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A Study on Existing Rubber Elasticity Theories for Stress-Strain Behavior of Rubber-like Networks

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ABSTRACT : The Edwards-Vilgis slip-link theory and the Kaliske-Heinrich extended tube theory were tested experimentally using published experimental data on networks of natural and isoprene rubber and on polysiloxane networks. All parameters were adjusted to achieve an optimum fit. The data description obtained with the EV theory is not satisfactory and the parameter values tend to lie outside their reasonably expected range. But for the region of low strains, the Kaliske-Heinrich theory offers a satisfactorily accurate data description which is able to serve for practical purposes. Its crosslink term, however, is based on approximations which lead to a questionable prediction and values determined for the exponent in the entanglement term lie outside the range expected by the KH model. Thus, the title question cannot be given a positive answer.
Conclusions published earlier that the trapped entanglements contribute both to the crosslink and constraint (entanglement) term are supported by the present data analysis. Experimental equibiaxial data on hydrocarbon networks do not show any maximum on their stretch ratio dependence, contrary to the predictions of molecular theories. The stretch ratio dependences of relative reduced stresses do not sensitively reflect differences in the chemical nature of the chain backbone (hydrocarbon vs. siloxane) and in the crosslinking method (end-linking vs. random crosslinking).

Keywords : rubber elasticity theory, natural rubber, isoprene rubber

Ⅰ. Introduction

The Gaussian rubber-elasticity theory is based on a simple phantom network model.[1,2] For uniaxial extension (UE) it predicts the following dependence of the nominal (engineering) stress, σ_{UE}, on the strech ratio λ:

$$\sigma_{UE} = G\,(\lambda - 1/\lambda^2)$$

G is the shear modulus which is predicted to be proportional to the network density.

The reduced stress, σ_{red}, is commonly defined as the ratio of stress and the corresponding stretch ratio function calculated in the Gaussian theory. For uniaxial extension (UE), equibiaxial extension (EBE), longitudinal pure shear (PS1) and transversal pure shear (PS2) it reads as follows:

$$\sigma_{red,UE} = \sigma_{UE} / (\lambda - 1/\lambda^2) \qquad \sigma_{red,EBE} = \sigma_{EBE} / (\lambda - 1/\lambda^5)$$

$$\sigma_{red,PS1} = \sigma_{PS1} / (\lambda - 1/\lambda^3) \qquad \sigma_{red,PS2} = \sigma_{PS2} / (1 - 1/\lambda^2)$$

The reduced stresses predicted by the Gaussian theory should be independent of the stretch ratio. On the other hand, the reduced stresses calculated from experimental data show a complex behavior. Typically, the experimental $\sigma_{red,UE}$ decreases at low

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strains (low-strain softening) and increases at high strains (high-strain hardening). The latter phenomenon is generally ascribed to the finite extensibility of network chains while for the former phenomenon a number of explanations and theoretical models have been proposed.[2]

At the present time, two theoretical approaches aiming to calculate the stress-strain behavior of rubber-like networks in different deformation modes up to large strains are available: the slip-link theory of Edwards and Vilgis[3] (EV) and the extended-tube theory of Kaliske and Heinrich[4] (KH). Both these theories assume a model with two additive contributions, one from stable network junctions (chemical crosslinks), the other from physical crosslinks (entanglements, slip-links). Both contain four parameters the values of which are calculated (estimated) from structural considerations. Recently, another approach has been proposed by Boyce and Arruda.[5] They combined their two-parameter Langevin-statistics-based theory[6] of the high-strain hardening effect with the two-parameter Flory-Erman constrained-junction theory of the low-strain softening effect.[7] However, the resulting equation does not give a sufficiently satisfactory data description. The EV theory has been tested experimentally several times[8-13] with both negative and positive conclusions. The KH theory has been shown by the authors[4] to give a satisfactory description of the well-known set of Treloar data on a natural rubber network. Quite recently, five molecular approaches including the EV and KH theory were compared with biaxial stress-strain data obtained on an end-linked poly(dimethylsiloxane)[12] and the EV model was found to fit the data most successfully.

