Thermodynamics of swelling in unfilled and filler-loaded networks*)

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Abstract: Within the framework of the van der Waals-network model a consistent interpretation of swelling and simple extension in differently crosslinked networks is presented. It is observed that the excess parameters in the Staverman–Koningsveld–Kleintjens version do not depend on the degree of crosslinking. Swelling of filler-loaded rubbers shows universal features because of not depending on the type and the properties of the filler. By introducing the Einstein–Smallwood modification in an adequate manner one understands this phenomenon without any further parameter adjustments. It is the consequence of having "quasi-permanent" filler-to-matrix contacts that are not modified in presence of solvent molecules. The excess-parameters in the swollen matrix are not affected. The entropy elastic stress due to the swelling induced deformation of the matrix is apparently too small as to enforce chain-slippage. The strength of the adhesion of the polymer inhibits filler-to-solvent contacts. These results defend the mean-field treatment of the boundary problem as presented by Einstein–Smallwood, and allows a valuable proof of the thermodynamics of swelling in networks.

Key words: Van der Waals-networks; swelling of networks; filler-loaded networks; thermodynamics; Einstein–Smallwood modification

Introduction

All known theories of equilibrium swelling in networks implicate substantial simplifications [1–5]. The mixing entropy is taken to be identical with the one of a polymer solution [8, 9]. In the classical Flory–Rehner approach the network is, in addition, represented as a single infinitely large molecule. It is, on the other hand, clear that the properties of real networks are controlled by the finite length of chains [1–6]. It is significant that it was found that the autonomy of network chains remains relatively large. This is the reason why modified single-chain models are successful [1–5]. In this situation, it appears to be interesting to prove whether it would not be consequent to define the network chains themselves as thermodynamic components to which the free enthalpy of mixing

should be related [4, 5]. If this approximation holds true, this represents another interesting extension of classical thermodynamics [7–9]: A swollen network as a super macromolecule should display nearly the same distinguishable configurations as a reference polymer solution without crosslinks and with a molecular weight distribution which is identical with the chain length distribution in the network. The "limited localization" of statistically indistinguishable chains should not matter so much provided that the chains are long enough, essentially, in comparison with the size of the solvent molecules.

In this paper this idea is condensed by linking thermodynamics of polymer solutions and the van der Waals network theory. We introduce, in addition, the interaction parameter as formulated by Koningsveld et al. [10]. Equilibrium swelling data

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*) Dedicated to Prof. H. H. Kausch on the occasion of his 60th birthday

obtained for differently crosslinked unfilled and filled networks are then studied for proving the reliability of the model.

Theory I: unfilled networks

The chemical potential of the solvent

We apply the thermodynamics of polymer solutions in the Flory–Huggins version [1–9, 11–14]. The difference between the chemical potential of the solvent in the solution and in the pure system is defined by

$$\frac{\Delta\mu_{mix,1}}{RT} = \ln(1 - \varphi_p) + \left(1 - \frac{y_1}{y_p}\right)\varphi_p + \chi\varphi_p^2 ,$$

$$\tag{1}$$

where R is the gas constant and T, the absolute temperature. The volume fraction of the polymer may be written as

$$\varphi_p = \frac{n_p y_p}{n_p y_p + n_1 y_1} .$$

$$\tag{2}$$

y_i gives the volume of the ith component related to an arbitrary unit of reference. n_p and n_1 are the mole numbers of the polymer and the solvent. The second term on the righthand side of Eq. (1) is the activity coefficient that accounts for particle size modification of the entropy of mixing. χ is the Flory–Huggins interaction parameter.

Taking Eq. (1) as a definition of the free enthalpy of mixing in a swollen network is equivalent to treating the chains of mean length y_p as particles in spite of their being linked in the network. This unconventional treatment is justified if the equilibrium configuration of the chains does not depend on their being linked in the network. The entropy of mixing should be about the same as the one in the polymer solution of reference. Under equilibrium conditions the chains operate, on the average, as "undistinguishable particles". Hence, the interpenetration volume of only the neighboring chains matters. Within this volume it must be guaranteed that about the same solvent–polymer configurations are realized as in the solution of reference. These conditions are likely to be approximated if the network chains are not too short [8, 9]. A swollen network can then be treated as a quasi-

binary system [15] with chains of length y_p:

$$y_p = \sum_{\eta=1}^{y_{max}} x_\eta \eta ;$$

$$\tag{3}$$

x_η = mole fraction of chains of length η.

