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## Thermomechanics of bimodal end-linked polydimethylsiloxane networks with one of the chains much short<sup>\*</sup>)

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### Summary

A novel equation of state for bimodal networks with extremely short chains as solid intrusions is developed proceeding from the van der Waals theory of molecular networks. Stress-strain and thermoelastic measurements on bimodal end-linked polydimethylsiloxane model networks can satisfactorily be described. The physical reasons behind that representation will be discussed.

### Key words

Networks, bimodal, polymethyl siloxane, equation of state.

### Introduction

Bimodal networks comprised of very short and relatively long polydimethylsiloxane (PDMS) chains have been prepared and found to be usually tough elastomers (1–7). Of particular interest are systems with a short chain molecular weight which is sufficiently small as to let these chains behave like rigid elements. Understanding of the deformation behavior of these model systems is attractive from various reasons for example also related with the question to the origins behind reinforcement of networks by an active molecular filler (8, 9).

A phenomenological description of the stress-strain behavior as well as of the thermomechanics of bimodal networks letting one of the components act as rigid intrusions is given in this study. Proceeding from the van der Waals

equation of state (10–14) we derive an adequate formulation of an equation of state for heterogeneous networks of this type.

### The van der Waals-equation of state

In spite of having a system in a condensed state, it is appropriate to consider the network to be represented as a formelastic fluid letting the chains behave like “particles in a conformational gas with weak interactions” (10–13). Equipartition of energy always present, the energy of deformation is simply obtained as the sum over the total number of chains each one contributing in the statistical average the same amount of energy. Hence we arrive at the stress-strain energy density

$$W = nw(T, L, \sigma_i) \quad [1]$$

where  $n$  is the number of chains per unit volume,  $w$  the average energy of deformation of a single chain which is uniquely defined in the coordinate system  $(T, L, \sigma_i)$  for uniaxial extension experiments (12).  $\sigma_i$  are the principal stresses in perpendicular direction to the applied stress, invariant under constant pressure conditions.  $L$  is defining the actual length of the system in direction of the stress  $\sigma$  which should be given by the mechanical equation of state

$$\sigma = \frac{NkT}{V_0} \frac{\langle r^2 \rangle}{\langle r_0^2 \rangle} D[B - aD] \quad [2]$$

where  $k$  is Boltzmann's constant,  $T$  the absolute temperature,  $V_0 = L_0^3$  the volume of the unstrained system.  $D$  is equal to

$$D_m = \lambda - \lambda^{-2}. \quad [3]$$

<sup>\*</sup>) Dedicated to Professor Dr. K. Ueberreiter on his 70th birthday.

With  $\lambda_m = L_{\max}/L_0$  assigned to the maximum strain of the system which is clearly related to the limited chain extensibility, we have

$$D_m = \lambda_m - \lambda_m^{-2} \quad [4]$$

such that

$$B = D_m/(D_m - D). \quad [5]$$

The van der Waals parameter  $a$  is taking into consideration weak interactions between the chains affecting their conformational abilities.  $\langle r^2 \rangle / \langle r_0^2 \rangle$  is the well known correction term which appears necessarily in actual networks with thermal expansion and non-isoenergetical rotational isomers (14–17).

### The bimodal network

To begin with let the rigid components in the bimodal network be represented by spheres. Since the displacement components within the rigid inclusions are assumed to be zero, energy of deformation can only be stored within the long-chain parts of the network.

With the short chain components being sufficiently small and homogeneously dispersed in the elastic matrix of the long-chain network, we may define the average length of the sample  $L$  by

$$L = L_{SO} + L_R \quad [6]$$

where  $L_{SO}$  and  $L_R$  correspond to the contributions of the solid and the rubber elastic component. With the length in the undeformed body written as

$$L_0 = L_{SO} + L_{RO} \quad [7]$$

we are led to the expression

$$\begin{aligned} \lambda &= L/L_0 \equiv L_{SO}/L_0 + (L_{RO}/L_0)\lambda_R; \\ \lambda_R &= L_R/L_{RO} \end{aligned} \quad [8]$$

thus, relating the average macroscopic strain  $\lambda$  to the actual average strain in the rubber matrix  $\lambda_R$ . Denoting the volume fraction of the solid chains by

$$v_s = (L_{SO}/L_0)^3 \quad [9]$$

we obtain

$$\lambda = v_s^{1/3} + (1 - v_s^{1/3})\lambda_R \quad [10]$$

which may be cast into the form

$$\begin{aligned} \lambda_R &= (\lambda - v_s^{1/3})/(1 - v_s^{1/3}) \\ &= \lambda \frac{1 - v_s^{1/3}/\lambda}{1 - v_s^{1/3}}. \end{aligned} \quad [11]$$