In the present paper the ability of the structure-based equations to describe the stress-strain behavior of rubberlike networks in different deformation modes up to high strains is tested using available literature data. According to the view adopted here, data description is classified as satisfactory if the relative deviations of the experimental data from the optimum-fit theoretical curves are non-systematic and do not exceed the level of 5 - 7 %. Attention is also given to the ability of the equations to predict the value of the modulus from structural considerations.

1. Definitions

The equilibrium deformation behavior of an elastic material is described by the strain energy density function W (elastic free energy, constitutive equation). In a biaxial extension experiment with stresses along the directions 1, 2, the stress along the direction 3 is zero and the principal nominal (engineering) stresses σ_i ($i = 1, 2$; $\sigma_3 = 0$) are obtained from the general relation

$$\sigma_{i\ (i=1,2)} = \frac{\partial W}{\partial \lambda_i} - \frac{\lambda_3}{\lambda_i}\frac{\partial W}{\partial \lambda_3} \tag{1}$$

At constant volume, $\lambda_3 = 1/\lambda_1\lambda_2$; in uniaxial extension $\lambda_2 = 1/\lambda_1^{0.5}$, in pure shear $\lambda_2 = 1$, in equibiaxial extension $\lambda_2 = \lambda_1$.

II. The slip-link theory of edwards and vilgis

1. Theoretical

The slip-link model is based on reptation concepts and considers a randomly crosslinked polymer melt where some trapped entanglements between crosslinks are present. At low deformations the trapped entanglements are able to slide and behave as slip-links. This leads to a decrease in the reduced tensile stress (strain softening).[14] Edwards and Vilgis have shown that at high deformations, the trapped entanglements restrict the extensibility and contribute to strain-hardening. The elastic free energy (or, strain energy density function), W (= W_c + W_s), derived from the Edwards-Vilgis slip-link theory consists of the crosslink part, W_c, and of the slip-link part, W_s. The required derivative

$$\frac{\partial W}{\partial \lambda_i} = \frac{\partial W_c}{\partial \lambda_i} + \frac{\partial W_s}{\partial \lambda_i}$$

can be calculated from the EV free energy function in the form[13]

$$\frac{1}{N_c kT}\frac{\partial W_c}{\partial \lambda_i} = \lambda_i\left(\frac{1-\alpha^2}{Q^2} - \frac{\alpha^2}{Q}\right) \quad (2)$$

$$\frac{1}{N_s kT}\frac{\partial W_s}{\partial \lambda_i} = \lambda_i\left\{\frac{\alpha^2 PS}{Q^2} + \frac{P}{QR_i^2} + \frac{\eta}{R_i} - \frac{\alpha^2}{Q}\right\} \quad (3)$$

$$I = \sum_i \lambda_i^2 ;\; Q = 1 - \alpha^2 I ;\; R_i = 1 + \eta\lambda_i^2 ;$$

$$P = (1 - \alpha^2)(1 + \eta) ;\; S = \sum_i \frac{\lambda_i^2}{R_i}$$

The summation is performed over the three Cartesian components of the stretch ratio λ_i (i = 1, 2, 3). N_c is the concentration of tetrafunctional network junctions (crosslinks, 1/m^3), α the inextensibility parameter, k the Boltzmann constant, T the absolute temperature, N_s the concentration of slip-links (1/m^3); η, the slippage parameter, is a relative measure of the freedom of a link to slide. The inextensibility parameter $\alpha = b/a$ is predicted to be inversely proportional to the mean distance, a, between slip-links; b is the length of the Kuhn segment; η = 0.234 was calculated by Ball et al.[14] with the assumption that each slip-link can on average slide as far as the centres of its topologically neighbouring links. Later on, variable values of η were admitted.[3] Using Eqs (1)-(3), one can calculate the respective homogeneous stresses which are predicted by the Edwards-Vilgis equation for uniaxial extension (UE), equibiaxial extension (EBE) and pure shear (longitudinal, PS1, and transversal, PS2).