It is now an interesting step to introduce the interaction parameter in the Staverman–Koningsveld–Kleintjens version (SKK model) [10, 16]:

$$\chi = \alpha_0 + \left(\beta_0 + \frac{\beta_1}{T}\right)\frac{1 - \gamma}{(1 - \gamma\varphi_p)^2} .$$

$$\tag{4}$$

For isothermal experiments and with $\alpha_0 = 0$ the parameters β_0 and β_1 and $1 - \gamma$ can be replaced by χ_0. Equation (4) is, therefore, reduced to

$$\chi = \frac{\chi_0}{(1 - \gamma\varphi_p)^2} .$$

$$\tag{5}$$

γ is related to the ratio of the molecular surfaces σ_2/σ_1 of the components according to

$$\gamma = 1 - \frac{\sigma_2}{\sigma_1} .$$

$$\tag{6}$$

The strain energy of a van der Waals network

It is an advantage of the van der Waals network model that the strain energy W_α is analytically given in every deformation mode α [17–19]:

$$W_\alpha = -G\left[(I_{1,max} - 3)(\ln(1 - \eta_\alpha) + \eta_\alpha) + \frac{2}{3}a\left(\frac{I_\alpha - 3}{2}\right)^{3/2}\right],$$

$$\tag{7}$$

with the modulus defined by

$$G = \frac{\rho RT}{M_u \lambda_{max}^2} ,$$

$$\tag{8}$$

where ρ is the network density. M_u is the stretching-invariant unit. I_α defines the first strain invariant in the deformation mode α. When defining λ as the strain in the direction of a uniaxial stress, we arrive for simple extension at

$$I_1 = \lambda^2 + \frac{2}{\lambda}: \quad \text{uniaxial} .$$

$$\tag{9}$$

Calling the strain in a swollen network $\lambda_3 \equiv \lambda_q$ we are led to the strain invariant in the equitriaxial

mode:

$$I_3 = 3\lambda_q^2: \quad \text{equitriaxial} . \tag{10}$$

The strain invariants become identical at the maximum strain $\lambda_{\alpha,max}$, where the chains themselves are considered to be fully stretched [17, 20]. We may, therefore, always use the first strain invariant $I_{1,max}$,

$$I_{1,max} = \lambda_{max}^2 + \frac{2}{\lambda_{max}} = y_p , \tag{11}$$

which is uniquely related to the chain length parameter y_p. For $\lambda_{max} \gg 1$ we are led to the approximate relation

$$\lambda_{max} \approx \sqrt{y_p} , \tag{12}$$

which involves the maximum strain of a phantom chain of the length y_p. The function η_α is defined by

$$\eta_\alpha = \sqrt{\frac{I_\alpha - 3}{I_{1,max} - 3}} . \tag{13}$$

a is the second van der Waals parameter that accounts for global interaction between network chains. The size of this parameter depends on the functionality of the junctions. This is believed to be the consequence of having the junctions fluctuation regulated by the functionality [5].

The mechanical equation of state
(simple extension)

From Eq. (7) the nominal force in the mode of simple extension is derived to be given by

$$f = \frac{\partial W_1}{\partial \lambda} = GD \left[\frac{1}{1 - \eta_1} - a \sqrt{\frac{I_1 - 3}{2}} \right] . \tag{14}$$

D is the derivative of $(I_1 - 3)/2 \equiv \phi_1(\lambda)$ $= (\lambda^2 + 2/\lambda - 3)/2;$

$$D = \lambda - \lambda^{-2} . \tag{15}$$

The elastic term of the elastochemical potential of the solvent

The equilibrium swelling of a network is described by introducing an additive term in the Gibbs function [1–5]. This means that the strain energy is a form of energy that may be exchanged independently. For the equitriaxial swelling deformation we derive the elastic component of the

elastochemical potential:

$$\frac{\Delta\mu_{elast,1}^{van}}{RT} = \frac{1}{RT} \left(\frac{\partial(W_3 V)}{\partial n_1} \right)_{T,p}$$
$$= \frac{y_1}{y_p} \left(\frac{1}{1 - \eta_3} - a \sqrt{\frac{I_3 - 3}{2}} \right) \varphi_p^{1/3} , \tag{16}$$

with V as the volume. Comparing this equation with the mechanical equation of state [Eq. (14)] one realizes the analogous analytical form of the van der Waals modification. But one has to keep in mind that the mode of deformation is different. The maximum strain parameter in the equitriaxial mode of deformation $\lambda_{max,3}$ is substantially shorter than the one in simple extension:

$$\lambda_{max,3} = \frac{\lambda_{max}}{\sqrt{3}} . \tag{17}$$

Under equitriaxial extension the van der Waals network is mechanically much more stable than under simple extension. The finite chain length as the essential structure parameter determines the maximum strain and the density of chains. In the heuristic limit of infinitely long chains, one arrives at a value of [Eq. (16)]

$$\lim_{y_p \to \infty} \Delta\mu_{elast,1}^{van} = 0 . \tag{18}$$

This makes it clear that in the van der Waals network model the eigenvolume of the chains is accounted for in a very natural manner.

To formulate the elastic potential of the Gaussian network [1] the density of phantom chains has to be introduced additionally. This leads to the elastic term of the elastochemical potential:

$$\frac{\Delta\mu_{elast,1}^{gauss}}{RT} = \frac{y_1}{y_p} \varphi_p^{1/3} , \tag{19}$$

where the factor y_1/y_p enters irrespective of whether or not the network is comprised of Gaussian chains of infinite contour length.