We learn from these considerations that the intrinsic strain of the long-chain matrix is markedly increased on bringing the volume fraction of the rigid chains to higher values. The assumptions imply an apparent reinforcement of the bimodal network. This can easily be estimated for a Gaussian rubber matrix at higher strains. The macroscopic density of the chains should be reduced in the bimodal network in proportion to  $1 - v_s$ , thus, yielding for simple extension the asymptotic behavior

$$\begin{aligned} \sigma &\sim (1 - v_s)\lambda_R \\ &\sim \lambda(1 - v_s)/(1 - v_s^{1/3}). \end{aligned} \quad [12]$$

If we express the pure Gaussian network stress at high elongations by  $\sigma_g \sim \lambda$ , we have therefore

$$\sigma/\sigma_g \sim (1 - v_s)/(1 - v_s^{1/3}) > 1; v_s < 1 \quad [13]$$

such that an overall reinforcement results on account of the extremely heterogeneous deformation in the bimodal network under discussion.

### The van der Waals approach

Under the above circumstances the problem of finding an adequate description of the bimodal networks is mainly solved if the equation of state of the rubber matrix can be expressed by means of equation [2]. Then we are immediately led to

$$\begin{aligned} \sigma &= (N_R k T \langle r^2 \rangle / \langle r_0^2 \rangle / V_0) \\ &D_R [B_R - \langle a \rangle D_R]. \end{aligned} \quad [14]$$

With the partial volume of the rubber matrix  $V_R$  related to the total volume of the system,  $V_0$ , we may rewrite equation [14]

$$\begin{aligned} \sigma &= v_R (n_R k T \langle r^2 \rangle / \langle r_0^2 \rangle) \cdot \\ &D_R (B_R - \langle a \rangle D_R) \end{aligned} \quad [15]$$

where  $n_R = N_R/\bar{V}_R$  is defining the density of the chains in the pure rubber matrix,  $v_R = V_R/V_0$  the volume fraction of this component. The indices should indicate that according to

$$D_R = \lambda_R - \lambda_R^{-2}. \quad [16]$$

$\lambda_R$  as the intrinsic strain in the rubber matrix has to be used. Hence,  $\sigma/v_R$  is formally identical with the equation of state of a homogeneous rubber having finite extensibility of its chains which is characterized by its belonging maximum strain,  $\lambda_m$ . Yet, the interaction parameter in the bimodal system is allowed for taking values which are different from the values for pure rubber systems. This is indicated with the brackets in equation [15].

At this point, it appears profitable to check whether an adequate fit to experiments on bimodal model networks of Zhang and J. E. Mark (7) can be obtained with the aid of the above equation of state.

**First comparison with experiments**

For the pure tetrafunctional long-chain network of PDMS the ‘‘Mooney plot’’ ( $\sigma^* = \sigma/(\lambda - \lambda^{-2})$  against  $\lambda^{-1}$ ) delivers a straight line in

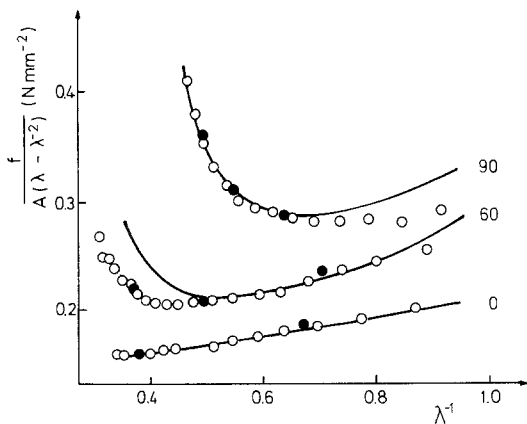


Fig. 1. Representative stress-strain isotherms for the bimodal PDMS networks in elongation at 225 K according to Zhang and Mark (7). Each curve is labeled with the mol% of the much shorter chains. The open circles locate the results gotten using a series of increasing values of the elongation  $\lambda$ , and the filled circles the results obtained out of sequence to test the reversibility. The solid lines are giving the isotherms computed with the aid equation [15] using the set of parameters listed in table 1 ( $\sigma = f/A$ ,  $A$  initial cross-section)

the medium range of elongations. This is shown in figure 1 giving the data published by Zhang and Mark (7). The bimodal networks have values of  $\sigma^*$  which increase after a linear decay at ‘‘high elongations’’, thus, giving unusually large values of the ultimate strength. Adopting the interpretation that the final upturn arises from the limited chain extensibility, it should be possible to determine  $\lambda_m$  of the rubber matrix very accurately by fitting the data with the aid of equation [13].