2. Testing

The EV theory is tested here using published biaxial experimental data obtained on hydrocarbon and siloxane networks (see Appendix 1). The dependences of logarithm of reduced stress vs. stretch ratio are used because of their advantage in showing relative deviations of experimental points from the fitted theoretical curves in the whole range of strain with the same sensitivity.

In Figure 1, the reputable data on natural and isoprene rubber networks are collected and compared with the EV curves drawn using two sets of paramers. With values of η = 0.5, the remaining three parameters can be adjusted to obtain a good description of UE data and a

somewhat less satisfactory description of low-strain EBE and PS2 data. To obtain a satisfactory fit in the high-strain EBE region, the slippage

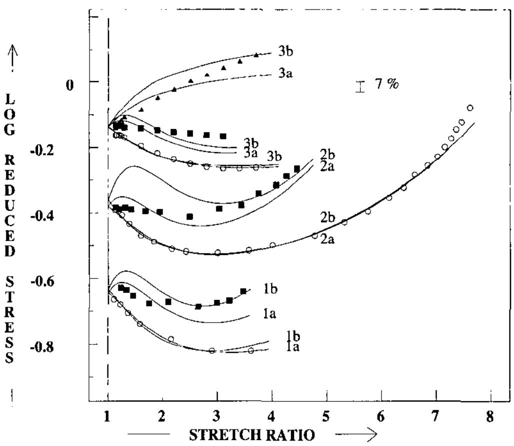

Figure 1. Comparison of the EV equation (curves) with experimental data on natural and isoprene rubber networks (points). Circles UE; squares EBE; triangles PS2. Curves are drawn using parameter values given below.
1a, 1b NR A; 2a, 2b NR B; 3a, 3b IR. Vertical shifts (curves+points): NR A Δ = -0.20; NR B Δ = 0; IR Δ = + 0.25.

	NR A	NR B	IR	NR A	NR B	IR
Curves	1a	2a	3a	1b	2b	3b
η	0.50	0.50	0.50	0.75	1.30	0.75
α	0.082	0.087	0.055	0.100	0.088	0.055
$N_c kT$ (MPa)	0.173	0.220	0.265	0.156	0.205	0.268
$N_s kT$ (MPa)	0.395	0.410	0.310	0.590	1.100	0.420

parameter values must be increased. However, in either case the overall data description remains unsatisfactory. In Figure 2, data on siloxane networks are shown. Recent data of Urayama et al.[12] are compared with the curves drawn using their set of parameters (1a); Urayama et al. have chosen N_s/N_c = 7 in order to reflect the actual known entanglement/crosslink ratio in the PDMS A network. To obtain a good fit to data, Urayama et al.[12] had

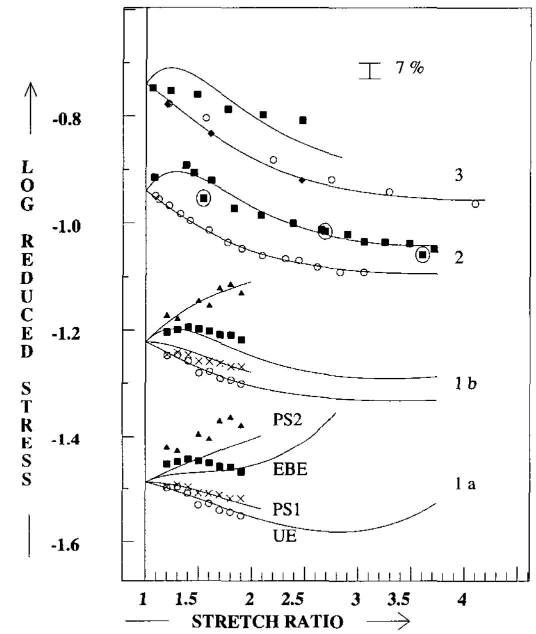

Figure 2. Comparison of the EV theory (curves) with experimental data on PDMS (points). Circles UE; diamonds UE measured on decreasing strain; squares EBE; squares+circles EBE measured out of sequence; crosses PS1, triangles PS2. Curves are drawn using parameter values given below.
1a,1b PDMS A; 2 PDMS B; 3 PDMS C. Vertical shifts (points+curves): 1a Δ = -0.30; 1b Δ = -0.05; 2 Δ = 0; 3 Δ = + 0.20.