Flory–Rehner approach vs. the van der Waals approach

In the Flory–Rehner approach the network is comprised of infinitely long Gaussian chains. We are led to the relationship [1–5]

$$\frac{\Delta\mu_{gauss}}{RT} = \ln(1 - \varphi_p) + \varphi_p + \chi\varphi_p^2 + \frac{y_1}{y_p} \varphi_p^{1/3};$$
$$\lambda_3 = \lambda_q = \varphi_p^{-1/3} . \tag{20}$$

In the van der Waals network model chains of mean length y_p are introduced. This length is now assumed to characterize the size of the polymer component in the mixture:

$$\frac{\Delta\mu_{vdw}}{RT} = \ln(1 - \varphi_p) + \left(1 - \frac{y_1}{y_p}\right)\varphi_p + \chi\varphi_p^2$$

$$+ \frac{y_1}{y_p}\left(\frac{1}{1 - \eta_3} - a\frac{\sqrt{I_3 - 3}}{2}\right)\varphi_p^{1/3}.$$

(21)

It is instructive to show the reduced elastic term of the elastochemical potential $\Delta\mu_{elast,1}^{\alpha}/RT\varphi_p^{1/3}$ plotted against λ^{-3} as the Mooney plot in the equitriaxial mode of deformation (Fig. 1). For the networks under discussion the equilibrium swelling deformation of both networks lies in the range $1 \geq \varphi_p \geq \varphi_p^* \approx 0.025$, where the reduced van der Waals force falls below the constant value of the Gaussian network. It is for this reason that the degree of swelling of these real networks is larger than the ones computed with the help of the Gaussian model. Finite chain extensibility and global interaction have measurable influence on the equilibrium degree of swelling of real networks. It was also shown that the activity coefficient $1 - y_1/y_p$ comes into play essentially if the size of the solvent is comparable with the length of the network chains [8, 9].
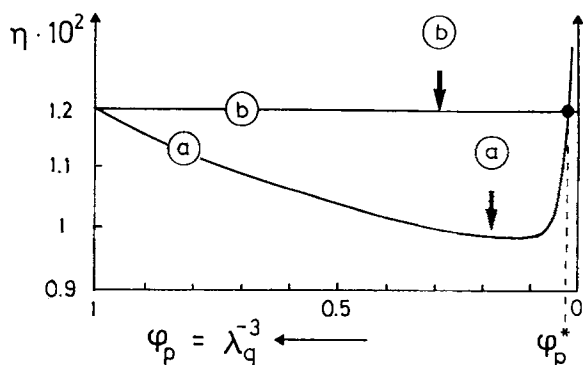
Comparison with experiments

Swelling experiments

With the Flory–Rehner relation every description of differently crosslinked networks should lead to a typical dependence of the interaction parameter on the density of junctions. It would substantially support our approach if equilibrium swelling of differently crosslinked networks could be described with a constant set of SKK parameters. Such a finding would be reasonable because solvent–polymer interaction is a very local phenomenon. Under these circumstances, the network's entropy of mixing is expected to be modified by the particle size effect only $((1 - y_1/y_p)\varphi_p)$ [8, 9].

To prove this hypothesis, let us rewrite Eq. (2) as

$$\frac{1}{\sqrt{\chi}} = \frac{1}{\sqrt{\chi_0}}(1 - \gamma\varphi_p).$$

(22)

If the SKK approach is adequate, we should observe a linear dependence of $1/\sqrt{\chi}$ on φ_p. It is evident from Fig. 2 that this holds true in all the systems studied here. It is, therefore, easy to deduce the parameters χ_0 and γ (see Tables 1 and 2). Experimental data for (natural rubber) NR–solvent systems as measured by McKenna [21, 22], Table 3, are shown in Fig. 3. The χ_0- and γ-values are collected in Table 4. The Flory–Huggins χ-parameter of our experiments on NR swollen in benzene (Fig. 3) are fairly well computed with the

Fig. 1. Mooney plot of the reduced equitriaxial swelling force of the van der Waals network $\eta_{vdw} = y_1/y_p\{1/(1 - \eta_3) - a[(I_3 - 3/2)]^{1/2}\}$ and the Gaussian network $(\eta_{gauss} = y_1/y_p = const)$ (crossing over φ_p^*) as a function of $\varphi_p = \lambda_q^{-3}$ (parametetrs $\lambda_{max} = 10.7$, $a = 0.27$, $T = 295$ K, $M_u = 68$ g mol^{-1}, $y_1 = 1.335$); the arrows indicate the equilibrium swelling of (a) the van der Waals network and (b) the Gaussian network
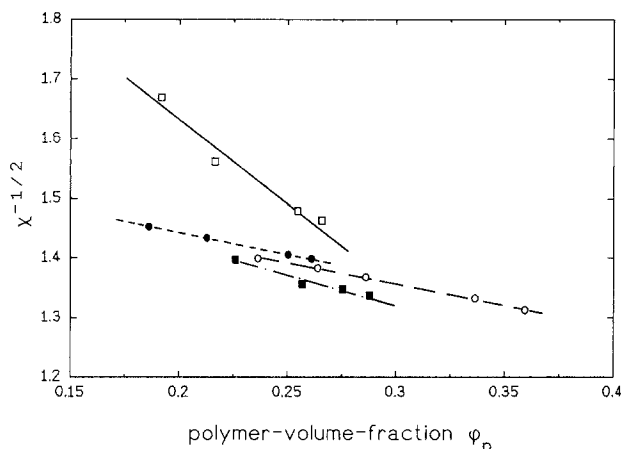

