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Langevin-elasticity-theory-based description of the tensile properties of double network rubbers

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Abstract

A previously proposed and successfully tested constitutive equation denoted by the ABGIL code (a combination of the Arruda–Boyce equation based on the Langevin elasticity theory and a constraint term based on tube theories; strain-induced increase in the finite extensibility parameter is assumed) has been found to provide a good basis for quantitative interpretation of the stress–strain data recently obtained by Mott and Roland on double networks of natural rubber, prepared by introducing additional crosslinks (second network) into a first network stretched to various extents. Experimental information on properties of the first and second networks has been used to obtain their ABGIL parameters and to calculate, under the common assumption of additivity of contributions, the stress–strain properties and residual stretch of the resulting double networks. The predictive ability of the ABGIL equation has been found to be very good. Effects of the finite extensibility of network chains appear to be significant in double networks while the possible role of orientational crystallization cannot be excluded.

Keywords: Theory of rubber elasticity; Double network rubbers; Experimental testing

1. Introduction

A rubbery material with a double network structure can be prepared by introducing additional crosslinks into a stretched primary network [1]. In a recent paper, Mott and Roland [2] prepared a series of peroxide-crosslinked natural rubber networks having both isotropic and double network structures with the residual stretch (permanent set) of the latter ranging from 2.5 to 4.5. They measured mechanical and optical properties of the networks and interpreted the results using the diffused constraint model of rubber elasticity [3] and the assumption of independent, additive contributions from the two component networks [4,5]; a generalization of the two-network hypothesis was published by Baxandall and Edwards [6]. Mott and Roland found [2] that the diffused constraint model underestimated the residual stretch (by 9–21%) and ascribed this discrepancy to the error in the rubber elasticity model. According to their measurements [7], constraint theories of rubber elasticity generally overestimate the stress in compression and this, they conclude [2], is the reason why we cannot expect more than qualitative predictions for double networks.

Recently, we have analyzed published biaxial stress–strain data obtained on elastomeric networks [8]. For that purpose we have proposed and tested the ABGI equation, which is a combination of the Arruda–Boyce equation [9] based on the Langevin elasticity theory, with a constraint term based on tube theories [10]. For natural and isoprene rubber networks, the fit of the ABGI equation to both uniaxial and biaxial data was satisfactory. The deviations of experimental points from the fitted curves generally did not exceed 5% and only in the low-strain region they showed a tendency to increase systematically up to 10–12%. For a satisfactory data representation in the region of high strains, the ABGIL equation—which is a generalized form of the ABGI equation and is based on the concept of a strain-induced increase in the finite extensibility parameter—was successfully applied [8].

The aim of the present paper is to show that using the assumption of additive contributions of the two component networks, the ABGIL equation is able to provide satisfactory

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estimates of the residual stretch of the Mott–Roland double networks and a reasonably good description of their tensile stress–strain dependences in the whole range of the strain studied.

2. Theoretical

2.1. The ABGI equation

For uniaxial extension/compression and equibiaxial extension at constant volume, the ABGI equation [8] can be written in the form:

$$\sigma = 2C_1 \frac{\lambda_{cm}}{3\lambda_c} L^{-1}\left(\frac{\lambda_c}{\lambda_{cm}}\right) D_A + 2C_2 \frac{2D_B}{n} \tag{1}$$

The functions λ_c, D_A, D_B, are given as

	Uniaxial extension/compression	Equibiaxial extension
λ_c	$(1/3^{1/2})(\lambda^2 + 2/\lambda)^{1/2}$	$(1/3^{1/2})(2\lambda^2 + 1/\lambda^4)^{1/2}$
D_A	$\lambda - \lambda^{-2}$	$\lambda - \lambda^{-5}$
D_B	$\lambda^{n-1} - \lambda^{-(n+2)/2}$	$\lambda^{n-1} - \lambda^{-(2n+1)}$