	PDMS A	PDMS A	PDMS B	PDMS C
Curves	1a	1b	2	3
η	0.08	0.60	0.70	0.50
α	0.150	0.05	0.05	0.05
N_ckT (MPa)	0.0084	0.046	0.069	0.058
N_skT (MPa)	0.0588	0.0525	0.128	0.125

to adjust the inextensibility parameter α to a rather high value (0.15) and this leads to the prediction of an early upturn in $\sigma_{red,EBE}$. However, the Xu and Mark measurements[15] up to high strains on an end-linked network of a similar structure, PDMS B, do not show any signs of such an early upturn. Assuming a more probable lower value of α = 0.05 (comparable to that of PDMS B), we have found an almost satisfactory data description with N_s/N_c = 1.14 (curves 1b) and N_ckT distinctly higher than that calculated from the crosslink concentration by Urayama et al. Our result is in line with the previous conclusion of Thirion and Weil[8] obtained on polyisoprene networks that a significant fraction of trapped entanglements does not behave as the sliding links of the EV model but gives the same contribution to the stress as the chemical crosslinks.

In an earlier analysis[21] based on a simpler (Mooney-Rivlin) model we have suggested practically the same interpretation: to explain the observations, two kinds of entanglements must be assumed to exist in the network. The sliding ones determine the C_2 part of the UE stress, the more stable non-sliding entanglements behave as crosslinks and contribute to the C_1 term of the Mooney-Rivlin equation. In the natural rubber networks explored, the numbers of the sliding and non-sliding entanglements (extrapolated to networks without free chain ends) were comparable.[21] It is interesting to note that at least in one theory (Rubinstein and Panyukov[22]) trapped entanglements are calculated to contribute both to the crosslink and entanglement (constraint) parts of the stress.

The data description obtained with the PDMS B network (curves 2) leaves some uncertainty owing to large experimental scatter at low strains. The results obtained with the PDMS C network (curves 3) show unsatisfactory features similar to those shown for hydrocarbon networks in Figure 1.

3. Conclusions

(1) The EV model does not give a satisfactory

description of the stress-strain behavior in different deformation modes. The experiment-theory deviations tend to be systematic and higher than 5 - 7 %. (2) The experimentally obtained W_c contribution to the strain energy is higher than predicted by the EV model from the knowledge of the crosslink concentration. This supports the view that entanglements present in an uncrosslinked polymer contribute, after crosslinking, both to N_c and N_s. (3) Modeling of the high-strain singularity in entropy is done in the EV theory using intentionally a rather simple approximation and, as a result, the calculated stresses of a slip-link free network should be looked upon as mere approximations of a conceivable rigorous treatment.[13]

Ⅲ. The extended tube model

1. Theoretical

Similarly to the slip-link model, the KH strain energy density function consists of two terms, the crosslink part and the entanglement (constraint) part:

$$\frac{1}{G_c}\frac{\partial W_c}{\partial \lambda_i} = \lambda_i\left(\frac{1-\delta^2}{Q^2} - \frac{\delta^2}{Q}\right) \tag{4}$$

$$\frac{1}{G_e}\frac{\partial W_e}{\partial \lambda_i} = \frac{2\lambda_i^{\,n-1}}{n} \tag{5}$$

