

van der Waals Model for Filled Rubbers with Modified Interfacial Contacts

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Synopsis

It is shown how the global deformation mechanism in filler-loaded vulcanizates were modified by additional filler-to-matrix bonds. A quantitative description is given in terms of an extended van der Waals treatment including the formulation of a reduced mechanical equation of state. An interpretation of the Mullins softening is presented.

INTRODUCTION

To show symmetries on many planes is the reason behind the rubber's universal behavior on deformation:^{1,2}

- the strain energy is equiparted over the subsystems of deformation;
- the phantom-chain model is found to be appropriate for describing the strain energy per chain;
- finite chain length—and global interactions—have to be described with the aid of a van der Waals approach that also allows us to formulate a reduced mechanical equation of state;³⁻⁵
- rubbers behave like “elastic liquids,” thus showing no defect contributions to the strain energy at all: The strain energy is of “global origins.”

Every interpretation of stress-strain pattern of rubbers is therefore equivalent in discussing the global deformation mechanism alone.

For composites like filled rubbers additional effects come into play originated with the operation of the solid particles plunged into an elastically soft rubber matrix. Quasipermanent adhesion to the surfaces of the filler particles always granted, a definite boundary value problem comes into existence. Based on ideas of Einstein and Smallwood,⁶⁻⁸ the boundary value problem can fortunately be brought to a very universal description.^{9,10} Excellent chances are therefore given for drawing from an analysis of the stress-strain pattern how deformation mechanism and colloid structure are related.

It was found that the displacements of the filler particles were enforced into are different for different filler-to-matrix contacts.^{9,10} Two limiting cases have been studied:

- the “filler-network,” that is constituted by only linking the polymer to the filler particles so as to form rigid crosslink bunches of extremely large functionalities;
- the “filled rubber,” where solid colloid particles and crosslinked matrix contact on each other by adhesion.

Both of the composites display an inverse reinforcement: Showing at smallest strains no strengthening at all, the filler network is then observed to become continuously reinforced at elevated strains, hence behaving inversely as to what is known to happen in filled rubbers.⁹⁻²²

This paper aims to extend the state of knowledge by studying filled rubbers wherein the solid particles were additionally linked to different degrees to the matrix ("filler-network-rubber"). To come to a full description of quasistatic deformation cycles on the use of an extended van der Waals approach there is an outstanding chance of interpreting the stress-strain pattern in terms of parameters that characterize the way the elements within the composite cooperate on deformation. It should be checked whether it is possible to bring along these lines the Mullins softening to a finer understanding.

THEORY

Every interpretation of deformation in filled systems is based on the knowledge of how rubbery matrix and filler particle ensemble act on each other. What is not easily brought to a description in all details are the collective processes the filler particles themselves are submitted to. What simplifies any description is the experience that the quasistatic deformation of the composite depends uniquely on the macroscopic strain.^{9,10}

When static equilibrium is achieved, the deformation in the composite has to run such as to match the mechanical equilibrium condition

$$\langle f(\lambda_{fe}) \rangle = \langle f(\lambda_r) \rangle \quad (1)$$

with λ_{fe} and λ_r as the elastic strain parameters of the filler particle ensemble and of the rubbery matrix.

The filler ensemble is very often submitted to large plastic rearrangements, leading to the total strain

$$\lambda_{tot} = \lambda_p \lambda_{fe} \quad (2)$$

where plastic components in general increasingly exceed the tiny Hookian-type elastic deformation of the filler particles themselves.

In spite of not exactly knowing the mechanism running off in the filler-particle's ensemble, it is possible due to relation (1) to interpreting the stress-strain behavior of filler-loaded vulcanizates by only describing the response of the rubbery matrix. With the aid of the van der Waals network model,^{2,9,10} the characterization of the rubbery matrix can be made quantitative by defining the maximum chain extensibility, by characterizing global interactions, and by formulating how the intrinsic matrix strain and the macroscopic extension are related.

One point to be stressed is that the maximum chain extensibility should be determined by the configuration of the whole set of permanent crosslinks essentially embracing the bunches of filler-to-matrix bonds formed by the numerous chains which emerge from each of the solid colloid particles. Hence, for describing the deformation of filled systems two questions should be

answered:

- What are the ways of cooperation between the crosslink bunches and the rubbery matrix?
- Can this cooperation be interpreted in terms of an “equivalent network”?

When coming to a positive answer in regard to the last point every description is simplified by taking advantage of all of the known symmetries of molecular networks.

The Maximum Extensibility

For networks in use the modulus is found to uniquely be determined by the density of subsystems of deformation (in the simplest model taken to be identical with the network chains):^{1,2,9,10,23}

$$G = \beta(\rho RT/M_c) \quad (3)$$

where R is the gas constant, T the absolute temperature, and β a factor by which unknown effects on the energy storage properties should be accounted for. With the molecular weight of the stretching invariant unit, M_0 , the average molecular weight of the energy-equivalent chains, M_c , can be related to the average molecular weight of the statistical Kuhn segment, M_s , according to^{2,9,10}

$$M_c = y_s M_s = y_s \beta M_0 \quad (4)$$

where the maximum chain extensibility is then expressed by

$$\lambda_m = \sqrt{y_s} \quad (5)$$

so that the maximum strain of the network chain is believed to be approximated by the use of the Gaussian chain model.^{1,24} On the use of these definitions we are led to rewrite the modulus as given in eq. (3):

$$G = \beta[\rho RT/(y_s M_c)] = \rho RT/[(\lambda_m)^2 M_0] \quad (6)$$

For filler-network-rubbers new aspects come into play: According to Figure 1 all of the crosslinkages within a single filler-to-matrix bunch are strictly bound to the displacement of the solid particle itself. It is easily realized when the polymer matrix is not crosslinked (“filler-network”) that most of the chains of different lengths included in each of the filler-to-matrix bunches are therewith brought into states of different “conformational energies,” due to “nonaffine” conformations the tie molecules were forced into.