The first term on the right-hand side of Eq. (1) is the network-junction contribution to the stress given by the Arruda–Boyce equation [9], the second term is the constraint contribution written in the phenomenological form [10]. σ is the nominal (engineering) stress, $\lambda = L/L_0$ the stretch ratio, i.e. the ratio of deformed and undeformed length, L^{-1} the inverse Langevin function (the Langevin function $L(x) = \coth(x) - 1/x$), λ_c the network-chain stretch ratio (the ratio of the deformed and undeformed chain end-to-end distances), λ_{cm}, the hypothetical highest possible chain stretch ratio (finite extensibility parameter, locking stretch), is predicted to be given by the square root of the number N of statistical segments in a network chain, $\lambda_{cm} = N^{1/2}$. $2C_1 = \nu RT$ is the modulus component proportional to the network chain density, ν [9], and R, T, have their usual meaning. $2C_2$ is the modulus component given by physical constraints to the mobility of network chains [10], n is the parameter in the constraint term which in different tube theories [10] is predicted to assume values ranging from -1 to $+1$. For natural rubber and isoprene rubber networks, we have found values of n in the -0.2 to $+0.2$ range [8].

The ABGI equation contains four adjustable parameters: C_1, C_2, λ_{cm}, n. The two elastic constants, C_1, C_2, determine the Young's modulus, E, (and the shear modulus, $G = E/3$) of the ABGI material; for large N's, $G = 2C_1 + 2C_2$. The high-strain behavior is increasingly determined by $\lambda_{cm} = N^{1/2}$ and the hypothetical highest possible stretch ratio λ_{max} can be calculated for uniaxial and equibiaxial extension from λ_{cm} using the relations given above. The value of n affects, i.e. the ratio of equibiaxial to uniaxial stress.

The reduced stress, σ_{red}, is defined as the ratio of stress and of the corresponding stretch ratio function D_A :

$$\sigma_{red} = \sigma/D_A \tag{2}$$

The reduced stress in equibiaxial extension is equal to that in uniaxial compression if the equibiaxial stretch ratio λ_{EBE} and the uniaxial compression stretch ratio λ_{UC} are related by $\lambda_{EBE}^2\lambda_{UC} = 1$.

2.2. The ABGIL equation

In our previous paper [11] we have shown that at very high strains the increase in stress of real networks is less steep than predicted by the Langevin elasticity theory. The experimental behavior can be interpreted and described by applying the concept of a strain-induced increase in the finite extensibility parameter [8,11]. The following empirical power function gives a good description of the dependence of λ_{cm} on the chain stretch ratio λ_c [8]:

$$\lambda_c \le \lambda_{c,a}: \qquad \lambda_{cm} = \lambda_{cm,a},$$

$$\lambda_c > \lambda_{c,a}: \tag{3}$$

$$\lambda_{cm} = \lambda_{cm,a} + (\lambda_{cm,b} - \lambda_{cm,a})[(\lambda_c - \lambda_{c,a})/\lambda_{c,b} - \lambda_{c,a})]^a$$

For chain stretch values lower than $\lambda_{c,a}$, the finite extensibility parameter λ_{cm} is constant and equal to $\lambda_{cm,a}$. With increasing strain and chain stretch ratio higher than $\lambda_{c,a}$, the finite extensibility parameter increases and at $\lambda_{c,b}$ it attains the value $\lambda_{cm,b}$. Parameters of Eq. (3) are determined by comparing experimental data with Eq. (3) [8]. The combination of Eqs. (1) and (3), i.e. the ABGI equation with a strain-dependent finite extensibility parameter, is denoted by the ABGIL code.

