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Equilibrium swelling of rubber networks loaded with modified silica: an interesting version of Langmuir adsorption

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Abstract: Equilibrium swelling of silica-loaded natural rubber networks in presence of surface active adsorbents is studied. "Reinforcement" is systematically reduced when parts of the silica surface are occupied by the adsorbent (silanes or glycol). Extending the description of the swelling of networks loaded with carbon black or silica within the framework of the van der Waals network model, this observation can be described as adsorption equilibrium. Langmuir adsorption turns out to be a good approach. This elucidates the dynamics in the filler surfaces. Interesting is the finding that the phenomenological Einstein–Smallwood modification of the modulus can be reformulated so as to account for the reduction of "network-active" adsorption sites. The description of the experimental data reveals different adsorption behavior of silanes and of glycol. The physical consequences are discussed.

Key words: van der Waals network – swelling – silica – silanes – Langmuir adsorption

Introduction

Rubbers loaded with spherical solid particles (carbon black or silica) show mechanical reinforcement [1–3]. In comparison with the pure network of the same crosslinking density, increased strain energies are necessary in the first stretch. It is an attractive idea to relate this phenomenon to the universal Einstein–Smallwood modification of the modulus. Postulating permanent tack of the rubbery matrix to the solid filler particles (diameters in the range of 20 to 60 nm) the modulus should increase in a universal manner. But this single particle approach does not include the existence of clusters. Here, chains in parallel arrangements become important. On deformation shortest intra-cluster chains store very large energies so that chain slip is enforced [2]. The resulting stress-strain hysteresis then is controlled by critical adhesional strengths. But despite the slip debonding does not occur. The filler-to-matrix contacts (*FM-contacts*) must have a *rapid dynamics* [4–9]. Strong enough thermodynamic factors of adsorption must guarantee that the density of filler-to-matrix contacts remains invariant even under largest strains.

We now want to prove the existence of the adsorption dynamics by studying adsorption equilibrium of a very active adsorbent solved in a swollen filler-loaded rubber [10]. The crucial point is that the interaction of the adsorbent with the filler should be so large that the adsorbent is preferably deposited. Keeping the concentration of the adsorbent low the contact sites on the filler's surface are only partially occupied by the adsorbent. If the solvent shows so weak attraction to the filler particles surface it does not participate in the adsorption competition. Those parts of the filler's surface which are not contacted by the adsorbent should then altogether be occupied by polymer segments. Because of having the segments linked in the permanent network the effective density of junctions is increased in clear dependence of the "free" sites available. This leads to a defined modification of the maximum degree of swelling. By changing the concentration of the adsorbent, we should be able to observe adsorption isotherms in vivo. It is attractive that this can be studied for different degrees of loading so as to prove the laws of adhesion in situations which are otherwise not realizable.

The key problem is how do we arrive at a solid description. Equilibrium swelling was described with the aid of a Flory–Rehner approach [11–13] modified by introducing the van der Waals network model [14] and the Stavermann–Konings veld–Kleintjens interaction parameter. The swelling pressure is usually not so high that adhesional contacts of the polymer segments are released. Hence, it is clear that the solvent does not make any contact with the filler. In these circumstances a monolayer only comprised of polymer chain segments is formed covering each of the primary particles. The Einstein–Smallwood model turns out to be fully appropriate for describing the reinforcement of the swollen filler loaded rubber. Moreover, this approach explains straight forwardly the universal features of the swelling behavior of differently loaded systems (carbon black or silica loaded networks).

Yet, this description does not directly reveal the dynamics of adhesional contacts [15–17]. To achieve this we now study adsorption of a few very active small molecules with a mean adhesional energy that is so large as to displace polymer segments at the surface of the filler particles. Because the solvent is "inactive" the adsorption competition between adsorbent and polymer segments must only be considered. The laws of stationary adsorption should then determine how the adsorbent molecules are partitioned on the surface of the filler particles and in the rubbery matrix. The description of the maximum swelling then informs about the fraction of polymer segments anchored to the filler.