It is not a trivial result that we succeeded, nevertheless, in giving a quantitative description of the stress-strain curves observed during the first stretch of filler-networks with varying volume fractions of equally sized filler particles: This is equivalent as to have nearly the same type of the chain-end-to-end distance distribution in all states of deformation so that the strain

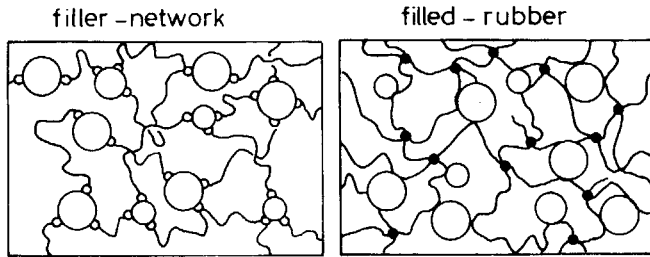


Fig. 1. Schematic drawings of (a) a filler-network and (b) a filled rubber.

energy can on the average invariably be related to an "equivalent network" assumed to be comprised of phantom chains of uniform lengths (identical with the average chain length within the filler-network).

When the rubber matrix is in addition bound to the filler particles, the question arises how the deformation energy is now stored in such "filler-network-rubbers." Having the filler-to-matrix bond bunches cooperating in a well-defined manner with the rubber, it is reasonable to believe that "energy-equivalent subsystems" were formed.

To describe the "equivalent network" it is convenient to define the density of the permanent energy-equivalent units by writing

$$\nu = \nu_r + \nu_f \quad (7)$$

where ν_r is the crosslinkage density within the rubber matrix while ν_f describes the density of the permanent crosslinks at the filler surfaces related to the whole rubber matrix. In terms of the van der Waals maximum strain parameters, we are thus led to

$$(\lambda_{me})^{-2} = (\lambda_m)^{-2} + k(\lambda_{mf})^{-2}, \quad 0 < k < 1 \quad (8)$$

λ_{me} represents the maximum strain parameter of the equivalent network, λ_m that one within the rubbery matrix while λ_{mf} describes the maximum strain parameter originated with tie molecules between next filler particles. It is then that the filler-network-rubber is additionally strengthened. The degree of additional "reinforcement" should depend on the surface density of the crosslinks attached to each of the filler particles described with the aid of the parameter k ($k = 1$ assigned to the maximum density of filler-to-matrix contacts).

The maximum strain parameter of a filler-network λ_{mf} can straightforwardly be computed when spherical filler particles with the radius R_f were homogeneously distributed across the system's volume. λ_{mf} is then predicted to depend on the volume fraction of the filler v and the surface density function $\alpha(R_f)$ according to¹⁰

$$(\lambda_{mf})^2 = \alpha(R_f) 2R_f \frac{1 - v^{1/3}}{v^{1/3}} \quad (9)$$

We learn from Table I that the maximum strain parameter in filler-network-rubbers should substantially decrease when the volume fraction of

TABLE I
The Maximum Strain Parameter of Filler-Rubber Networks ($k = 1$)

$v/\text{filler-vol. fract}$	$(\lambda_{mf})^2$	$(\lambda_{me})^2$	
0.00	Infinite	100	
0.01	654	87	$(\lambda_m)^2 = 100$
0.05	308	76	
0.10	207	68	$k = 1$
0.20	128	56	$2\alpha(R_f)R_f = 180$
0.30	89	47	

TABLE II

Prescription	DIV 50	A	B	C	D	E
Perbunan 3307		100				
Zinkoxide active		4				
ASM DDA		1				
Stearin-acid		1				
Plasticizer N 61		15				
Vulkasil N		30				
Si A 189		—	0.75	1.5	2.25	3.0
κ		0	0.25	0.5	0.75	1.0
Accel. J		3.2				
Accel. MBIS		1.65				
Rhenocure S		1.5				
Vulcanometer						
160°C (t_{10}, t_{75})		11.5/27.5	7.5/18.6	3.6/13.8	2.3/9.90	1.8/7
Vulcanization 165°C		35'	25'	20'	15'	10'

equally sized filler particles is increased whereby each of the filler particles is assumed to be linked to its maximum degrees ($k = 1$).

It would be extremely satisfactory if the apparent modulus would correctly be predicted on the use of

$$G = \rho RT / [M_0(\lambda_{me})^2] = G_0 / (\lambda_{me})^2 \quad (10)$$

The assumption would therewith be justified that the global kinetical energy within the equivalent network is equiparted across the effective subsystems of deformation. The apparent modulus shows then the "classical symmetry of being proportional to the total density of the subsystems." On saying this, one has to keep in mind that the density of the subsystems of deformation within the equivalent network is no more given by the number of chains present: "Tie molecules" between the filler particles operate as additional "functional elements" comprising numbers of chains which run as subsystems within the rubbery matrix too.