3. Comparison of experimental data with the ABGIL equation

3.1. Isotropic networks in uniaxial and equibiaxial extension

Equilibrium stress–strain dependences in uniaxial extension and compression were measured by Mott and Roland [7] using cylindrical specimens of natural rubber which were crosslinked using 1 (NR-1) and 2 (NR-2) weight parts of dicumyl peroxide (DCP) per hundred weight parts of rubber (phr). The obtained experimental dependences (given in Ref. [7], Fig. 4.) of reduced tensile stress on reciprocal stretch ratio are replotted in the coordinates of log σ_{red} vs. stretch ratio in Fig. 1 (circles and curves 2, 3) and in the coordinates of stress vs. stretch ratio in Fig. 2 (circles and curves 2, 4). The experimental dependences of tensile stress on stretch ratio (the Mott and Roland Fig. 2 in Ref. [7]) were also used and are given in Fig. 1 as crosses. The differences in position of the two kinds of markers

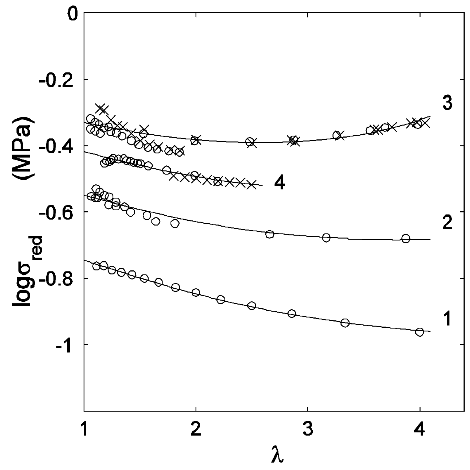

Fig. 1. Dependences of log(reduced stress) on stretch ratio in uniaxial extension for the Mott–Roland isotropic NR networks. 1-SA, 2-NR-1, 3-NR-2, 4-DA0; vertical shifts: 1: +0.4, 4: −0.06. Curves are drawn according to the ABGI equation using parameter values given in Table 1.

reflect the scatter in reading off the coordinates of points in the original graphs. The uniaxial compression data (Ref. [7], Fig. 4) were converted here to equibiaxial extension data and are shown in Fig. 2 as squares. In the same graph, the low-strain regions of three published experimental series [12–14] (circles + squares, curves 1, 3, 5) are shown for comparison. In these cases, the equibiaxial extension data were obtained using inflation of rubber sheets [12] and a biaxial extension apparatus [13,14] rather than the uniaxial compression arrangement [2]. Complete experimental series were compared with the ABGIL equation previously [8] and the parameter values obtained are given in Table 1. Both the

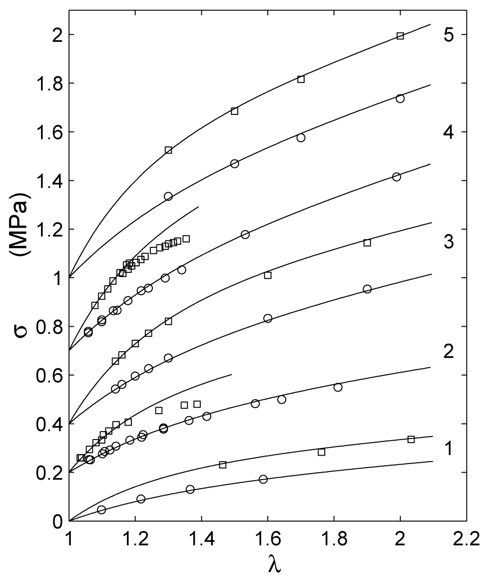

Fig. 2. Dependences of stress on stretch ratio for isotropic networks. Points: experimental; circles-uniaxial extension, squares-equibiaxial extension. Curves are drawn according to the ABGI equation for parameter values given in Table 1. 1-NR RS, 2-NR-1, 3-IR Kaw, 4-NR-2, 5-NR Jam. Vertical shifts of points and curves, 2: +0.2 MPa, 3: +0.4 MPa, 4: +0.7 MPa, 5: +1 MPa.

Table 1
Parameter values of the ABGI equation for isotropic networks and curves in Figs. 1 and 2

Network	Crosslinking system	n	C_1 (MPa)	C_2 (MPa)	λ_{cm}
SA [2]	DCP, 0.3 phr	0.5	0.0138	0.0218	(7.0)
NR RS [12]	Sulfur/accelerator	0.2	0.069	0.096	3.70
NR-1 [7]	DCP, 1 phr	0.5	0.067	0.072	(4.7)
IR Kaw [13]	Sulfur/accelerator	0.2	0.108	0.084	4.6
DA0 [2]	DCP, 0.3 + 1.7 phr	0.5	0.107	0.108	(4.2)
NR-2 [7]	DCP, 2 phr	0.5	0.132	0.094	3.4
NR Jam [14]	Sulfur/accelerator	0.2	0.150	0.078	3.54

uniaxial and equibiaxial stress–strain dependences of the three series (full lines) are described by the ABGI equation with a sufficient accuracy.