We measure the maximum degree of swelling in rubbers loaded with silica. First, the density of polymer *FM*-contacts is changed by adding different amounts of oligomer silanes as a very active adsorbent. In another experiment loaded networks were swollen in presence of glycol. It will be shown that the experimental results can in both cases be interpreted as Langmuir absorption. This indirectly informs about the dynamics and the nature of modifier-to-filler contacts. Moreover, we can discuss the possible structure within the monolayers each silica filler particle is covered with.

Thermodynamics

Colloid particles dispersed in a network modify macroscopic properties. The maximum swelling of carbon black or silica loaded rubbers is uniquely reduced when the filler volume fraction is increased. No dependence on the chemical and physical properties of the filler particles is observed [10, 17]. The Einstein–Smallwood approach explains this universal behavior.

For describing equilibrium swelling the van der Waals network model [18] is introduced into thermodynamics. The difference of the elastochemical potentials of the solvent in the solution μ_1^{solution} and in the pure solvent $\mu_1^{\text{reservoir}}$ should fulfill the condition.

$$\Delta\mu = \mu_1^{\text{solution}} - \mu_1^{\text{reservoir}} = 0 \, , \tag{1}$$

which is explicitly written as [14] :

$$\begin{aligned} \Delta\mu/RT &= \ln(1-\varphi_p) + (1 - y_1/y_p)\varphi_p + \chi\varphi_p^2 \\ &\quad + (y_1/y_p)[1/(1-\eta_3) \\ &\quad - a(\phi_3)^{1/2}]\varphi_p^{1/3} = 0 \\ \eta_3 &= (\phi_3/\phi_{m3v})^{1/2}; \\ \phi_3 &= 3/2(\lambda_q^2 - 1), \phi_{m3v} = \phi(\lambda_{m3v}) \\ \lambda_{m3v} &= \lambda_{m3}/(1 + C_0 v)^{1/2} \; \lambda_{m3} \simeq \lambda_m/3^{1/2}; \\ \lambda_m &= y_p^{1/2}, \lambda_q = \varphi_p^{-1/3} \, . \end{aligned} \tag{2}$$

The front terms formulate the entropy of mixing of polymer and solvent. Here, it is significant that the *network chains of different length are considered as the components in the thermodynamic system.* y_p, defined as number of strain-invariant units of the molecular weight M_u, then determines the mean size of the *polymer particles.* y_1 gives the size of solvent molecules also related to M_u.

$$y_p = \frac{M_c}{M_u}, \quad y_1 = \frac{M_1}{M_u} \, . \tag{3}$$

M_c and M_1 are the molecular weights of the network chains and the solvent molecules, respectively. R is the gas constant, T is the absolute temperature, φ_p is the volume fraction of the polymer in the swollen network that is defined by

$$\varphi_p = \frac{n_p y_p}{n_l y_l + n_p y_p}; \tag{4}$$

n_p and n_l are the mole numbers of the polymer chains- and the solvent molecules. λ_q is the degree of swelling in the matrix. Q is related to the experimental degree of swelling Q_{exp} according to

$$\lambda_q = Q^{-1}; \; Q = \frac{Q_{exp} - v}{1 - v}, \tag{5}$$

where v is the volume fraction of the filler in the dry network

$$v = \frac{m_{filler}}{m_{filler} + m_{rubber}\rho_{filler}/\rho_{rubber}}. \tag{6}$$

m_{filler} and m_{rubber} are the masses of the filler and the rubber, respectively. ρ_{filler} and ρ_{rubber} are the corresponding densities. The first van der Waals parameter λ_m is the maximum strain the single chains can on average uniaxially be stretched to. The effective maximum strain in the filler loaded network is defined by λ_{m3v} whereby the label 3 should indicate that swelling enforces equitriaxial extension of the network. It might here be stressed that the maximum strain λ_{m3} in the equitriaxial mode of deformation is lowered by the factor of $3^{-1/3}$ in respect to λ_m in simple extension. The second van der Waals parameter a accounts for global interaction. χ is the Flory–Huggins interaction parameter defined in the modified version of Staverman, Koningsveld and Kleintjens (SKK model) [19, 20]:

$$\chi = \frac{\chi_0}{(1 - \gamma\varphi_p)^2}; \quad \gamma = 1 - \frac{\sigma_p}{\sigma_s}. \tag{7}$$