From this consideration it comes out clearly that

- the modulus of networks can only be related to the density of the actual chains if there is a unique "functional network structure" wherein chains operate as the subsystems of deformation without forming clusters linked by tie molecules.

The Interaction Parameter of the Filler–Network Rubber

Chemical crosslinks bound to the filler surface cannot fluctuate at all.^{9,10} These crosslinks do not contribute to global interactions within the rubbery matrix. When now relating the van der Waals correction term to the representative subsystem of deformation, the average global interaction parameter of the filled-network–rubber should become reduced since it has been shown that the van der Waals interaction parameter disappears in filler-networks (constituted by nonfluctuating filler-to-matrix-bond bunches).

To arrive at an explicit formulation of the average interaction parameter, we ask of the relative fraction of each of the filler–surface crosslinks

$$x = v_r / (v_r + v_f) = 1 / \left[1 + k(\lambda_m / \lambda_{mf})^2 \right] \quad (11)$$

Since the fluctuation of crosslinks is found to be unaffected by the presence of the filler particles,¹⁰ the average interaction parameter is then straightforwardly given by

$$\langle a \rangle = x a_r \quad (12)$$

where a_r is taken to be the interaction parameter of the unfilled rubber matrix. For filler-networks without any global interaction,⁸ we are consequently led to

$$\lim_{k \rightarrow 1} \langle a \rangle = 0 \quad (13)$$

while for filled rubbers we are led to the trivial identity

$$\lim_{k \rightarrow 0} \langle a \rangle = a_r \quad (14)$$

The Intrinsic Strain within the Rubbery Matrix

The soft rubber matrix must be “overstrained” for satisfying the condition of mechanical equilibrium as formulated by eq. (1). To achieve a mathematical description, it is profitable to first ask of the asymptotic situations at minimum and maximum strain. These limits fixed, the full mathematical formulation of the intrinsic strain is then easily disposed of.

To consider the rubbery matrix as incompressible is the condition by which in the mode of simple extension a single independent strain variable is left. This independent variable is reasonably chosen to be identical with the intrinsic strain in the rubbery matrix λ_r . Its analytical formulation is given by^{9,10}

$$\lambda_r = (\lambda - u_i) / (1 - u_i) \quad (15)$$

[with u_i characterizing the deformation mode i . For both of the limited systems, the filler-network and the filled rubber, u_i is then written as

$$\begin{aligned} u_f &= [(\lambda - 1) / (\lambda_{mf} - 1) v]^{1/3} && \text{filler-network } (u_i = u_f) \\ u_r &= (v / \lambda)^{1/3} && \text{filled rubber } (u_i = u_r) \end{aligned} \quad (16)$$

The inverse deformation behavior for both of the network types is easily deduced from these relations: Not showing reinforcement at smallest strains is typical for filler networks, at raised strain becoming increasingly strengthened so as to finally approximate the "Bueche mode":

$$\lambda_r = (\lambda - v^{1/3}) / (1 - v^{1/3}) \quad (17)$$

A filled network, on the other hand, shows fading reinforcement approaching at largest strains the affine transformation of the composite.⁸

Behind that inversed deformation behavior, there are different deformation mechanisms originating with modified transformation modes of the filler particle's ensemble. It is indeed reasonable a finding that permanent filler-to-matrix-bond bunches in filler-networks induce operations different from the mechanism as observed in filled rubbers where the filler-to-matrix contacts are made by adhesion.

It suggests itself to assume that the filler-network-rubber should display an "intermediate" behavior. The simplest ad hoc assumption is to postulate additivity in the extensive variables as defined by

$$u_{fr} = [xu_r + (1 - x)u_f]^{1/3} \quad (18)$$

which might be taken as consequent within the logical demands of the equivalent network idea: a weighted superposition of the mechanism of both of the limiting models.

The Einstein-Smallwood Correction

It has been thoroughly discussed that the above "two-phase approach" neglects the physical consequences which unevitably arise when filler and polymer matrix act on each other by adhesion. To describe this boundary value problem, we take advantage of the ingenious treatments of Einstein^{6,7} and Smallwood,⁸ along these lines being led to

$$\lambda_{mfv} = \lambda_{mf}(1 + Cv)^{-1/2} \quad (19)$$

where C is the universal Einstein coefficient. For spherical colloid particles, C is assigned to the value of 2.5.^{6,7,9,18} What is extremely satisfactory is the finding that the "Einstein-Smallwood correction" as defined in eq. (18) seems indeed not to depend on the filler particle size in excellent accord with the demands of this mean-field approach. Form anisometry of the particles determines to which value the Einstein parameter C should be assigned.

The van der Waals Equation of Filler-Network-Rubbers

We are now in the position to formulate the van der Waals equation of state for filler-network-rubbers in the mode of simple extension^{9,10}

$$f = G_0 [(\lambda_{mfv})^{-2}] D_r \left((1 - D_r/D_{mfv})^{-1} - \langle a \rangle D_r \right) \quad (20)$$

where

$$\begin{aligned} D_r &= \lambda_r - (\lambda_r)^{-2} \\ D_{mfv} &= \lambda_{mfv} - (\lambda_{mfv})^{-2} \end{aligned} \quad (21)$$

The network is reinforced in a twofold manner, on the one hand, due to the Einstein–Smallwood factor $1 + Cv$, and, on the other hand, due to having the rubbery matrix “overdrawn” according to

$$\lambda_r = (\lambda - u)/(1 - u) \quad (22)$$

Anticipating the later treatment of the Mullins softening, we like to stress here that the above eq. (20) is only appropriate for describing the first stretch of a filler-network–rubber system.