The results of this fit are shown in figure 1 with the solid lines. The typical shift of the characteristic upturn to smaller elongations with the number of the short chains increased, is satisfyingly be obtained with an invariant maximum strain parameter of  $\lambda_m = 5.8$ . This is justifying the basic assumption of having nearly invariant intrinsic properties of the rubber matrix in all the bimodal networks under discussion. A systematic decrease of the average interaction parameters  $\langle a \rangle$  with rising values of the short chains has been found to be necessary to arrive at the best fit of the data. The characteristics of the model networks as well as the parameter used are given in table 1.

Table 1:

(I) The number-average of the molecular weights (7)

|                      |                              |
|----------------------|------------------------------|
| $M_n$ (long-chains)  | = 18 500 g mol <sup>-1</sup> |
| $M_n$ (short-chains) | = 200 g mol <sup>-1</sup>    |

(II) The composition of the bimodal samples in mol% and Wt% of the short chains<sup>a)</sup> and the belonging  $\langle a \rangle_{exp}$

| Sample | mol% | Wt%  | $\langle a \rangle_{exp}$ |
|--------|------|------|---------------------------|
| (1)    | 60   | 1.75 | 0.36                      |
| (2)    | 75   | 3.44 | 0.34                      |
| (3)    | 85   | 6.31 | 0.31                      |
| (4)    | 90   | 9.67 | 0.28                      |

<sup>a)</sup> the sample with 80 mol% is not considered here because of its unusual stress strain behavior

(III) The parameters of the van der Waals approach

$$N_R k T \langle r^2 \rangle / \langle r_0^2 \rangle = 0.25 \text{ Nmm}^{-2}; \lambda_m = 5.8$$

$$n = 0.3; m = 5$$

Pure PDMS-system:  $a = .39$ ; others see the fourth column in the table

**The short-chain contributions**

A straight forward improvement of the above considerations can be installed by taking into consideration a certain form-anisotropy of the short chains. Having rigid rods instead of spheres, orientation contributions of the short chains necessarily appear essentially at small elongations.

In the simplest model it is assumed that all rigid rods the largest principal axis of which are fully oriented in direction of the macroscopic force, will act as active rigid molecular inclusions. The complementary fraction should behave as a type of an "active plastic filler" the behavior of which will be defined now. We learn from the scetch in figure 2 that the length of the projection of the two-dimensional representation of a rod is given by

$$l_{si} = l_{so}(\xi \sin \phi_i + \cos \phi_i) \tag{17}$$

with  $\phi_i$  is the angle between the large principal axis  $l_{so}$  and the direction of the force.  $\xi = r_{so}/l_{so}$  is adequately defining the form anisotropy of the rods. We thus find that the fraction of rods initially oriented in direction of  $\phi_i$  delivers a maximum relative transformation of the projection under discussion given by

$$\lambda_i = \frac{l_{si}}{l_{so}} = (\xi \sin \phi_i + \cos \phi_i)^{-1} \tag{18}$$

Using now the simple condition

$$\lambda_i = \lambda \tag{19}$$

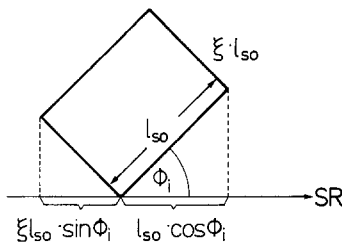


Fig. 2. Illustration of the two-dimensional cross-sectional area of a rod occupying the angle  $\phi_i$  with the axis of symmetry which is considered to be determined by direction of the uniaxial stress ( $r_{so} = \xi l_{so}$ )

that fraction of rods which is not yet fully oriented is obtained from

$$\eta(\lambda) = \int_{\phi(\lambda)}^{\pi/2} \sin \phi d\phi \tag{20}$$

provided that the rods have initially been randomly oriented. What is available for fitting is the form anisotropy parameter  $\xi$ . It is seen from table 2 that having  $\xi$ , equal to 0.5, a certain fraction of all the rods should only deliver relevant contributions in direction of  $L$  that means to the average elongation of the sample in direction of the force. This is indicated with the arrow in the third column in table 2 A.