The data of Mott and Roland on the NR-2 network [7] given in Figs. 1 and 2 (points) are described by the ABGI equation (curves) with parameter values that are reasonably well substantiated and are roughly comparable with those of similar networks (see Table 1). However, the scatter of uniaxial low-strain data is rather large and the equibiaxial stress calculated from compression data shows, at higher strains, a downward deviation not observed with the published three series (see [8]). A similar behavior to that of NR-2 is shown by the less crosslinked network NR-1. To obtain a reasonable data description, the higher-strain equibiaxial data were not taken into account and a somewhat higher value of the parameter n ($=0.5$) had to be used. It is difficult to see whether the downward deviation of equibiaxial stress at higher strains is a real effect or a consequence of possible lower reliability of the compression measurements. However, it should be mentioned that the equibiaxial data obtained on the NR-1, NR-2 networks (Fig. 2) are described sufficiently well up to the stretch ratio of $\lambda_{EBE} \sim 1.2$ and this, in uniaxial compression, corresponds to the stretch ratio of $\lambda_{UC} = 1/1.2^2 = 0.7$. The applicability range of the ABGI equation for the DA double networks of Mott and Roland is thus sufficient since in the unstressed condition the stretch ratios of the second networks do not decrease below 0.7 (see Figs. 4 and 5).

The lightly crosslinked SA network (0.3 phr of DCP) was used as the first network in the preparation of double networks of the DA series. The DA0 network was crosslinked in two steps (0.3 + 1.7 phr of DCP) under isotropic conditions and represents a limiting case of the double networks, the prestrain of the second network being equal to zero. Equilibrium tensile measurements on the SA and DA0 networks were taken from Ref. [2], Fig. 4, and are shown in Fig. 1 as circles (SA: curve 1, DA0: curve 4). The results of extension measurements at constant rate (2%/min) which are given for DA0 in Fig. 1 of Ref. [2] are plotted in Fig. 1 as crosses (curve 4). The measurements on SA and DA0 networks were limited to a strain range where the upturn in reduced stress is not yet sufficiently pronounced and thus, the conditions for an independent determination of all four parameters are not fully developed. Therefore, a simplifying assumption has been made here that the value of $n = 0.5$ obtained for the NR-2 network is applicable to all other networks of Mott and Roland, both isotropic and double ones. Values of λ_{cm} (given in Table 1 in parentheses) are rough estimates. Qualitatively, they conform to the expectation that the length of network chains N should decrease with increasing network density (C_1). The scatter in the determination of C_1 and C_2 is not large and the degree of fit of the ABGI equation to the data on the SA network (curve 1 in Fig. 1) and on the DA0 network (curve 4 in Fig. 1) seems satisfactory.

It should be noted that the application of the Arruda–Boyce theory to strain-crystallizing networks of natural and isoprene rubbers is subject to criticism based on the fact that the upturn in reduced stress may be affected both by finite extensibility of chains and by the formation of crystalline regions. We have found that when using the ABGI equation, a satisfactory formal description of the stress–strain dependences of strain-crystallizing networks is possible in many cases [15], at the expense, of course, of the N parameter losing its unambiguous physical interpretation.