THE REDUCED MOONEY REPRESENTATION

A discussion of the stress–strain behavior of filled systems in terms of a reduced mechanical equation of state provides some interesting and novel insights.

To derive the reduced mechanical equation of state in the mode of simple extension, let us rewrite the equation

$$\begin{aligned} f/G^+ &= (\lambda_{mfv})^{-2}(1 + Cv)TD_{mfv}\mu/(1 - \mu) \\ &\quad - (\lambda_{mfv})^{-2}(1 + Cv)\langle a \rangle T(D_{mfv})^2\mu^2 \\ \mu &= D_r/D_{mfv} \end{aligned} \quad (23)$$

by introducing the symbols

$$\begin{aligned} T^+ &= (1 + Cv)TD_{mfv}(\lambda_{mfv})^{-2} \\ a^+ &= (1 + Cv)\langle a \rangle T(D_{mfv})^2(\lambda_{mfv})^{-2} \end{aligned} \quad (24)$$

We are then led to

$$f^+ = f/G^+ = T^+\mu/(1 - \mu) - a^+\mu^2 \quad (25)$$

where

$$G^+ = \rho R/M_0 \quad (26)$$

Asking of the critical parameters, we have to seek these variables from the conditions

$$\begin{aligned} df^+/d\mu &= T^+(1 - \mu_c)^{-2} - 2a^+\mu_c = 0 \\ d^2f^+/d\mu^2 &= 2T^+(1 - \mu_c)^{-3} - 2a^+ = 0 \end{aligned} \quad (27)$$

here from being led to

$$\mu_c = 1/3, \quad (f^+)_c = (T^+)_c/8 = a^+/27, \quad (T^+)_c = 8a^+/27 \quad (28)$$

From the last one of these relations we derive with the use of eqs. (23) that for each critical system the condition

$$8\langle a \rangle D_{mfv}/27 = 1 \quad (29)$$

must be fulfilled. Accepting that the temperature dependence of the stretching invariant unit (M_0) is comparatively irrelevant, we come to the very interesting condition

$$d\langle a \rangle/dT \approx 0 \quad (30)$$

That means that

- the interaction parameter in the van der Waals equation of state should nearly be independent on the temperature, the "fluctuation term" is growing in proportion to temperature according to

$$a^+ = (1 + Cv)\langle a \rangle T \quad (31)$$

Defining the reduced variables by

$$d = \mu/\mu_c = 3\mu \quad (32)$$

$$t = T^+/(T^+)_c = T/T_c \quad (33)$$

$$f = f^+/(f^+)_c \quad (34)$$

the reduced mechanical van der Waals equation of state is straightforwardly derived to be given by³⁻⁵

$$f = d [8td/(3 - d) - 3d] \quad (35)$$

By means of theoretical data of filler-network-rubbers calculated under the condition to keep the maximum strain parameter λ_{mfv} constant, it is illustrated in Figure 2 that thermodynamical stabilization is brought about when the surface density of the filler crosslinks is raised to higher values. Growing distance to the critical stress-strain curve ($t = 1$) is a simple measure of increasing stability.

Due to these effects the slope in the reduced stress strain curves is depressed, very soon changing its sign to negative values.

- The apparent Mooney-Rivlin coefficient C_2 can be shown to be uniquely related to both of the global van der Waals parameters λ_{mfv} and a . The C_2 determination at constant degrees of crosslinking can thus be used for characterizing the average crosslink fluctuation uniquely determined by the average functionality of the crosslinkages.^{10, 25, 26}