$$J = \sum_i(\lambda_i^2 - 1);\; Q = 1 - \delta^2 J$$

G_c and G_e are the crosslink and entanglement (constraint) contribution to the modulus, respectively; $n = -2\,\gamma\beta$ is the exponent in the generalized strain invariant, γ represents the dependence of the tube diameter on the microscopic deformation and in the KH model (and in the Rubinstein-Panyuchov theory[22]) it is equal to 1/2; Gaylord et al. derived γ = -1/2 assuming a deformation-independent tube volume.[23] β correlates the microscopic and macroscopic deformation and for an affine deformation it is unity; Kaliske and Heinrich consider constraint release effects and allow β to vary: $0 \le \beta \le 1$. Thus, according to KH, n should assume values in the range between -1 and 0 while Gaylord et al.[23] predict n = +1. Equations (2) and (4) are similar, the inextensibility parameter being denoted as δ by KH. The difference between Eqs (2) and (4) looks insignificant but the low-strain predictions of Eq. (4) differ substantially from those of Eq. (2): for $\lambda_1 \rightarrow 1$, i.e., when J is small and Q close to unity, the expression in brackets on the right-hand side of Eq. (4) approaches $(1 - 2\,\delta^2)$ and is thus smaller than unity. In other words, the KH equation predicts that at low strains (for $J < 1$) the finite extensibility contribution to the stress is not positive but negative. This can hardly be true and probably results from some approximations involved in the calculation. Although for small values of δ the effect is small, it nevertheless detracts from the value of the KH equation. With very large inextensibilities, even the stress itself is predicted to become negative at low strains ($0 < J < 1$).

2. Testing

The KH equation is tested experimentally in Figures 3 and 4. Point-curve deviations appear at very low strains and the limiting reduced stresses obtained from the optimum-fit curves at zero strain, $G_{o,KH}$, are systematically lower than those obtained from the experimental reduced stresses by simple extrapolation, $G_{o,exp}$. EBE data in the region of stretch ratio ca 1.2 to 2.2 tend to show deviations from curves in the case of NR A and NR B networks. On the whole, however, the degree of fit of the KH curves to the data is better than that observed with the EV theory. The data description is generally satisfactory, in some cases very good. With proper adjustment of the parameter n, the ability of the KH equation to simultaneously describe the UE, EBE and PS1, PS2 data is also good and the inextensibility parameter assumes reasonable values which lie in the 0.06 - 0.10 region. With one exception, the ratio G_e/G_c is equal to 1 ± 0.4. It shows

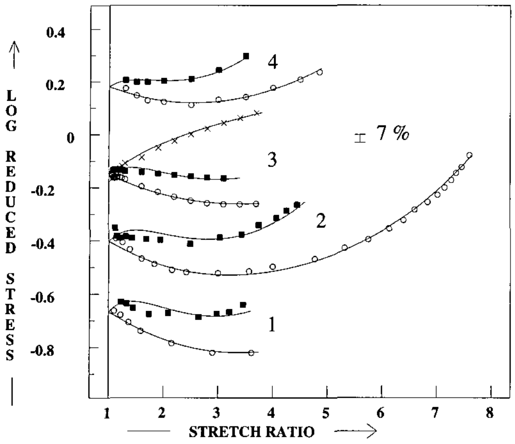

Figure 3. Comparison of the KH equation (curves) with experimental data on natural and isoprene rubber networks (points). Circles UE; squares EBE; crosses PS2. Curves are drawn using parameter values given below.
1 NR A; 2 NR B; 3 IR; 4 NR C. Vertical shifts (curves+points): NR A Δ = -0.20; NR B Δ = 0; IR Δ = + 0.25; NR C Δ = + 0.50.

	NR A	NR B	IR	NR C
Curves	1	2	3	4
n	0.20	-0.05	0.32	0.40
δ	0.100	0.096	0.082	0.109
G_c (MPa)	0.143	0.196	0.215	0.295
G_e (MPa)	0.200	0.202	0.183	0.190
G_e / G_c	1.40	1.03	0.85	0.64