For the sake of simplicity it is introduced now that the fraction  $\eta(\lambda)$  behave like an ideal plastic filler storing no energy of deformation. The only effect of its existence is then that the intrinsic strain in the rubber matrix is reduced in definite dependence on the "effective relative volume fraction" of rigid rods,  $v_s(\lambda)$ , given by

$$v_s(\lambda) = (1 - \eta(\lambda)) v_s(\lambda) \tag{21}$$

It is seen from table 2 B that the characteristics of  $v_R(\lambda)$  can analytically be represented by the empirical equation.

Table 2.  $v_s(\lambda) = (1 - \eta(\lambda_i)) v_{so} \cong (1 - \eta/\lambda^m)^3 v_{so}$

| A | $\phi_i$ | $1 - \eta(\phi_i)$ | $\lambda_i(\xi = 0.5)$ |
|---|----------|--------------------|------------------------|
|   | 10       | .015               | .93                    |
|   | 20       | .06                | .9                     |
|   | 30       | .13                | .9                     |
|   | 40       | .23                | .92                    |
|   | 50       | .36                | .97                    |
|   | 60       | .5                 | 1.07                   |
|   | 70       | .66                | 1.23                   |
|   | 80       | .83                | 1.50                   |
|   | 90       | 1.0                | 2.0                    |

| B | $(1 - n/\lambda^m)^3$ | $\lambda$ | $1 - \eta(\phi_i)$ |
|---|-----------------------|-----------|--------------------|
|   | 1.05                  | .44       | .48                |
|   | 1.15                  | .62       | .55                |
|   | 1.25                  | .73       | .66                |
|   | 1.35                  | .78       | .71                |
|   | 1.5                   | .88       | .83                |
|   | 2                     | 1         | 1                  |

$$n = 0.3; m = 5$$

$$v_s(\lambda) \cong v_{s0} (1 - n\lambda_m^{-2})^3; \quad [22]$$

$$0 < n < 1$$

by a proper adjustment of the parameters  $n$  and  $m$  ( $n = 0.3, m = 5$ ). The correction due to the above processes are confined to the range of small elongations ( $\lambda < 2$ ).

The shape and relative position of the load-deformation curves in the Mooney plot can now be fitted for the total set of binary networks no more having relevant discrepancies at small deformations. This can be seen by evidence from figure 3. The systematic deviations of the calculated upturn of  $\sigma^*(\lambda)$  from the data observed for lower valued shortchain component networks may be originated by very small differences in the actual structure of the network.

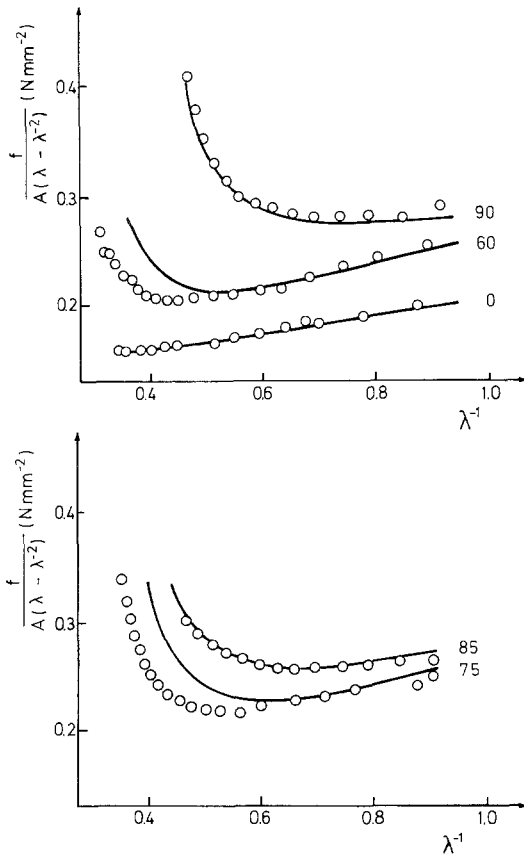


Fig. 3. Fit to Zhang-Mark's stress-strain measurements (parts of them also given in fig. 1) substantiated by means of the equations [15] and [22] employing the parameters listed in table 1 and table 2. The calculated results are given by the solid lines

### General remarks

First of all we learned from the preceding treatments that molecular reinforcement in bimodal networks having chain-components one of them of extreme shortness, is simply produced by a definite increase of the intrinsic strain in the rubber matrix. Reinforcement is obtained in all cases in spite of the decreased overall density of the long chains.