Fig. 2. $\chi^{-1/2}$ vs. the volume fraction of the network measured at room temperature: ● NR/toluene, ○ NR/n-dodecane, ■ EPDM/toluene, □ EPDM/n-dodecane
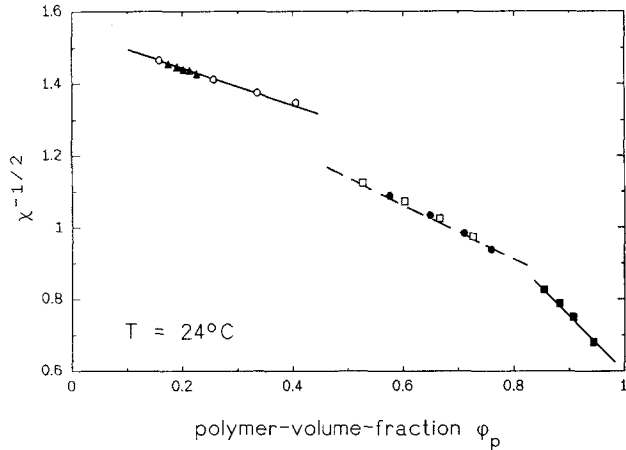
Fig. 3. $\chi^{-1/2}$ vs. the volume fraction of NR networks swollen in ○ benzene, ● methylene ethylene ketone, □ ethylene acetate, ■ acetone (after [20]), ▲ in benzene

Table 2. χ_0 and γ

	NR		
	toluene	*n*-dodecane	benzene
y_1	1.355	2.505	1.147
χ_0	0.3976	0.4033	0.4164
γ	0.4481	0.4575	0.3470

Molecular weights of the stretching-invariant units: $M_u(\text{NR}) = 68\,\text{g mol}^{-1}$

Table 3. Experimental data of McKenna [20]

	Benzene	Methyl ethyl ketone	Ethyl acetate	Acetone
M_1	78	72	88	58
y_1	1.147	1.059	1.294	0.853
phr DCP	φ_p	φ_p	φ_p	φ_p
1	0.158	0.575	0.527	0.854
3	0.256	0.648	0.602	0.882
5	0.335	0.709	0.665	0.907
10	0.405	0.759	0.725	0.943

Table 1. NR, $a = 0.27$

		toluene $(y_1 = 1.355)$		*n*-dodecane $(y_1 = 2.505)$	
phr DCP	λ_{max}	φ_p	χ	φ_p	χ
0.07	11.8	–	–	–	–
1.08	10.7	0.1859	0.4732	0.2639	0.5222
1.35	10.0	–	–	0.2861	0.5336
1.62	9.7	0.2126	0.4856	–	–
1.89	8.7	–	–	0.3364	0.5619
2.20	8.6	0.2502	0.5048	–	–
2.35	8.3	0.2610	0.5096	0.3595	0.5789

Table 4. χ_0 and γ

NR	χ_0	γ
benzene	0.4255	0.3020
methyl ethyl ketone	0.4117	0.5221
ethyl acetate	0.4300	0.4957
acetone	0.2027	0.7334

NR/benzene, $a = 0.3$, $y_1 = 1.147$

phr DCP	λ_{max}	φ_p	χ	$1/\sqrt{\chi}$
1.08	10.30	0.1745	0.4718	1.4559
1.35	9.65	0.1905	0.4775	1.4471
1.62	9.27	0.2014	0.4822	1.4401
1.89	8.80	0.2131	0.4841	1.4373
2.03	8.47	0.2256	0.4909	1.4273

Table 5. NR–benzene, $a = 0.3$, $y_1 = 1.147$

λ_{max}	φ_p	χ	$\chi_{calculated}$
10.30	0.1745	0.4718	0.4716
9.65	0.1905	0.4775	0.4790
9.27	0.2014	0.4822	0.4823
8.80	0.2131	0.4841	0.4860
8.47	0.2256	0.4909	0.4900

same SKK parameters as deduced from McKenna's data (Table 5).

The solvent–polymer interactions should be controlled by local contacts. γ gives the ratio of contact surfaces between polymer segments and solvent molecules [10, 16]. We obtain here the ratio of the contact surfaces of NR with toluene or benzene:

$$\frac{\sigma_{tol}}{\sigma_{benz}} = \frac{\sigma_{tol}}{\sigma_{NR}}\frac{\sigma_{NR}}{\sigma_{benz}} = \frac{1 - \gamma_{benz}}{1 - \gamma_{tol}} = 1.17\ , \qquad (23)$$

which is in satisfactory accordance with Koningsveld's value of 1.24 [10].

Hence, isothermal equilibrium swelling in differently crosslinked networks is successfully interpreted with constant SKK interaction parameters. Global interaction between network chains seems not to be modified in the presence of small solvent molecules.