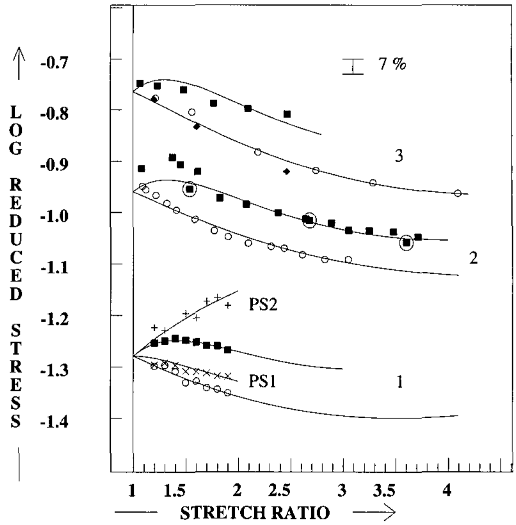

Figure 4. Comparison of the KH equation (curves) with experimental data on PDMS networks (points). Circles UE; diamonds UE measured on decreasing strain; squares EBE; squares+circles EBE measured out of sequence; crosses PS1, PS2. Curves are drawn using parameter values given below.
1 PDMS A; 2 PDMS B; 3 PDMS C.Vertical shifts (points+curves): PDMS A Δ = -0.10; PDMS B Δ = 0; PDMS C Δ = +0.20.

	PDMS A	PDMS B	PDMS C
Curves	1	2	3
n	0.30	0.60	0.80
δ	0.08	0.06	0.085
G_c (MPa)	0.0346	0.050	0.032
G_e (MPa)	0.0320	0.060	0.077
G_e / G_c	0.92	1.20	2.41

a certain tendency to decrease with increasing degree of crosslinking (decreasing ratio of the number of entanglements to crosslinks) of NR and IR

networks but it is rather low (smaller than unity) for the PDMS network of Urayama et al.[12] where the entanglement/crosslink ratio is known to be several times higher than unity. This result again suggests that the experimental G_c term is higher than that expected theoretically from the knowledge of the existing crosslink concentration and that it receives some contribution from entanglements. The determined values of the exponent n lie in the 0 - 0.8 range, quite differently from the expectation of the KH theory. A simple formal interpretation of this result suggests that β is not constant and γ = -1/2, in conformity with Gaylord et al.[23]

3. Conclusions

(1) But for the region of low strains, the KH model is able to describe the stress-strain behavior of NR, IR and PDMS networks with a satisfactory accuracy. (2) The inextensibility parameter and the modulus components assume reasonable values; n lies outside the range expected by KH. (3) The G_e/G_c

ratio does not reflect the high entanglement/croslink ratio of an end-linked PDMS. For NR and IR networks explored, it shows a tendency to decrease slightly with increasing degree of crosslinking. (4) The crosslink term of the KH equation leads to an erroneous prediction which becomes significant for more highly crosslinked networks. (5) The KH equation can be used for practical purposes of data description; its limitations, however, should be born in mind.

Ⅳ. Some conclusions based on experimental data

Figure 5 shows the Mooney-Rivlin plot of UE and EBE data for NR and IR networks and for stretch ratios lower than 2.2, where the contribution of finite extensibility to the stress may be expected to be negligible. Very low strain data are not included to avoid the puzzling effect of the increasing experimental scatter. The UE points are described very well by straight lines which in the limit of the unit stretch ratio define the values of the limiting reduced UE stress $G_{o,exp}$. For all three networks the reduced EBE stresses at low strains are practically equal to $G_{o,exp}$ and with increasing strain (decreasing reciprocal stretch ratio) tend to decrease slowly. The first derivative of the experimental reciprocal stretch ratio dependence of the reduced uniaxial extension/compression stress shows an abrupt change in the vicinity of zero strain. These phenomena are at variance with the results of theoretical treatments which predict no

sudden change of the derivative and a more or less pronounced maximum on the stretch ratio dependence of the reduced EBE stress: EV theory (Figure 1), KH theory (Figures 3, 6), constrained junction, constrained chain and other theories (not shown here). This result gives the impression that the existing theoretical models may rely on assumptions that may require some revision.

It was suggested that the biaxial stress-strain behavior of PDMS networks composed of a siloxane backbone can be expected to be fundamentally different from that of the hydrocarbon networks. To test this possibility, we have plotted the equibiaxial (EBE) and pure shear (PS1, PS2) reduced stress-