The basic autonomy of the chains in the rubber is fully maintained such that the intrinsic properties of the matrix are clearly determined by a network structure which turns out to be practically identical with that of the pure PDMS system. Only the interaction parameter is found to be dependent on the presence of the rigid short-chain elements. Energy stored in these short chains, this happens as in solids by exceedingly small strains. Contributions of these origins can thus fairly well be neglected in describing the elongation in such bimodal networks. A partial "softening" essentially at lowest elongations is considered to be attributed to orientational effects of the formanisotropic rigid elements.

### The size of the statistical segments

The question arises whether any relationship between the maximum strain value of  $\lambda_m = 6$  and the number-average of molecular weight of the long chains can be found. We want to demonstrate that we are in the position of giving such an estimate on the basis of the van der Waals approach. This explanation is deeply related to the fact that the entropy of conformation of chains of finite length does depend on the size of the statistical segments.

Let us define the average length of the chains by

$$y = n_{st} y_{st} \quad [23]$$

where  $y$  is the number of periodic units in the chain which is considered to be comprised of  $n_{st}$  statistical segments of the length  $y_{st}$ . In the limited case of a freely jointed Gaussian chain the maximum strain should be given by (8, 13, 14, 15).

$$\lambda_m = y_{st} n_{st} / y_{st} (n_{st})^{1/2} = n_{st}^{1/2} \quad [24]$$

such that we calculate from the experimental value of  $\lambda_m = 6$  an average number of statistical segments in the chains of

$$n_{st} = (\lambda_m)^2 = 36. \quad [25]$$

Hence, we see that we are led to an average molecular weight of the statistical segments in the long chains of

$$M_{st} = M_n/36 = 18500/36 = 514 \text{ g mol}^{-1} \quad [26]$$

where we have used the number-average of the molecular weight of the long PDMS-chains which has been reported by Zhang and Mark (7). We observe therefore that the length of the short chains having a molecular weight of  $M_{\text{short}} = 220 \text{ g mol}^{-1}$  (7), is apparently only half as long as the statistical segments thus bringing about justification of the basic idea of treating the short chain segments as rigid molecular inclusions. Moreover, the size of the statistical segments computed from these considerations appears to be represented by a reasonable number, at least obtained by a straight forward analysis of the shape of the stress-strain curve in the mode of simple elongation (13).

### The average interaction parameter

Of substantial interest is now the systematic decrease of the average interaction parameter  $\langle a \rangle$  in the bimodal networks under discussion when the amount of the rigid short chains is steadily risen to higher values. This phenomenon is indicating that the dynamics in the network concerned with the local exchange of momentum mainly at the junctions (11), should be affected by the incorporation of very short chain segments acting as rigid segments. Hence, because of linking two junctions by a "rigid rod", the fluctuations of the junctions involved should be reduced such that the exchange of momentum at these junctions is correspondingly improved. This is in principle agreement with the asymptotic behavior in a Gaussian network where the perfect exchange of momentum is based on the absence of any autonomous fluctuations of the crosslinks (8, 14, 15). The interpretation seems to elucidate deeper origins of the "interaction parameter"  $a$  of the van der Waals equation of state by also relating this phenomenological parameter to the fluctuations of

the crosslinks the existence of which was first discussed by Guth (14) more recently considered in the theory of phantom networks by Allegra (20) and Flory (18, 19).

In a tetrafunctional bimodal network each of the long chains is linked at each end with three other chains such that for a statistically random distribution of the components four crosslinks of different chemical compositions appear (see the sketch in fig. 4). If differently composed crosslinks possess different fluctuations  $\langle \delta r_i^2 \rangle$ , the total fluctuation may be expressed in terms of these individual contributions by

$$\begin{aligned} \langle \delta r^2 \rangle = & (1 - x_s)^3 \langle \delta r_1^2 \rangle \\ & + 3(1 - x_s)^2 x_s \langle \delta r_2^2 \rangle \\ & + 3(1 - x_s) x_s^2 \langle \delta r_3^2 \rangle \\ & + x_s^3 \langle \delta r_4^2 \rangle \end{aligned} \quad [27]$$

where  $(1-x_s)$  and  $x_s$  are giving the a priori chances for choosing a long or a short chain. Thus, the probability of having a tetrafunctional junction comprised of long chains only, is defined by  $(1 - x_s)^3$ . Replacing one of the long chains by a short segment, we consequently arrive at the probability factor  $3(1 - x_s)^2 x_s$ , etc. Relating the total fluctuations to the fluctuation of the pure PDMS network  $\langle \delta r_{\text{PDMS}}^2 \rangle$ , we are led to the following representation of the phenomenological interaction parameter

$$\begin{aligned} \langle a \rangle = a_{\text{PDMS}} [ & (1 - x_s)^3 \\ & + 3(1 - x_s)^2 x_s \eta_2 \\ & + 3(1 - x_s) x_s^2 \eta_3 + x_s^3 \eta_4 ] \end{aligned} \quad [28]$$

