[22] et al. on natural rubber (NR) networks swollen in n-decane. The solid lines show the predictions of eq 25. The parameters of the two-network potential, G_X and G_N, were obtained from stress–strain measurements on the dry network as $G_X = 0.107$ MPa and $G_N = 0.144$ MPa. The value of $m = 0.34$ was used for all predictions. As can be seen from the figure, the predictions of the theory are excellent for the first three volume fractions, $v_2 = 1.00$, 0.798, and 0.61. For $v_2 = 0.42$ and $v_2 = 0.36$, the predictions are fair but not as good. For $v_2 = 0.24$ the agreement becomes rather good again.

Figure 10 shows the data of Flory and Tatara[23] on poly(dimethylsiloxane) (PDMS) networks swollen in benzene. The experiments were made at constant solvent

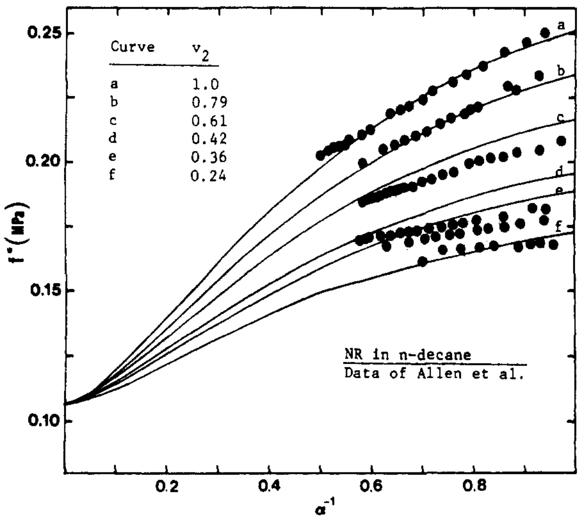

Figure 9. Stress–strain behavior of a swollen network, compared to the predictions of the 2NW potential.

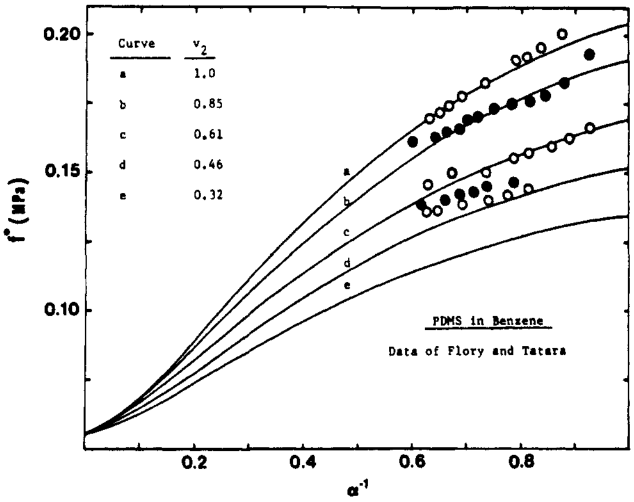

Figure 10. Stress–strain behavior of a swollen network, compared to the predictions of the 2NW potential.

activity rather than constant composition. Again the two parameters of the 2NW potential were obtained from the data on the dry network, and a value of $m = 0.34$ was used. The moduli were obtained as $G_X = 0.056$ MPa and $G_N = 0.149$ MPa.

Figure 11 shows data of Yu and Mark[24] on a PDMS network swollen to the same volume fraction in three different diluents. The points in Figure 11 were calculated by using the values of $2C_1$ and $2C_2$ reported by Yu and Mark.[24] At $v_2 = 0.80$ the data points for all three diluents lie on the same curve. At $v_2 = 0.60$, differences between the three diluents become apparent.

Figure 12 shows the data of Erman and Flory[25] on poly(ethyl acrylate) (PEA) networks swollen in bis(2-ethoxyethyl) ether at 25 °C. The experiments were made on networks cross-linked to different degrees which were then swollen to equilibrium. The open circles are the experimental points for dry networks, and the closed circles are the experimental points for the swollen networks. The solid lines show the predictions of eq 24 with $m = 0.34$, and the two moduli obtained from the dry network stress–strain data. The agreement is seen to be very good. It should be pointed out here that Flory and Erman[26] have examined the same data using the Flory–Erman theory. The value of the phantom modulus they obtain from their analysis is always larger than our G_X, even though both values are supposed to represent the same quantity, the phantom network contribution to stress. We cannot address the reason for this difference at present but hope to do so in a later publication.