If the interaction parameters are known, it is possible to elicit the maximum strain parameter (that means the density of quasipermanent junctions) from equilibrium swelling experiments.

Simple extension

The nominal force in simple extension experiments of the dry networks is correctly calculated with the same network parameters as used above (Fig. 4).

Conclusions

Different experiments like simple extension of dry networks or swelling of networks are consistently described with an invariant set of network parameters (M_u, λ_{max}, a). Since the strain energy is equipartitioned, chains of different lengths are energy-equivalent. This allows one to describe the elastic properties of the actual network by an equivalent monomodal network with the chain length equal to the mean chain length in the real network. If the network chains are defined as the polymer components, equilibrium swelling in networks is

fairly well understood in terms of a quasibinary solution.

The above result makes it clear that in a swollen network the strain energy is stored in the network itself. Moreover, the presence of small solvent molecules does not appreciably affect the overall network properties. This allows one to consider a real network as a "weakly interacting van der Waals conformational gas".

Theory II: filled networks

The general situation

It is now a significant and indicative finding [23] that the equilibrium degree of swelling for carbon black or silica fillers (Fig. 5) is uniquely reduced, not showing any dependence on the chemical and physical properties of the filler particles investigated. We must, therefore, develop thermodynamics of the swelling of filler-loaded rubbers that reproduces this finding. It is self-evident that one can make use of the Einstein–Smallwood relation.

Some definitions

v is the filler volume fraction defined by

$$v = \frac{V_{filler}}{V_{filler} + V_{rubber}} . \tag{24}$$
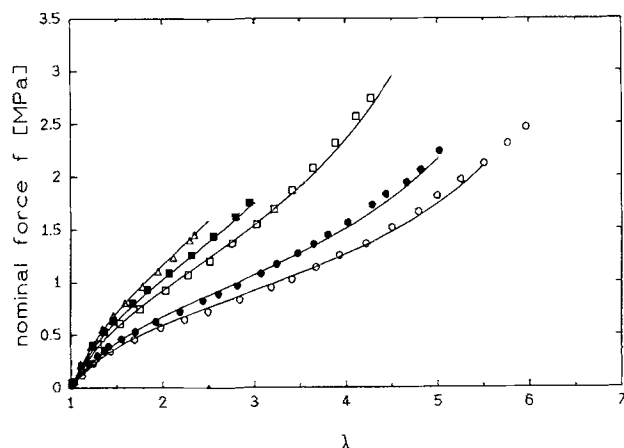
Fig. 4. Nominal force NR networks at 353 K stretched with a strain rate of $v_{def} = 0.66\%$ min^{-1}; λ_{max}: ○ 10.6, ● 10.0, □ 8.7, ■ 8.3, △ 7.85; $a = 0.27$; $M_u = 68$ g mol^{-1}
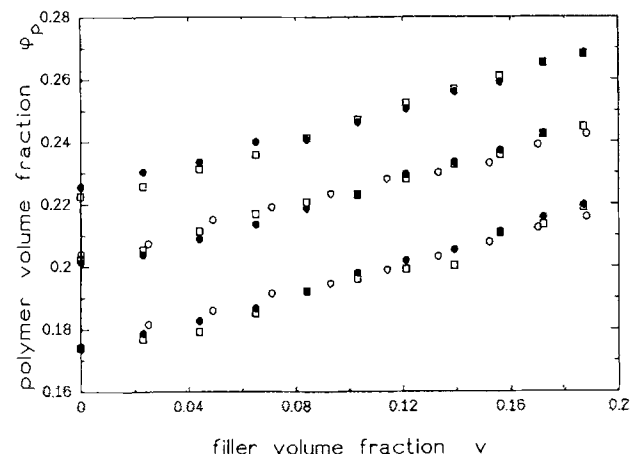

Fig. 5. Volume fraction of the NR networks swollen in benzene as a function of the volume fraction of the filler (○ N110, ● Ultrasil VN2, □ Aerosil 130 V)

This volume fraction is related to the filler weight fraction w_{filler} according to

$$v = \frac{w_{filler}}{w_{filler} + w_{rubber}\rho_{filler}/\rho_{rubber}} , \quad (25)$$

where the densities of the constituents ρ_α come into play. The filler mass fraction is often expressed in terms of parts of filler per hundred parts of rubber (phr) as

$$w_{filler} = \frac{phr}{phr + 100} . \quad (26)$$

What we have to find out is how the intrinsic strain of the rubber-elastic matrix $\lambda_3 \equiv \lambda_q$ is interrelated with the macroscopic degree of swelling Q_{exp}:

$$Q_{exp} = \frac{V_{filler} + V_{rubber} + V_{solvent}}{V_{filler} + V_{rubber}} . \quad (27)$$

V_α gives the volume of the constituents, the filler particles, the rubbery matrix and the solvent. From the degree of swelling in the rubbery matrix defined by Eq. (27) we arrive at the following expression for the intrinsic degree of swelling:

$$Q = \frac{V_{rubber} + V_{solvent}}{V_{rubber}} = \frac{Q_{exp} - v}{1 - v} , \quad (28)$$

$$\lambda_q = Q^{1/3} . \quad (29)$$

The van der Waals–Flory approach

Swelling in filled networks enforces an equitriaxial deformation of the rubbery matrix with distortions in the next neighborhood of each filler particle or particle aggregate. The filler-to-matrix contacts being quasipermanent, these boundary effects can be accounted for by the Einstein–Smallwood modification of the network modulus [24–30]:

$$G_v = \frac{\rho RT}{M_u \lambda_{max}^2} (1 + Cv) , \quad (30)$$

where C is a universal parameter depending only on the form of the colloid particles. If the filler particles or aggregates are spheres, C is equal to 2.5, independent of the size. One arrives, therefore, at the same value for monodispersed or polydispersed filler ensembles provided that the particles and aggregates are spherical in shape.