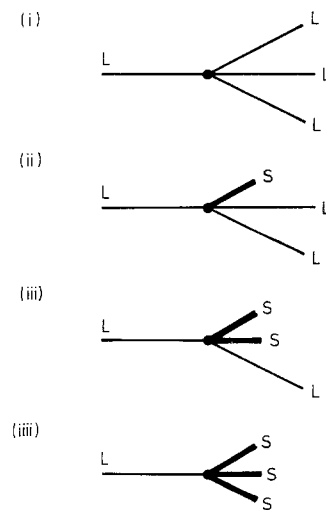


Fig. 4. Sketch of various junctions which occur in tetrafunctional bimodal networks

Table 3.  $\eta_2 = \eta_3 = 1$ ;  $\eta_4 = 0.5$ ;  $a = 0.39$ 

| $v_s$  | $\langle a \rangle_{\text{exp}}$ | $\langle a \rangle$ |
|--------|----------------------------------|---------------------|
| 0.0175 | 0.36                             | .354                |
| .0344  | .342                             | .34                 |
| .0454  | .33                              | .33                 |
| .0631  | .312                             | .319                |
| .0967  | .28                              | .299                |

calculated with the aid of equation [28]

with  $\eta_i = \langle \delta r_i^2 \rangle / \langle \delta r_1^2 \rangle \cdot a_{\text{PDMS}}$  is assigned to the interaction parameter in the pure PDMS system. Using the set of  $\eta_i$ 's listed in table 3, the interaction parameter can apparently be calculated in good accord with the experimental results (see also table 3). If the given representation of letting the fluctuations of the crosslinks be determined upon its composition is reasonable, then, it turns out that such fluctuations should primarily be altered by junctions where all the additional segments are rigid chains ( $\eta_4 = 0.5 < \eta_2 = \eta_3 = 1$ ).

It is important to notice that in any case, having decreasing values of  $\langle a \rangle$  in bimodal networks with one of the chains being a solid short chain component, the thermomechanical stability of these systems is on principal improved (10–13).

 Table 4.  $f_b/f$  calculated with the aid of equation [31].

$$\frac{\partial \ln \langle r_0^2 \rangle}{\partial T} = 0.002 \text{ K}^{-1}, \beta_R = 3 \cdot 10^4 \text{ K}^{-1}, \beta_S = 3 \cdot 10^{-6} \text{ K}^{-1}, a = 0.39$$

| A | $v_s/\lambda$ | 1.2   | 1.25  | 1.5   | 2     | 3     | 4     | 5     | (9)  |
|---|---------------|-------|-------|-------|-------|-------|-------|-------|------|
|   | 0             | 0.805 | 0.406 | 0.277 | 0.208 | 0.173 | 0.195 | 0.237 | 0.39 |
|   | 0.0175        | 0.585 | 0.292 | 0.198 | 0.127 | 0.142 | 0.190 |       | 0.37 |
|   | 0.0344        | 0.535 | 0.270 | 0.185 | 0.143 | 0.148 | 0.192 |       | 0.34 |
|   | 0.0967        | 0.431 | 0.222 | 0.158 | 0.129 | 0.150 |       |       | 0.29 |

| B | $v_s/\lambda_R$ | 2      | 3     | 4     | 5     | 1.5   | 1.1   |
|---|-----------------|--------|-------|-------|-------|-------|-------|
|   | 0               | 0.209  | 0.173 | 0.195 | 0.237 | 0.277 | 0.805 |
|   | 0.0965          | 0.1522 | 0.128 | 0.136 | 0.158 | 0.213 | 0.    |
|   | $\nu$           | 0.72   | 0.74  | 0.70  | 0.67  | 0.77  | 0.73  |

$$\nu = (f_b/f)_{\text{bimod}} / (f_b/f)_{\text{PDMS}}, v_s = 0.0967$$

## The thermo-elasticity

With the parameters listed in table 4 we arrive at the fit to the force-temperature data of the bimodal system with  $v_s = 0.0344$  reported by Zhang and Mark (7). In the calculations shown in figure 5, we used the constitutive equations [15] letting the ratio of the mean square roots be