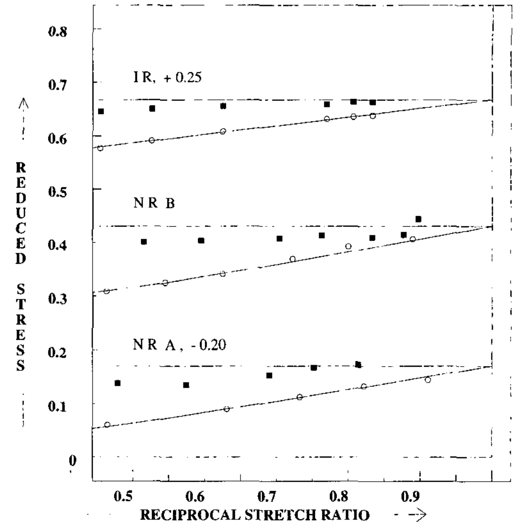

Figure 5. Experimental data on natural and isoprene rubber networks in the plot of reduced stress vs. reciprocal stretch ratio. UE circles, EBE squares. Vertical shifts of the points and lines belonging to the respective networks are indicated in the graph.

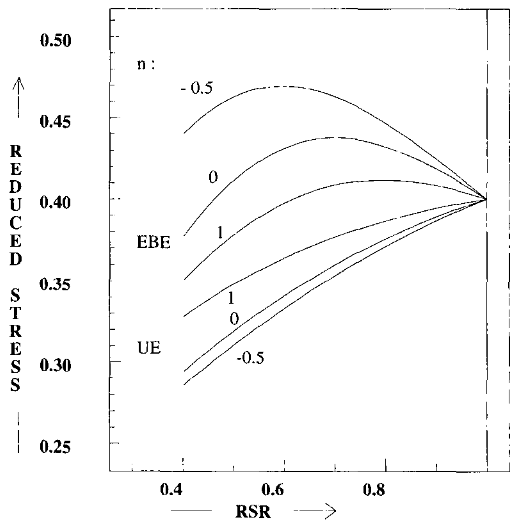

Figure 6. The KH function in the plot of reduced stress vs. reciprocal stretch ratio for $\delta = 0$ and $G_e / G_c = 1$.

stretch ratio data obtained on the isoprene rubber network[19] in the same graph together with the data on a siloxane network; in the latter case, only points with stretch ratios higher than 1.5 are shown. Relative values of the reduced stress are given by the ratio σ_{red}/G_0 where G_0 was obtained by extrapolating the stretch ratio dependence of the reduced EBE and PS2 stresses to unit stretch ratio. In this way, the PS2 and EBE data of the two networks are made to superimpose within the experimental scatter; the PS1 data obtained on the two networks differ but slightly. From this result one can conclude that the biaxial stress-strain behavior does not seem to sensitively reflect the chemical nature of the chain backbone and the nature of the crosslinking process (end-linking of precursor molecules vs. random crosslinking of long chains). In a similar way the data on PDMS A network prepared by end-linking in solution were compared with data on the corresponding melt end-linked PDMS network (no diluent) and found not to differ significantly.

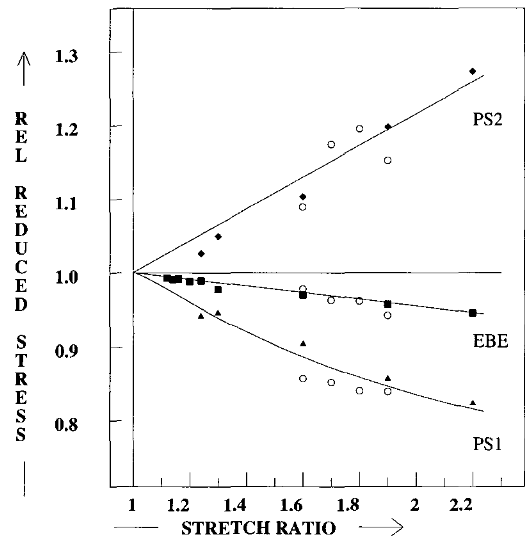

Figure 7. Dependence of the relative reduced stresses σ_{red}/G_0 on the stretch ratio of isoprene (IR) and siloxane (PDMS A) networks. IR: diamonds, squares, traingles. PDMS A: circles. Straight lines (PS2, EBE) and curve (PS1) are empirical fits to IR data.