By writing

$$G_v = \frac{\rho RT}{M_u \lambda_{m,v}^2} , \quad (31)$$

we may define the effective maximum strain parameter $\lambda_{max,v}$ as

$$\lambda_{max,v}^2 = \frac{\lambda_{max}^2}{1 + Cv} \equiv y_{p,v} . \quad (32)$$

Hence, the Einstein–Smallwood modification may be interpreted as a reduction of the maximum chain extensibility.

If the interaction parameter a is invariant, the upturn in simply extended filled rubbers should be shifted to lower strains. Such a shift is, in fact, observed and fairly well described within the framework of one of the first versions of the van der Waals formulation of the mechanic equation of state of filled rubbers including the formulation as in Eq. (32) (Fig. 6) [31–34]. Under the premise that the filler-to-matrix contacts are quasipermanent, so that the density of the effective crosslinks in the swollen network is fixed, the above approach is elegant and correct (discussed later).

It is now unconventional and interesting to use the equivalent chain length $y_{p,v} = y_p/(1 + Cv)$ in the mixing term of the elastochemical potential as well. The boundaries around each filler particle or particle aggregate are assumed to diminish the
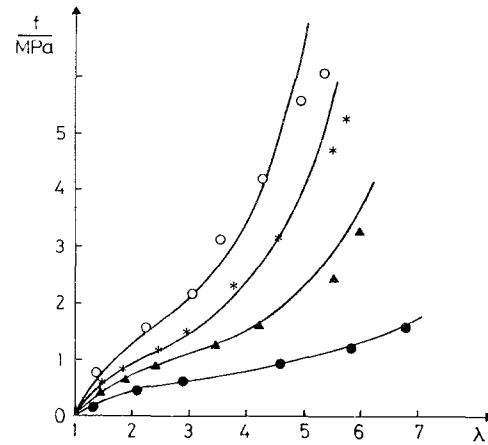

Fig. 6. Stress–strain pattern of NR filled with TiO_2-filler particles. The solid lines are computed from Eq. (14): ● $v = 0$, ▲ $v = 0.091$, ★ $v = 0.167$, ○ $v = 0.239$, $\lambda_{max} = 10.7$, $a = 0.28$, $M_u = 45\,g\,mol^{-1}$; filler: TiO_2; $C = 2.5$, $\lambda_{max,v} = \lambda_{max}/(1 + Cv)^{1/2}$ replacing λ_{max}, $\lambda_i = [\lambda - (v/\lambda)^{1/3}]/[1 - (v/\lambda)^{1/3}]$ replacing λ

mean entropy of mixing in the matrix according to $(1 - y_1/y_{p,v}) \varphi_p$.

Comparison with experiments

The equilibrium degree of swelling can then be computed with the help of Eq. (21) in the equitriaxial mode of deformation whereby $\lambda_{max,v}$ has to replace λ_{max}. With the help of the same parameters as in the unfilled NR network (Table 2), we arrive at the representation of the measurements (Fig. 5) as depicted in Fig. 7.

We come to the following conclusions:

(a) The mean-field approach based on the thermodynamics of filled van der Waals networks is adequate.

(b) Quasipermanent filler-to-matrix adhesion reduces the effective chain length so that the entropy of mixing in swollen filler-loaded networks is diminished. The reduction is fairly well defined by the Einstein–Smallwood modification.

(c) Filler-to-matrix contacts are quasipermanent. The adhesion of NR segments is in any case strong enough to inhibit any exchange with solvent molecules. This explains the universal features in the swelling behavior of filler-loaded rubbers.

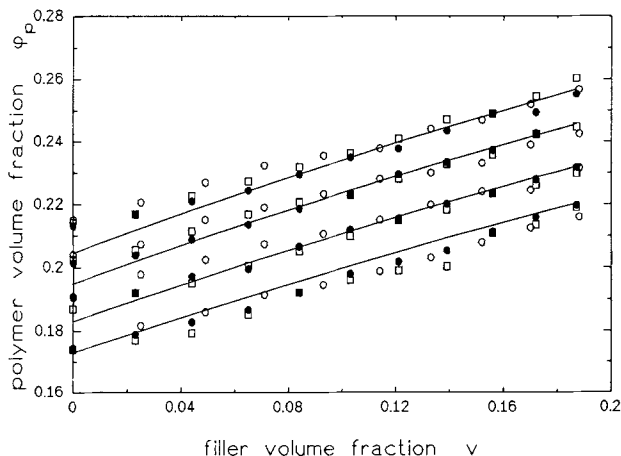(d) The cluster ensemble of filler particles like carbon black or silicates should form aggregates of spherical symmetry in accordance with the results of electron microscope studies (Fig. 8).