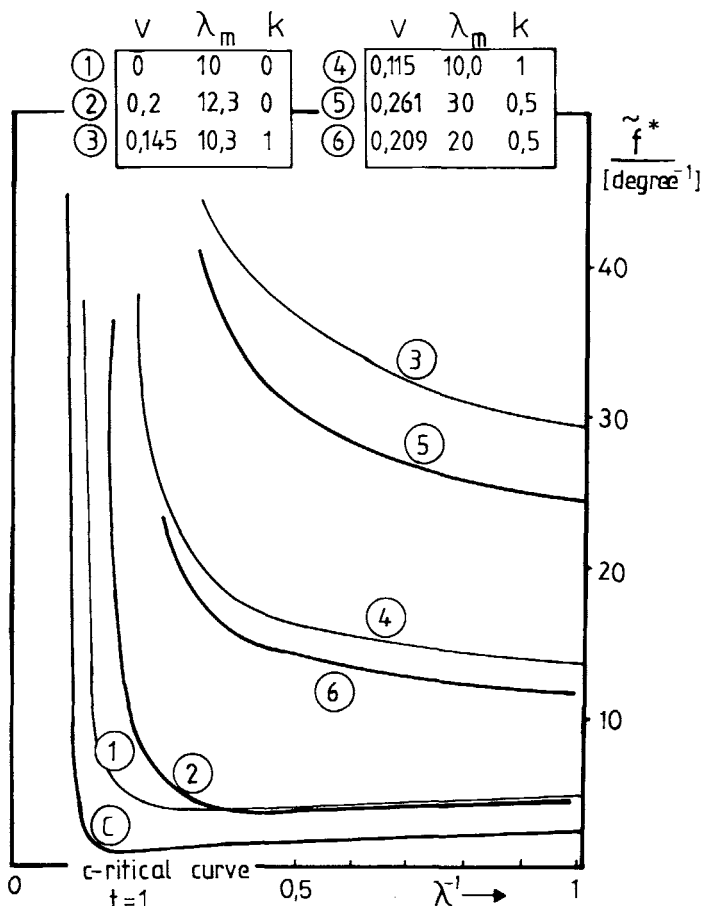


Fig. 2. Filler-network-rubbers stress-strain curves in terms of the reduced variables calculated with the aid of eq. (35) on the use of the parameters: $\alpha = 0.15$; $G_0 = 40$ MPa; $C = 2.5$; all the other parameters are indicated in the figure.

To have the crosslinks fluctuations as destabilizing factor in van der Waals networks (filled or unfilled) leads to the interesting consequence that for sufficiently large fluctuations a phase-transition is predicted to occur.² Disregarding thermal expansion and compressibility, the entropy only “jumps” at the phase transition. This also occurs in filled systems so that it is elucidated that such heterogeneous colloid-systems show the same topological phase-transition phenomena as a single component system.

A consequence of general interest is to have shown on hand of our model that energetical attraction is not necessary for getting a phase transition: The “nonstable van der Waals network” represents an outstanding model system which might undergo a phase transition that purely originated with entropic origins.

STRUCTURE-STRESS-STRAIN CORRELATION

Increasing average crosslinking densities per filler particle were described with increasing values of the parameter k defined in eq. (6). Starting with the

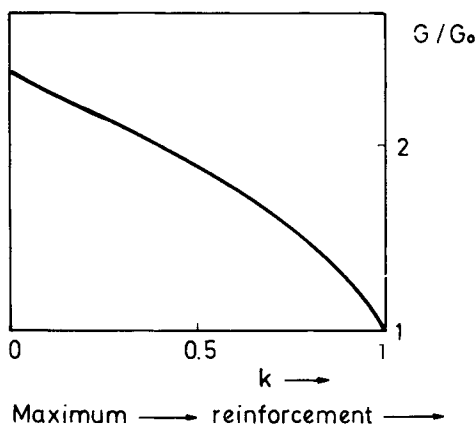


Fig. 3. Apparent small-strain modulus of filler-network-rubbers with an invariant total number of crosslinks against κ , the fraction of the filler-to-matrix crosslinks per filler surface: $c = 2.5$; $\alpha = 0.2$; $\lambda_{mf} = 9.22$.

maximum modulus at $k = 0$ (filled rubber mode), the apparent small-strain modulus of filler-network-rubbers is then continuously depressed to lower values, reaching its minimum in the filler-network limits for $k = 1$ (see Fig. 3).

At large extensions, this situation is found to be inverted what is demonstrated with the crossing over in the reduced Mooney plot drawn out in Figure 4 calculated with the aid of

$$f/[D(1 + Cv)TG_0] = (D_r/D) \left[(1 - D_r/D_{mf_0})^{-1} - \langle \alpha \rangle D_r \right] \quad (36)$$

Hence we are led to the statement:

- The global properties for rubbers with the same density of permanent crosslinks and the same filler-volume fraction can be manipulated by changing the fraction of permanent contacts to the filler particles.

The resulting reduced stress-strain patterns lie in between the limits that are fixed by both of the “antipodes,” the filler-network and the filler rubber (see Fig. 4).

It is important to realize that

- the apparent small strain modulus can only uniquely be related to the actual density of the permanent crosslinks if the network is homogeneous.

By this result it is suggested that global inhomogeneties in real networks that operate on principles similar to filler particles might be one of the reasons behind the problem of not always being able to uniquely relate the modulus to the density of permanent crosslinks.

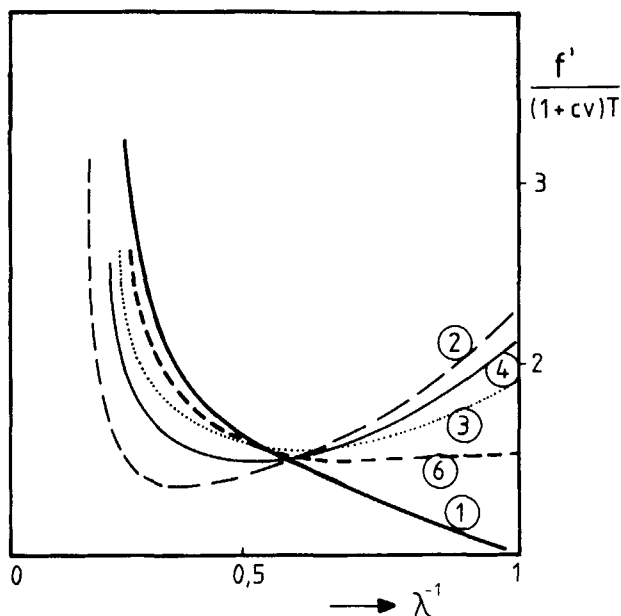


Fig. 4. Mooney plot of various filler-network-rubbers with a constant total number of permanent crosslinks against the fraction of "filler bounds." The parameters as given with Figure 2.