3.2. Double networks in uniaxial extension

The Mott–Roland dependences of uniaxial engineering stress (force per unit of unstressed cross-section) on stretch ratio of double-networks DA0, DA1, DA2, DA3, DA4, prepared at various stretch lengths of the SA first network, are given in Fig. 1 of Ref. [2]. They are shown in Fig. 3 in the Mooney–Rivlin coordinates. The stretch ratio $\lambda = L/L_0$ of the first network is the ratio of its stressed, L, and unstressed, L_0, length; L_R is the length of the unstressed double network, $\lambda_R = L_R/L_0$ is the stretch ratio of the unstressed double network with respect to the length of the unstressed first network (the residual stretch ratio; permanent set); $\lambda/\lambda_R = L/L_R$ is the stretch ratio of the double network, i.e. ratio of its stressed, L, and unstressed, L_R, length; L_X is the length at which crosslinks of the second network were introduced.

The values of the stretch ratio $\lambda_X = L_X/L_0$ of the first network at which the second network was formed are given in Table 2 together with the corresponding values of the measured residual stretch ratio λ_R. The experimental dependences of reduced stress on reciprocal stretch ratio of double networks given in Fig. 3 are formally compared with the ABGI equation. This treatment of data has a character of a zeroth-order approximation since the Arruda–Boyce theory is not designed for networks containing, in the unstressed state, oriented chains. The resulting parameter values are given in Table 2 and conclusions based on them should be regarded as having only a qualitative value. The main result is not surprising and seems to be well documented: with increasing λ_X, an upturn in the reduced stress appears and shifts progressively to lower strains, i.e. the (average) value of $\lambda_{cm} = N^{1/2}$ decreases. The increase in stress at 100% strain with increasing λ_X observed by Mott and Roland [2] and the increase in the zero-strain reduced stress, $\sigma_{red,\lambda=1,calc}$, which is systematic and amounts to 20% (Table 2), both appear to be attributable, for the most part, to the diminishing finite extensibility of the double networks (a contribution, however, from an increasing orientational crystallizability cannot be excluded). The effect is an obvious consequence of the increasing prestretch, λ_R, of the first network in the unstressed double network. On the other hand, the increase in the sum of the two network-density-reflecting parameters, $(C_1 + C_2)$, with λ_R is less significant and does not exceed 9%.

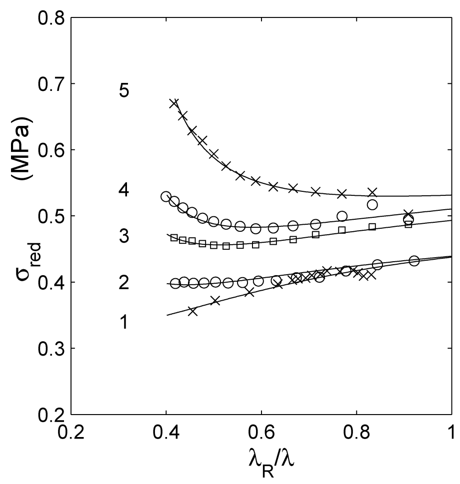

Fig. 3. Dependences of reduced stress in uniaxial extension on reciprocal stretch ratio for double networks of natural rubber. Points: experimental [2]. Curves are drawn according to the ABGI equation for parameter values given in Table 2. 1-DA0, 2-DA1, 3-DA2, 4-DA3, 5-DA4.

4. Calculation of tensile properties of double networks using the ABGIL equation

In conformity with previous treatments, it is assumed here that the mechanical response of a double network is equal to the sum of the individual contributions of the two component networks. The stress, $\sigma(\lambda)$, of the double network is then given by the sum of the stresses of the

Table 2
Parameter values of the ABGI equation for double networks (curves in Fig. 3). Experimental values of λ_X, λ_R, given by Mott and Roland [2]