V. Tensile stress - strain dependences

The problem of a sufficiently precise description of the tensile stress-strain curves of both unfilled networks and networks reinforced with fillers or hard polymer domains was addressed in our previous papers.[10,24-26]. It was found that the stress-strain dependences measured on a decreasing strain approach a simple behavior which can be described by a combination of the molecular and phenomenological approach. The proposed equation which we denote by the JGC2 code is composed of the Langevin-statistics based James-Guth (JG) equation and the phenomenological C_2 term of the Mooney-Rivlin equation.[27,17] The latter term is equivalent to the KH entanglement term (Eq. (5)) for uniaxial extension with $n = -2$, $2C_2 = G_e$. An extensive data analysis based on the JGC2 equation has identified two main effects which make the general tensile stress-strain behavior of rubber networks to deviate from the JGC2 equation: (a) formation/disruption of networks of filler particles and/or hard polymer domains at low strains; it can be accounted for by introducing a modified C_2 term, (b) stress-induced topological changes at high increasing strains; they can be represented using the concept of a strain-dependent finite extensibility parameter. Tensile stress-strain curves of rubber networks of all kinds (unfilled amorphous and strain-crystallizing, bimodal, filler reinforced, thermoplastic elastomers with semicrystalline or glassy domains; specimens virgin, pre-strained; increasing and decreasing strain) have been found to show the same general features, the differences between networks being a matter of degree rather than of kind.[25,26]

The combination of a molecular and phenomenological approach can, in principle, be also used for biaxial extension. The James-Guth equation must be replaced with the Arruda and Boyce equation[6] which gives a rigorous molecular basis for the crosslink term and a correct prediction for the finite extensibility effects in biaxial stress-strain behavior. (For uniaxial extension, the two equations give practically the same prediction.[10]) In the first step, the experimental stress-strain behavior in uniaxial extension is analyzed and the Arruda-Boyce contribution and the C_2 contribution to the experimental UE stress are determined. The AB contributions to stresses in other geometrical modes can then be calculated and the differences between the experimental and the respective AB stresses analyzed and described phenomenologically. The analysis of experimental biaxial data is simplified in the absence of finite extensibility effects in which case the reduced AB stress is equal to the reduced Gaussian stress and is thus predicted to be constant and the same for all deformation modes. In the example given in Figure 7 no upturn of reduced EBE stress is apparent at low and medium strains. Simple linear stretch ratio dependences of the reduced stresses in EBE and PS2 are seen; linear dependences (not shown here) also appear for other posible σ_2 stresses with b = const., $\sigma_2 = \sigma_1^{(b/2)}$, $-1 < b \leq 2$. These data can thus easily be described using a simple phenomenological approach. The reduced stress in PS1 and other possible reduced σ_1 stresses with b = const., $-1 \leq b < 2$ show simple dependences on reciprocal stretch ratio and are also amenable to phenomenological representation. The combination of the two-parameter Arruda-Boyce equation with the phenomenological term and its parameter values enables data description without systematic deviations and may serve as a tool for comparison of different networks.

Summary

The Edwards-Vilgis slip-link theory and the Kaliske-Heinrich extended tube theory were tested experimentally using published experimental data on networks of natural and isoprene rubber and on polysiloxane networks. All parameters were adjusted to achieve an optimum fit. The data description obtained with the EV theory is not satisfactory and the parameter values tend to lie outside their reasonably expected range. But for the region of low strains, the Kaliske-Heinrich theory offers a satisfactorily accurate data description which is able to serve for practical purposes. Its crosslink term, however, is based on approximations which lead to a questionable prediction and the values determined for the *n*-parameter lie outside the range expected by the KH model. Thus, the title question cannot be given a positive answer.

The conclusions published earlier that the trapped entanglements contribute both to the crosslink and constraint (entanglement) term are supported by the present data analysis.

Experimental equibiaxial data on hydrocarbon networks do not show any maximum on their stretch ratio dependence, contrary to the predictions of molecular theories. The stretch ratio dependences of relative reduced stresses do not sensitively reflect differences in the chemical nature of the chain backbone (hydrocarbon vs. siloxane) and in the crosslinking method (end-linking vs. random crosslinking).

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