THE MULLINS EFFECTS

A pronounced hysteresis observed in the first stress-strain cycle of filler rubbers (Fig. 5) manifests irreversible processes even for experiments that were done under quasistatic conditions.^{9,11-22} The next constant strain rate cycles are then always nearly reproduced showing in general a weak hysteresis mainly originated with relaxation (see Fig. 5).

A phenomenological treatment of this effect was given by Mullins et al.^{15-20,27} while Bueche has offered an molecular-statistical interpretation based on the discussion of tearing loose or breaking of tie molecules between filler particles.^{11,14}

Stretching microcalorimeter investigations give strong evidence that the rubbery matrix is under quasistatistical conditions brought into the state of internal equilibrium.²⁸ The Mullins softening must therefore be originated with irreversible global constraints developed during the first stretch.

The Intrinsic Strain

As a concrete model, let us assume that the filler particle's ensemble is irreversibly brought into a configuration that should stay invariant on shrinking and redrawing so as to keep the strain-induced filler ensemble's processes characterized by a fixed ratio of the plastic to the elastic components unaltered. In terms of the intrinsic strain as defined in the eq. (22), we should thus believe that it is appropriate to write

$$\lambda_{r-} = (\lambda - u_-)/(1 - u_-) \quad (37)$$

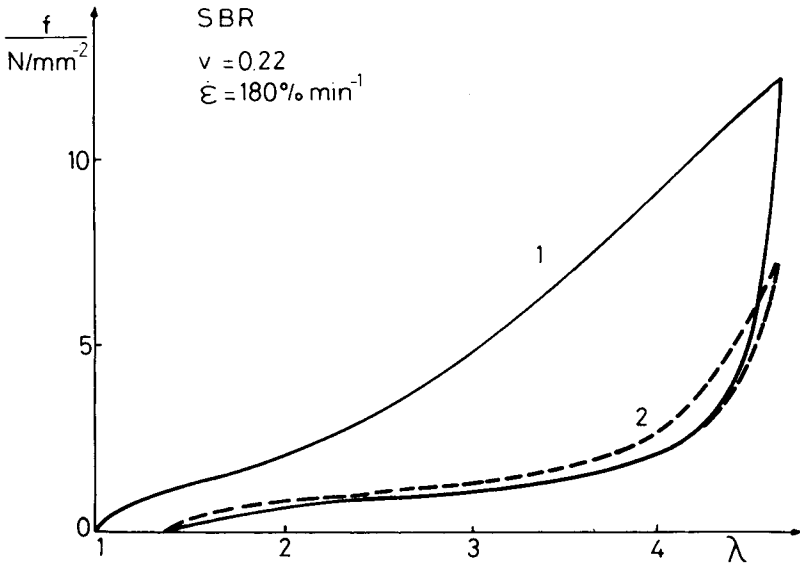


Fig. 5. Stress-strain cycles of a styrene-butadiene rubber at room-temperature.

where

$$u_- = \left\{ \nu \left[x/\lambda_{\max} + (1-x)(\lambda_{\max} - 1)/(\lambda_{mf\nu} - 1) \right] \right\}^{1/3} \quad (38)$$

Since λ_{\max} and $\lambda_{mf\nu}$ are constant for $\lambda \leq \lambda_{\max}$, all of these processes are understood as a response of a composite showing a quasipermanent global structure. The “history of the prestretch” up to λ_{\max} seems to be frozen in due to constraints which cannot be unlocked by weak inherent rubber-elastic retracting forces.

After the first unloading (see Fig. 5), a small remanent strain is observed to be left. Since no distinct understanding in terms of our model is available, we account empirically of this effect by extending eq. (36) to the form

$$\lambda_{r-} = (\lambda - \lambda_b - u_-)/(1 - u_-) \quad (39)$$

where λ_b has to be drawn from the experimental results.

The Smallwood-Einstein Effect

To arrive at a quantitative interpretation of the Mullins softening, it turns out to be necessary to consider another irreversible phenomenon. We assume that the bound rubber will also be only deformed during the first stretch, being left on shrinking or redrawing under the condition of $\lambda \leq \lambda_{\max}$ in a frozen state of deformation. Strain energy is thus believed to be stored within glassy layers encapsulating each of the filler particles. In the first stages of shrinking, a minor reorganization assumed to be just allowed, fading quickly out with increasing degrees of shrinkage, these processes may be described with the aid of

$$C_- = C \exp[-\delta(\lambda_{\max} - \lambda)] \quad (40)$$

where δ is considered a phenomenological parameter that must be adjusted to get a best fit to the experiments.

COMPARISON WITH EXPERIMENTS

The quality of fitting calculations to experiments with the aid of the eqs. (21), (38), and (39) is to be seen by evidence from the plots drawn out in Figure 6.

According to our representations, the Mullins softening is interpreted by three irreversible effects

- irreversible elements in the strain-induced reshuffling of the filler-particle's configuration,
- the peculiar "one-way" deformation of the bound rubber,
- the effects behind the remanent strain.