Network	λ_X	λ_R	n	C_1, (MPa)	C_2, (MPa)	λ_{cm}	$\sigma_{red,\lambda=1,calc}$
DA0	1	1	0.5	0.107	0.108	(4.2)	0.439
DA1	2.86	2.52	0.5	0.128	0.082	(3.00)	0.439
DA2	3.95	3.30	0.5	0.137	0.094	2.50	0.493
DA3	4.93	4.13	0.5	0.140	0.094	2.22	0.510
DA4	5.76	4.50	0.5	0.200	0.030	2.08	0.531

first, $\sigma_1(\lambda)$, and second, $\sigma_2(\lambda/\lambda_X)$, networks [2]:

$$\sigma(\lambda) = \sigma_1(\lambda) + \sigma_2(\lambda/\lambda_X) \tag{4}$$

$\lambda/\lambda_X = L/L_X$ is the stretch ratio of the second network. The double network is unstressed when $\lambda = \lambda_R$ and this condition enables the calculation of the residual stretch ratio (permanent set, $\lambda_R - 1$) [2]:

$$\sigma_1(\lambda_R) + \sigma_2(\lambda_R/\lambda_X) = 0 \tag{5}$$

The stresses of the component networks are described here through the application of the ABGI or ABGIL equation.

The experimental stress of the first network, SA, was measured by Mott and Roland up to $\lambda = 4$ only, while the calculation of tensile properties of the double networks requires its knowledge up to much higher stretch ratios ($\sim$10.8 for DA4). In order to obtain such information, we have prepared three natural rubber networks crosslinked by 0.2, 0.3 and 0.4 phr of DCP and we have measured their stress–strain dependences under conditions similar to those used by Mott and Roland. From these three dependences plotted together with the SA data we have obtained, by interpolation, a reasonable estimate of the stress–strain dependence of the SA network up to the required high stretch ratio. Assuming $n = 0.5$, we have then evaluated its ABGIL parameters which are given in Table 3.

The stress contribution of the second network to the stress of the isotropic double network DA0 has been assumed to be determined by the stress difference between the DA0 and SA networks. From this difference the parameter values for the second network were calculated and are given in Table 3. The exact value of the finite extensibility parameter of the second network appears to be of less importance since the highest stretch ratios of the second networks in the extended double networks remain only moderate, being always much smaller than those of the first network ($\lambda/\lambda_X < \lambda$). The parameter values summarized in Table 3 were then used, together with the Mott–Roland values of λ_X (Table 2), to calculate the stress contribution of the second networks in the stretched double networks.

The application of Eqs. (1), (3) and (4) to the DA1 and DA3 networks is shown in Figs. 4 and 5, respectively. The experimental points and calculated stresses are plotted vs. the stretch ratio, λ, of the first network. Curves 1 and 2 are drawn for the first and second networks, respectively, while curves 3 are their sums. The data on the isotropic double network DA0 are included. The experimental stress-stretch

Table 3
Parameter values of the ABGIL equation for the first and second network (curves 1, 2 in Figs. 4 and 5)

	n	C_1, (MPa)	C_2, (MPa)	$\lambda_{c,a}$	$\lambda_{cm,a}$	$\lambda_{c,b}$	$\lambda_{cm,b}$	a
1st Network	0.5	0.0138	0.0218	4.053	6.5	6.644	7.9	1.25
2nd Network	0.5	0.094	0.086	–	–	–	4.2[a]	–

[a] Strain-independent finite extensibility parameter, $\lambda_{cm} = \lambda_{cm,b}$.

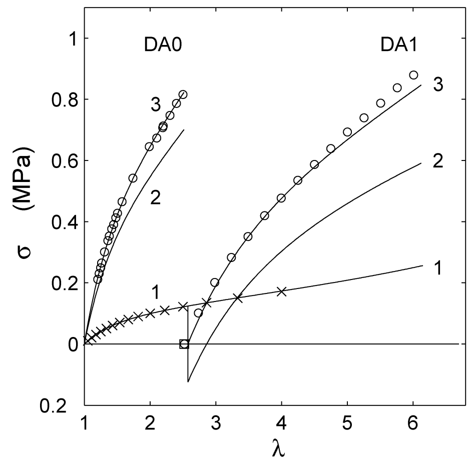

Fig. 4. Dependences of uniaxial engineering stress on stretch ratio (expressed per unit length of the unstressed first network) for double network DA1 and for isotropic double network DA0. Points: experimental [2]. Curves 1 (first network SA) and 2 (second network) are drawn according to the ABGIL (or ABGI) equation for parameter values given in Table 3. Curves 3 are sums of curve 1 and the respective curves 2.