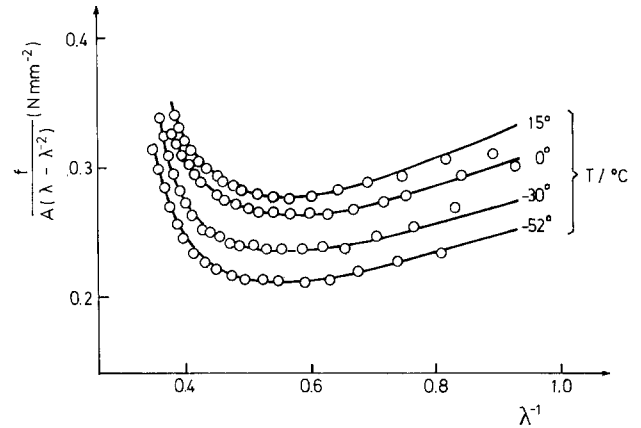


Fig. 5. Typical results of stress-strain isotherms for networks containing 75% of short chains at the temperatures indicated which each of the curves. The solid lines are computed with the aid of the equations [13] and [22] employing the parameters:  $\lambda_m = 6.3$ ;  $\langle a \rangle = 0.342$ ;  $n = 0.3$ ;  $m = 5$ ;  $N_R k T \langle r^2 \rangle / \langle r_0^2 \rangle = 0.25 \text{ N mm}^{-2}$  at  $T = 225 \text{ K}$

independent upon temperature. By the excellent reproduction of the data the basic assumption of considering the rubber matrix as an thermo-mechanically autonomous part of the sample (with exception of the dependence of  $\langle a \rangle$  upon the fraction of short chains) is again fully verified.

When taking relation [15] as the constitutive mechanical equation of state, its general meaning can be checked by considering the thermoelastic properties of the bimodal network. Zhang and Mark (7) obtained a characteristic decrease of  $f_e/f$  for  $\lambda = 2$ ,  $T = 225$  K in bimodal networks employing thermoelastic relations in the Gaussian approach. The question arises whether an interpretation of this effect can be given proceeding from the new equation of state to the belonging thermo-elastic relations.

From the equilibrium stress referred to the unstrained cross-section in the deformation mode of simple elongation

$$\sigma = (NKT/V_0)D_R[B_R - \langle a \rangle D_R] \quad [29]$$

we will derive the ratio of the enthalpy component  $f_b$  to the thermodynamically defined total force  $f$  employing the relation (10, 14)<sup>1)</sup>

$$\sigma_b/\sigma \equiv f_b/f = -T^2 \frac{\partial}{\partial T} (f/T)_{P,L}. \quad [30]$$

Thus, we arrive at

$$f_b/f = T \left[ \beta_0 - \frac{\bar{D}_R}{D_R} - \frac{\bar{B}_R - \langle a \rangle \bar{D}_R}{B_R - \langle a \rangle D_R} - 2\beta_R + \frac{d \ln \langle r_0^2 \rangle}{dT} \right] \quad [31]$$

with the definition

$$\frac{\partial D_R}{\partial T} \equiv \bar{D}_R = (1 + \lambda_R^{-3}) \partial \lambda_R / \partial T \quad [32]$$

where  $\partial \lambda_R / \partial T$  is equal to

$$\partial \lambda_R / \partial T = (1 - v_s^{1/3})^{-1} [v_s^{1/3} (\lambda_R - 1) (\beta_s - \beta_0) - \lambda \beta_0]. \quad [33]$$

<sup>1)</sup> On defining the Gibbs-function by means of the adequate Legendre transformation (1) in the co-ordinate system ( $T, L, \sigma$ ) with  $\sigma_s = P_0 = \text{const.}$ , equation [30] has been shown to be correct for simple extension experiments (11).

Having the linear thermal expansion coefficients of the rubber matrix and the rigid components given by

$$\begin{aligned} \beta_R &= \partial \ln L_{RO} / \partial T; \\ \beta_s &= \partial \ln L_{SO} / \partial T \end{aligned} \quad [34]$$

we are led to the expansion coefficient of the bimodal network

$$\begin{aligned} \beta_0 &= 1/L_0 (\partial L_0 / \partial T) \\ &= L_0^{-1} [\partial L_{RO} / \partial T + \partial L_{SO} / \partial T] \\ \beta_0 &= \frac{L_{RO}}{L_0} \beta_R + \frac{L_{SO}}{L_0} \beta_s \\ &= (1 - v_s^{1/3}) \beta_R + v_s^{1/3} \beta_s. \end{aligned} \quad [35]$$