The interpretation presented applies equally well in all cases including rubbery systems with a very different colloid structure. The bound rubber is always present, apparently operating in a very universal manner:

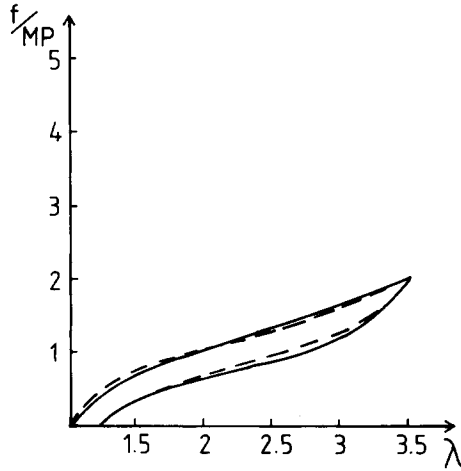
- The Einstein–Smallwood effect is well represented by a mean-field approach showing no particle-size dependence in the maximum strain modification.
- The properties within the interfacial layers do not depend on the kind of the interfacial contacts whether there are permanent chemical bounds, contacts by adhesion, or a mixture of both of them.
- The effects are identical and independent of the type of the global deformation mechanism.
- To freeze deformed states of matter seems to represent a general phenomenon.²⁹

Fully analogous arguments can be put forth in discussing the filler particle's transformation. Constraints were developed which are quasipermanently trapped after the first stretch so that on shrinking or redrawing there exists a quasipermanent colloid structure provided that the strain is kept below the maximum strain enforced with the first stretch.

It is much surprising that the totality of the deformation mechanism in rubber–fillers networks can be described on the basis of two limiting models, the filled rubber and the filler-network. It is that permanent subsystems of deformation become operative in any case such that an equivalent network can always be defined showing symmetries like homogeneous networks (as for example gaslike conformation behavior or the equipartition of kinetical energy on the global level). The density of the subsystems of deformation is not in each case represented by the chains themselves. In filler-network–rubbers network, the "matrix chains" store additional energy as segment of a "tie molecule" which operates predominantly between the next filler particles. Filler-network–rubbers show therefore global mechanism of a more complex nature. Every modification of the fraction of the filler-to-matrix bonds brings about global system properties lying between the limits as fixed by the filled rubber and the filler-network.

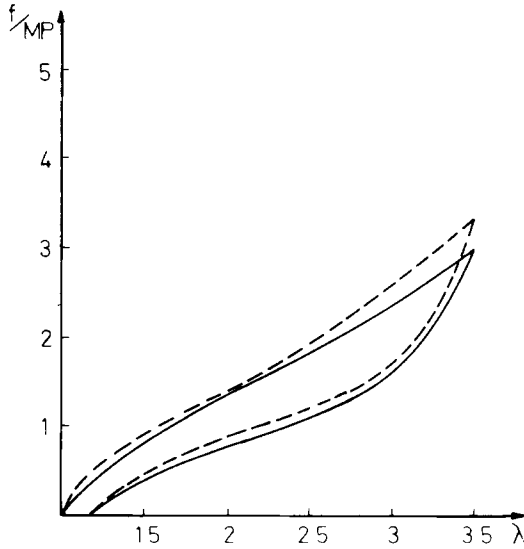
30: Vulkanil N (BET 130 g/m²)

$$k = 0$$



(a)

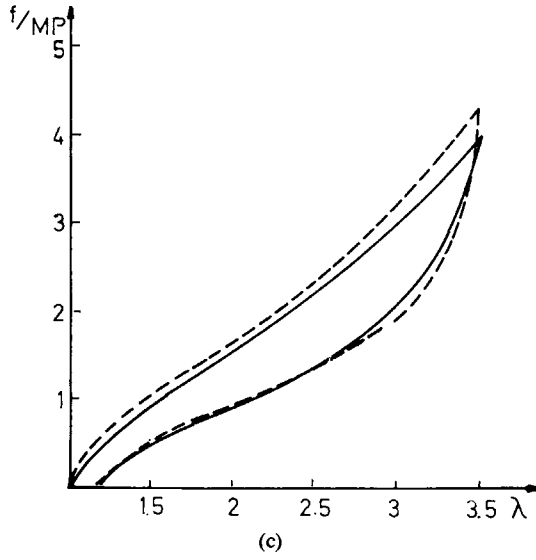
$$k = 0.25$$



(b)

Fig. 6. Stress-strain cycles of filler-network-rubbers with a constantly crosslinked natural-rubber matrix with additional filler-to-matrix bonds. The fraction of these bonds related to its maximum value is indicated with each of the drawings (parameter k): (---) calculated with the aid of eqs. (19), (39), and (40) on using the parameters $\delta = 5$; $\alpha(R_f) = 120$; (—) found.

$k = 0.5$



$k = 0.75$

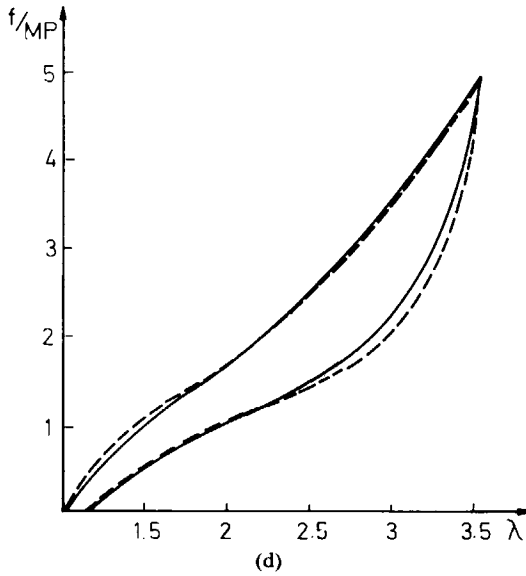
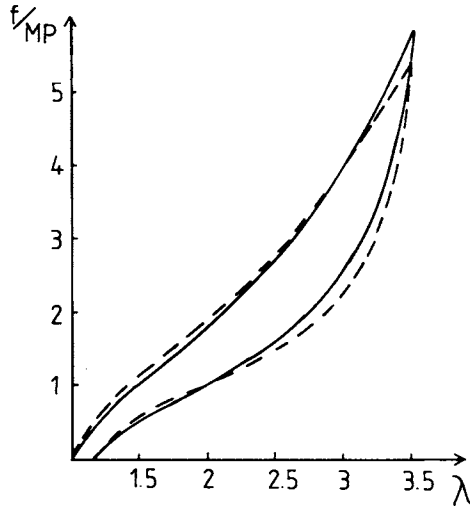