ratio dependence of the DA1 network in Fig. 4 (points) is described by Eqs. (1) and (4) (curve 3) reasonably well. The calculated residual stretch ratio, $\lambda_{R,calc}$, which follows from Eq. (5) and is indicated by the vertical line connecting curves 1 and 2, differs from the experimental one (plotted as square) by 2% only (see Table 4). Fig. 5 shows a similar type of plot for the network DA3. A reasonably good description of the experimental data (curve 3) is obtained. It is clearly visible that, for the calculation of the uniaxial extension behavior of the composite networks the knowledge of the high-strain behavior of the first network is essential.

The stress–strain dependences were calculated for all double networks and they are compared with experimental

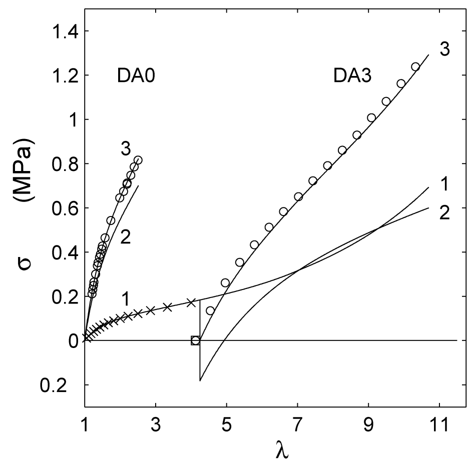

Fig. 5. Dependences of uniaxial engineering stress on stretch ratio (expressed per unit length of the unstressed first network) for double network DA3 and for isotropic double network DA0. Points: experimental [2]. Curves 1 (first network SA) and 2 (second network) are drawn according to the ABGIL (or ABGI) equation for parameter values given in Table 3. Curves 3 are sums of curve 1 and the respective curves 2.

Table 4
Experimental and calculated values of the residual stretch and calculated values of the zero-strain reduced stress $\sigma_{red,\lambda=1,calc}$

	$\lambda_{R,exp}$	$\lambda_{R,calc}$	δ^a	$\sigma_{red,\lambda=1,calc}$
DA0	1	1	0	0.439
DA1	2.52	2.575	+2.1	0.457
DA2	3.30	3.470	+5.2	0.479
DA3	4.13	4.245	+2.8	0.504
DA4	4.50	4.876	+8.4	0.529

[a] Percent difference between the calculated and experimental residual stretch ratio.

data of Mott and Roland in the coordinates of log(reduced stress) vs. stretch ratio in Fig. 6. The calculated curves are closely similar in shape to the dependences observed experimentally. Systematic experiment–theory deviations, both positive and negative, can be seen which, however, do not exceed some 5%. The calculated values of the residual stretch ratio (Table 4) tend to be somewhat higher (2–8%) than the experimental ones. Whether this is mainly due to some inadequacy of the theory or to a possible experimental uncertainty remains to be decided by further experiments.

The value of the parameter $n = 0.5$ determined in the present paper for the peroxide-crosslinked natural rubber networks is slightly higher than are the values lying in the range between -0.2 and $+0.2$ determined previously from the data on four sulfur/accelerator crosslinked natural and isoprene rubber networks. The value of $n = 0.5$ is predicted by an early version of the tube theory, which its authors Heinrich and Straube [16] characterize as a simple attempt to simulate chain-constraining effects. In quite a recent paper, Rubinstein and Panyukov [17] developed a new molecular model, designated as the slip-tube model, which combines and generalizes several ideas introduced over the years in the field of the rubber elasticity. The exact solution for the stress is obtained using numerical calculations but the reduced entanglement stress for the uniaxially deformed network can be satisfactorily approximated by the function $F \equiv (\sigma_{red} - G_c)/G_e = 1/(0.74\lambda + 0.61\lambda^{-0.5} - 0.35)$ where G_c and G_e are the phantom and entanglement contributions to the elastic modulus. The exact solution for the entanglement part of the reduced stress (points) is compared with the approximate expression F in Fig. 7 (thin line). In the same graph, the corresponding function following from the ABGI equation, Eq. (1) for $n = 0.5$ and $\lambda_{cm} = \infty$, is drawn (thick line). It is rather surprising to see that the two widely differing models lead to predictions that are almost identical. The description obtained with $n = 0.4$ (not shown here) is even somewhat better than that obtained with the Rubinstein–Panyukov approximation F. It thus appears that the ABGI equation includes the result of the slip-tube model as one of its special cases.