(e) The calculations are altogether done with the same van der Waals parameter a. Overall interactions within the rubber matrix should not be changed very much in the presence of the filler.

(f) The Einstein–Smallwood reinforcement must be a local phenomenon because in the opposite case one should find particle–particle interaction effects [35, 36]. Straightforwardly argued, it may be that the elastochemical potential $\mu(x, y, z)$ is

a)
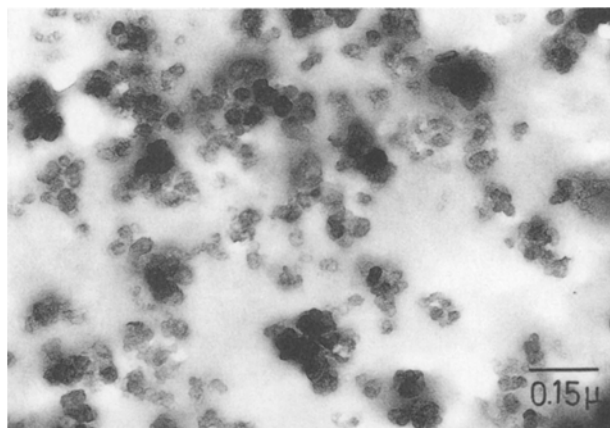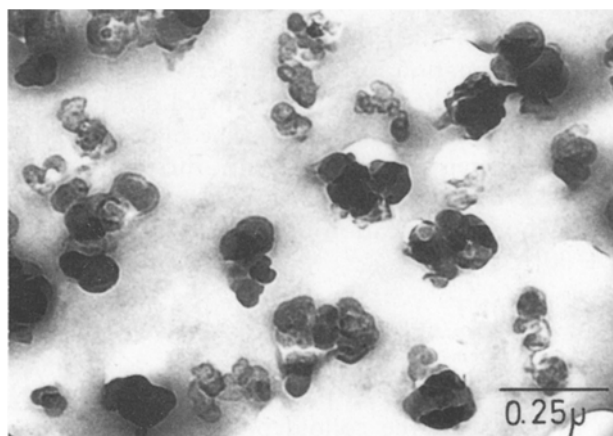
Fig. 8. Electron microscope picture of a filler-loaded NR (carbon black) (a) N110 and (b) N660, $v = 0.18$); total magnification 10^5

b)

filler volume fraction v

Fig. 7. Equilibrium swelling of filled NR–benzene against the filler volume fraction (Fig. 5). Solid lines, computed (parameters Table 5)

brought to its constant value simply by adjusting the concentration within a relatively small layer around each filler particle or filler particle aggregate.

It is the last suggestion which needs justification.

Finite-element calculations

The thermodynamic description as a mean-field approach allows one to apply the method of finite-element calculations based on the material equations [Eqs. (7) and (21)] [37]. The network parameters M_u, λ_{max} and a, as well as the thermodynamic parameters, are altogether kept invariant. Hence, the calculations are done with an a priori homogenous matrix whereby permanent adhesion at the filler particle surface is introduced as a boundary condition. By establishing equilibrium, we are led to the pattern of iso-concentration lines as depicted in Fig. 9. When approaching the filler surface the degree of swelling is continuously reduced; in the present case down to about 60% as in the matrix far off (see also [38]). One learns from this calculation that the thickness of the modified layers is comparable to the radius of the filler particle. The Einstein–Smallwood approach, therefore, seems to be a good approximation, even in swollen networks with surprisingly high loadings (in the present case $v \leq 0.2$–0.22). This is different than in the stress–strain behavior of filler-loaded rubbers [37].

Fig. 10. λ_q against $\lambda_{max,v}$ of differently filled networks ($\bigcirc v = 0.13$, $\bullet v = 0.17$, $\square v = 0.2$) swollen in benzene. The stars represent the experimental data on unfilled NR networks

By plotting the strain λ_q against $\lambda_{max,v}$, it is seen from Fig. 10 that all the finite-element calculations fall onto a master curve, where we also find the experimental data of unfilled networks [39]. This verifies an interesting empirical correlation which is not yet explained. It defends, on the other hand, the mean-field representation of the finite-element calculation. We also find excellent agreement by comparing the thermodynamic calculations, with the help of Eq. (21) (the modified parameters for filled systems introduced), and the finite-element calculations (Fig. 11).
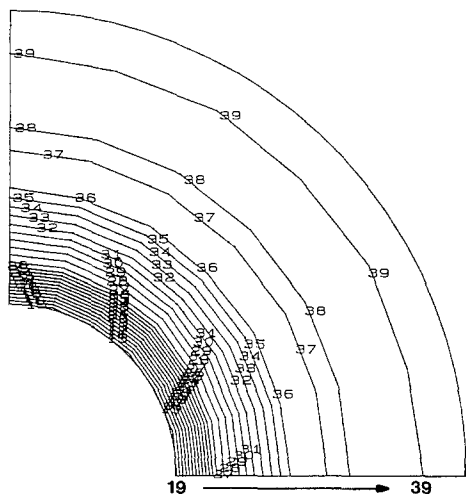