Fig. 6. (Continued from the previous page.)

$$k = 1$$



(e)

Fig. 6. (Continued from the previous page.)

The quasistatic constrained equilibrium states known, hope is engendered that the time-dependent phenomena could finally be interpreted by extending and applying the generalized relaxation theory developed recently.³⁰

FINAL REMARKS

Our description of the stress-strain pattern of filler-rubber networks brings out a set of interesting principles.

The question arises as to how a molecular interpretation of cooperative deformation mechanism in rubbery composites could be developed. It is in evidence that general principles should be implied. It could for example be suggested that the deformation mechanisms-structure relationship, its being uniquely related to the macroscopical strain, could be understood by the use of an extremum principle. To define the affine transformation as the minimum strain-energy mode of a filler-network appears to be self-evident, but the question is automatically provoked as to how the maximum reinforcement in the Bueche mode can be brought to a finer understanding. Clearly, a molecular interpretation of the "one-way constraints" is wanted, also since stretching-microcalorimeter measurements give evidence that the molecular-statistical model as given by Bueche^{11,14} cannot correctly account for the experimental energy-balance characteristics.

On seeking a molecular model interpretation, the treatments presented here may be helpful, essentially also due to their identifying the two global effects

that seem to govern the deformation phenomena:

- The filler–matrix cooperation with its quasistatically irreversible individual mechanism determined by the type of the permanent crosslink configuration (crosslink bunches implanted into a polymer network);
- The irreversible Einstein–Smallwood bound-rubber effects.

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References

1. L. R. G. Treloar, *The Physics of Rubber Elasticity*, 3rd ed., Clarendon, Oxford, 1975.
2. H. G. Kilian, *Polymer*, **22**, 209 (1981).
3. T. Vilgis and H. G. Kilian, *Polymer*, **24**, 949 (1982).
4. H. G. Kilian, *Colloid Polym. Sci.*, **260**, 985 (1982).
5. H. G. Kilian, *Kautschuk Gummis. Kunststoffe*, **36**, 959 (1983).
6. A. Einstein, *Ann. Phys.*, **19**, 289 (1906).
7. A. Einstein, *Ann. Phys.*, **34**, 581 (1911).
8. H. M. Smallwood, *J. Appl. Phys.*, **15**, 758 (1944).
9. H. G. Kilian, *Kautschuk Gummi Kunststoffe*, **39**, 689 (1986).
10. H. G. Kilian, H. Schenk, and S. Wolff, *Colloid Polym. Sci.*, **265**, 410 (1987).
11. F. Bueche, *J. Appl. Polym. Sci.*, **4**, 107 (1960).
12. L. Mullins, *Rubber Chem. Technol.*, **46**, 847 (1948).
13. G. Kraus, *Adv. Polym. Sci.*, **11**, 155 (1971).
14. Z. Rigbi, *Adv. Polym. Sci.*, **36**, 21 (1980).
15. L. Mullins and N. R. Tobin, *Rubber Chem. Technol.*, **30**, 355 (1957).
16. L. Mullins and N. R. Tobin, *J. Appl. Polym. Sci.*, **9**, 2993 (1965).
17. L. Mullins, *Rubber Chem. Technol.*, **42**, 339 (1969).
18. J. B. Donnet and A. Voet, *Carbon Black, Physics of Elastomer Reinforcement*, Dekker, New York, 1976.
19. E. M. Dannenberg, *Rubber Chem. Technol.*, **30**, 355 (1975).
20. A. F. Blanchard and P. Parkinson, *Ind. Eng. Chem.*, **44**, 799 (1952).
21. A. F. Blanchard, *J. Polym. Sci.*, **14**, 355 (1954).
22. J. A. C. Harwood, L. Mullins, and A. R. Payne, *J. Appl. Polym. Sci.*, **9**, 3011 (1965).
23. H. G. Kilian, H. F. Enderle, and K. Unseld, *Colloid Polym. Sci.*, **264**, 1 (1986).
24. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
25. T. Vilgis and H. G. Kilian, *Colloid Polym. Sci.*, **264**, 137 (1986).
26. I. Soës, candidate thesis, Mühlhausen, Université de Haute Alsace, (1987).
27. H. G. Kilian and H. Schenk, *Colloid Polym. Sci.*, (1986), to appear.
28. H. G. Kilian and T. Vilgis, *Colloid. Polym. Sci.*, **262**, 691 (1984).
29. H. F. Enderle, H. G. Kilian and T. Vilgis, *Colloid Polym. Sci.*, **262**, 696 (1984).
30. H. F. Enderle, H. G. Kilian and T. Vilgis, *Coll. Polym. Sci.*, **262**, 696 (1984).

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