5. Conclusion

The Mott–Roland experimental data on networks of peroxide-crosslinked natural rubber were compared with the ABGIL equation which is a combination of the Arruda–Boyce equation based on the Langevin elasticity theory with a constraint term calculated by different tube theories. The ABGIL equation gives a good description of the uniaxial extension/compression and equibiaxial extension stress–strain data on isotropic networks. The parameter $n = 0.5$ evaluated here using the Mott–Roland uniaxial extension/-compression data corresponds to the prediction of Heinrich and Straube [16] obtained under assumptions valid for high crosslink densities but it can be equally well interpreted using the recent slip-tube theory [17].

Using the assumption of additive contributions of the two component networks, the ABGIL equation is able to provide

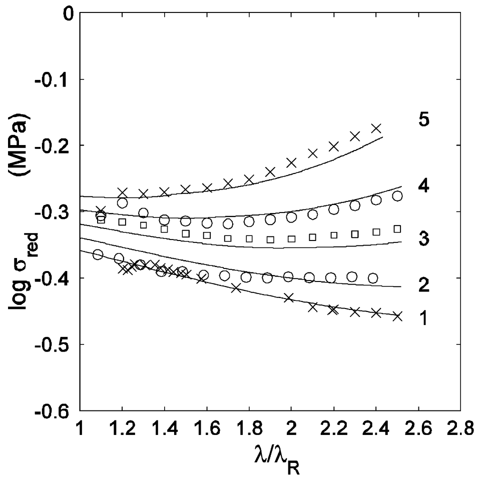

Fig. 6. Dependences of log(reduced uniaxial stress) on stretch ratio of double networks. Points: experimental [2]. Curves are drawn according to the ABGIL equation assuming additivity of contributions of the component networks for parameter values given in Table 3. 1-DA0, 2-DA1, 3-DA2, 4-DA3, 5-DA4.

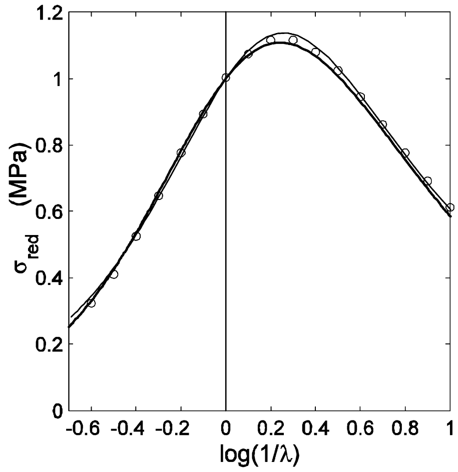

Fig. 7. Comparison of the exact solution of the slip-tube model (points) for the entanglement part of the reduced stress with the approximative expression F (thin line). The prediction of the ABGI equation for $n = 0.5$, $\lambda_{cm} = \infty$ is drawn by the thick line.

reasonable estimates of the residual stretch of double networks; these tend to be only slightly higher than the experimental ones (2–8%).

The tensile stress–strain dependences for double networks were calculated from the experimental information on the stress–strain dependences of the first and second networks. A unique set of the ABGIL parameters of the component networks was used to calculate tensile properties of all double networks prepared at different stretches during the second cross-linking. The theory-experiment deviations, although systematically positive or negative for individual double networks, do not exceed some 5%. This success of the ABGIL equation follows from its ability to model the upturn of reduced stress which is increasingly pronounced in double networks with increasing prestretch of the first network during insertion of the second network. Finite extensibility of oriented chains can be considered to be its main reason while orientational crystallization is a possible secondary factor.

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