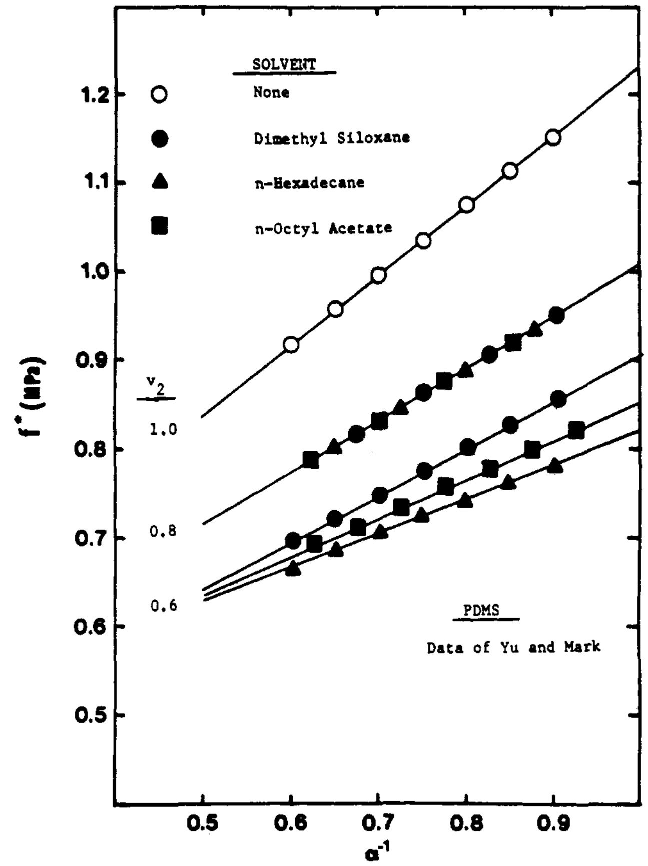

Figure 11. Stress–strain behavior of a PDMS network swollen in different solvents.

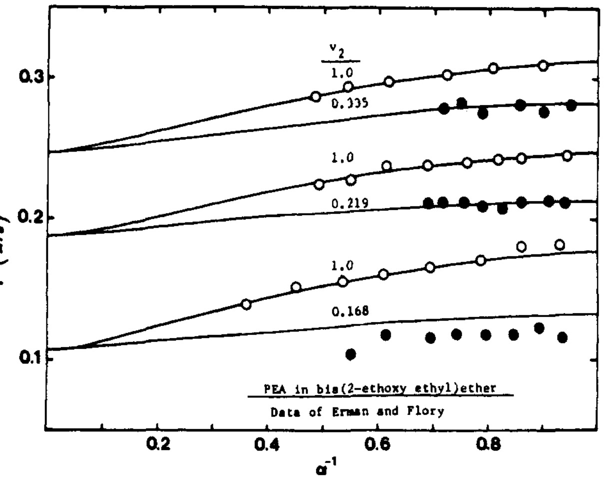

Figure 12. Stress–strain behavior of PEA networks cross-linked to different degrees swollen to equilibrium. Solid lines are the predictions of the 2NW potential.

If we look at Figures 9–12 again, it is clear that the agreement of experimental data on swollen networks with the predictions of the 2NW potential is quite satisfactory at relatively small degrees of swelling but is generally not as good at smaller values of v_2. Such a behavior would be expected from a concentration dependence of the Flory–Huggins χ_1 factor. However, a reviewer pointed out to us that such an explanation would require the chain configuration and its interaction with the diluent to be coupled and that this is not supported by experimental evidence. We cannot offer an alternative explanation at this time.

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Conclusions

We have demonstrated the constitutiveness, in the narrow sense, of the 2NW potential. We have shown further that it represents data on networks of varying cross-link densities adequately, with a G_N that is sensibly independent of the degree of cross-linking.

We have also examined the stress–strain properties of swollen networks. When the degree of swelling is not too high, parameters obtained from the dry network by the 2NW potential adequately describe the stress–strain behavior of swollen networks. This implies that, when a network is swollen, the topological environment around the network chains is not altered. The effect of the neighboring chains on a given network chain is diminished due to dilution only and is not changed in character. This observation casts doubt on the existence of trapped entanglements because, once swollen, their nature as well as their concentration would change.

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Behavior of Elastomer Networks in Moderately Large Deformations. 2. Determination of the Parameters of the Elastic Potential from Measurements in Small Deformations

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ABSTRACT: The proposed elastic potential is completely determined by two moduli, G_X and G_N. Their sum is the equilibrium modulus, G, which can be obtained from stress relaxation measurements on the cross-linked material, in the linear region. It is shown that G_N is proportional to G_N^0, the plateau modulus of a high molecular weight un-cross-linked sample of the same polymer. The proportionality constant appears to be independent of the cross-link density and of the nature of the polymer. Its best current estimate is 0.354.

Introduction

In two previous communications,[1,2] we proposed an elastic potential of the form

$$W = \frac{G_X}{2}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) + \frac{2G_N}{m^2}(\lambda_1^m + \lambda_2^m + \lambda_3^m - 3) \tag{1}$$

This potential was shown to be highly successful in describing arbitrary deformations (general biaxial tension) of rubberlike materials, if the deformations are moderately large, i.e., if they are restricted to the region below the upswing in a plot of the stress vs. the largest principal stretch ratio.

The potential contains three material parameters. Of these, the strain parameter m was originally left to be determined by experiment. Elsewhere,[2] however, we presented arguments which led to the adoption of a "universal" value of 0.34 for m. Of the remaining two parameters, G_X and G_N, the first represents the modulus ascribed to the presence of chemical cross-links in the network. The second expresses the contribution arising from topological constraints. The two moduli can be obtained from stress–strain experiments in simple tension for which eq 1 yields

$$\sigma_M = G_X + G_N\varphi_m(\lambda) \tag{2}$$

where

$$\sigma_M = \frac{\bar{\sigma}}{\lambda^2 - \lambda^{-1}} \tag{3}$$

$$\varphi_m(\lambda) = \frac{2(\lambda^m - \lambda^{-m/2})}{m(\lambda^2 - \lambda^{-2})} \qquad m = 0.34 \tag{4}$$

In these equations λ is the stretch ratio and $\bar{\sigma}$ is the true stress in the direction of the stretch. The two moduli are linked by the additivity relation

$$G_X + G_N = G \tag{5}$$

in which G is the shear modulus of the material. If any two of the moduli G, G_X, and G_N are known, the third can be obtained by using eq 5.