Hence,  $\bar{B}_R$  becomes

$$\begin{aligned} \frac{\partial B_R}{\partial T} &= \bar{B}_R = \\ &= \frac{1}{D_m - D_R} \left\{ \bar{D}_m - D_m \frac{\bar{D}_m - \bar{D}_R}{D_m - D_R} \right\} \partial \lambda_R / \partial T. \end{aligned} \quad [36]$$

In addition we used the known relation (15)

$$\partial \ln \langle r_0^2 \rangle / \partial T = 2\beta_R. \quad [37]$$

On deriving equation [30], independence of  $\langle a \rangle$  upon temperature has been assumed what is experimentally manifested in the approximate invariance found for the slope of the linear portions in the Mooney-Rivlin plots of bimodal networks at various temperatures drawn out in figure 5.

In order to fit the calculation with the value of  $f_e/f = 0.20 \pm 0.05$  which has been found for pure PDMS systems (21, 22), the values listed in table 4 have been assigned to the parameters as indicated. In good accordance with Zhang-Mark's findings of having clearly depressed values of  $f_e/f$  in bimodal PDMS-networks (7) at  $\lambda = 2$ , we calculate correspondingly smaller ratios of  $f_b/f$  at the same elongation and temperature (see table 4 A). The decrease is chiefly related to the dependence of the total expansion coefficient upon expansion of the rigid component which has been introduced in the above calculations. If we against that substitute  $\beta_s = \beta_R$  we are led to  $f_b/f = .2097$  for the bimodal network with a volume fraction of  $v_s = 0.0967$  at  $T = 225$  K for the elongation of  $\lambda = 2$  what is indeed the same value as observed



for pure PDMS networks in contradiction to the findings of Mark et al. (7).

Hence, there are clear evidences for having short chain segments with a kind of intrinsic solid state behavior as for example their "thermal expansion". Because of being localized within the "fluctuation-volume" of the crosslinks, the short chains can apparently not behave like longer chains with their liquid-like expansion which is produced on heating by the belonging increase of the concentration of "holes". Consequently the rigid elements should be found to reduce the fluctuations of the crosslinks.

From the calculations listed in table 4 B it can readily be seen that an approximately invariant relationship of the  $(f_b/f)_{\text{bimod}}/(f_b/f)_{\text{PDMS}}$  is indeed observed when these ratios are compared at the same values of  $\lambda_R$ , the intrinsic strain in the rubber. This is again manifesting the approximate autonomy of the rubber matrix in the short range properties on deformation.

It should finally be mentioned that the value of  $\partial \ln \langle r_0^2 \rangle / \partial T = 2 \cdot 10^{-4} \text{ degree}^{-1}$  is exceedingly smaller than other values reported in literature (23). No explanation can be given for this discrepancy.

### Final remarks

For bimodal networks comprised of chains of different lengths with one of these being sufficiently short as to appear as rigid segments, the characterization of the deformation behavior can properly be based on the assumption of an "a priori autonomy" of all the chains. Their intrinsic properties are consequently independently determined such that the chains in the networks may be considered as localized autonomous units like "molecules" (10). Adopting this view it is no more strange that these "species" of the bimodal system may be distinguished by a different number of internal freedoms, thus, having in our case in addition to the fluctuating long chains, solid molecular segments without any "internal conformational abilities". Hence, when equipartition of energy is present even in the strained equilibrium states, no conformational energy of deformation will be stored if there are spheres as rigid intrusions. Deformational effects on the short chain segments are then restricted to changings in the anharmonicity of the internal interaction poten-

tials in the above treatments represented by solid-state expansion. Energy balance measurements are wanted for directly proving this interesting hypothesis.

In the presence of approximately rigid short chains the intrinsic strain in the rubber matrix is accordingly increased at least producing an apparent macroscopic reinforcement of the bimodal network. Small modifications of this model come into play for form-anisotropic solid elements because of their defined solid body rotations within the rubber matrix.

Yet, the autonomy of all the chains is not fully achieved as it is manifested by the existence as well as by the changes of the average interaction parameter in the bimodal networks under discussion. When understanding these van der Waals corrections as "weak interactions" between the long chains in the bimodal network, a reduction of these interactions is observed by incorporating rigid molecular segments four-functionally crosslinked to their neighbours. This effect is probably due to the reduction of local fluctuations at the junctions which seems in the first place be originated by that crosslinks the long chain end of which is linked with three other rigid segments. Clearly the dynamics in the exchange of momentums at the junctions which is determining the macroscopic static stress, is improved in bimodal networks under discussion.

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