Fig. 9. Isoconcentration lines around a filler particle with permanent contacts plunged into a swollen matrix. The lower the numbers the lower the degree of swelling (19–39).
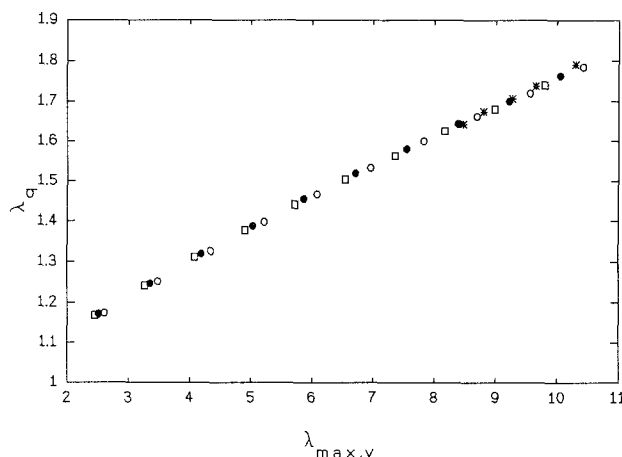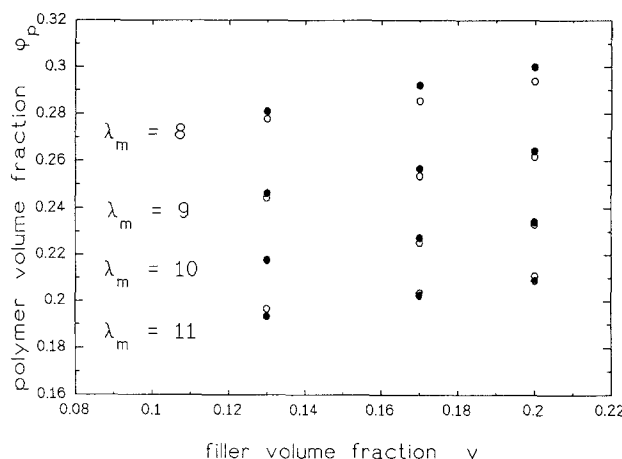

Fig. 11. Volume fraction of the network as a function of the volume fraction of the filler for different networks as indicated with each curve ($\bullet$ thermodynamics, $\bigcirc$ finite-element calculation)

This leads to the following consequences:

(a) Permanent filler–matrix contacts reinforces the rubber in the van der Waals network approach described by a well-defined reduction of the maximum strain parameter. This is equivalent to reducing the effective chain length. This can be quantified by using the Einstein–Smallwood relationship.

(b) The layer in which the concentration of the solvent is depressed is relatively thin so as to make the single-filler-particle model a good approximation up to filler volume fractions of about $\nu = 0.2$ (whereby this number depends on the mean size of the filler particles or filler particle aggregates).

(c) According to the finite-element calculations, actually, solid contact layers on the filler surface must be very thin.

The Einstein–Smallwood reinforcement seems to be related to entropy-elastic chains in parallel arrangements anchored at the filler surface.

Conclusions

It is shown that simple extension and equilibrium swelling can consistently be explained within the framework of the van der Waals network model. The overall behavior is fairly well characterized as that of a weakly interacting conformational gas.

Because of having achieved a quantitative understanding of swelling in differently crosslinked networks, it is justified that the network chains are treated as quasiautonomous particles in spite of their being linked in a network. Interaction of any kind (overall interactions as well as solvent–polymer interactions) seems to have local origins so as to be nearly identical in filled and in unfilled networks. The van der Waals type of description of polymer–solvent contacts as proposed by Staverman–Koningsveld–Kleintjens turns out to be a very reasonable approach.

In describing the equilibrium swelling in filler-loaded networks the Einstein–Smallwood approach is very adequate. The swelling is reduced in a universal manner because each filler particle is screened by a well-defined rubber layer. Within these shells the concentration of the solvent falls rapidly to very low values. The solvent does not contact the filler surface itself. This is the reason why in swollen filler-loaded rubbers the adhesion of the polymer segments is quasipermanent and independent of the filler's properties. The swelling-induced volume increase together with a non-homogeneous distribution of the solvent makes the "single-particle" approach of Einstein–Smallwood a very good approximation.

A new consequence of the Einstein–Smallwood approach is to assume that the entropy of mixing in filled rubbers should be diminished within the boundary layers of the filler particles. This suggests that this effect may be interpreted in terms of a reduced effective chain length $y_p/(1 + C\nu)$. This elucidates a spectacular power of the boundary problem as formulated by Einstein–Smallwood. Colloid particles embedded in a continuum and making quasipermanent contacts lead in very different physical situations to analogous and universal modifications of the macroscopic properties (viscosity, elasticity, rubber-elasticity, viscoelasticity, and thermodynamic properties like the mixing entropy).

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