γ is determined by the ratio of contact surfaces of polymer segments and solvent molecules (σ_p/σ_s). The solvent-polymer segment interaction is of local origins. Equilibrium swelling of differently crosslinked unfilled networks should therefore be describable with constant SKK parameters χ_0 and γ.

The fundamental network parameters a and λ_m are deduced by describing the quasistatic stress strain curve of the dry network with the aid of van der Waals equation of state [18, 21].

The last term in Eq. (2) describes the entropy change in the swollen network. It formulates the partial molar strain energy per network chain. It does not depend on the length distribution of network chains because strain energy is equipartitioned. Chains of different length are *energy-equivalent* like different molecules in a gas.

Hence, in contrast to that of Flory–Rhener, we consider a non-Gaussian system that accounts for finite chain extensibility and global interaction.

The Einstein Smallwood relation

The Einstein–Smallwood modification is a mean field approach where the elastic continuum is solidly bound at the surface of a single rigid colloid particle. We reflect its interpretation so that we learn how the "classical" Einstein–Smallwood approach can be used in order to later account for the adhesion of "non-network active adsorbent molecules".

The Einstein–Smallwood relation predicts that the modulus of the elastic continuum, the rubbery matrix in quasi-permanent contact with the filler particles [15, 16, 17] should be increased according to

$$G_v = G_0(1 + C_0 v); \tag{8}$$

C_0 as universal parameter only depends on the shape of the colloid particles.

In terms of a network model, we easily come to a new formulation. A monolayer with properties different than in the matrix is formed around each filler particle [22, 30]. Here, the polymer segments make local contacts on surface. The effective crosslinking density in the filler loaded network should be increased therewith. Treated as quasi-permanent, this effect can be translated into a reduction of the effective length of chains according to

$$\lambda_{m,v}^2 = y_{p,v} = \frac{y_p}{1 + C_0 v} = \frac{\lambda_m^2}{1 + C_0 v}. \tag{9}$$

This mean field interpretation deeply relies on the energy-equivalence of chains in a network. To have shorter chains concentrated around each filler particle does not matter. The whole set of surface contacts cooperates so as to build up

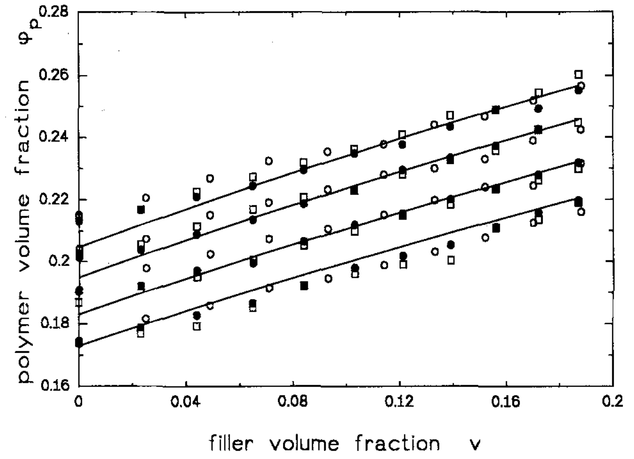

Fig. 1. Equilibrium swelling of different crosslinked (natural rubber) NR-networks in benzene against the volume fraction of the filler (○ Corax N110, ● Ultrasil VN2, □ Aerosil 130 V) at T = 293 K. Solid lines are theoretical (parameters in Table 1)

Table 1. NR in benzene, Corax N110, Ultrasil VN2, Aerosil 130V

$a = 0.3$, $y_1 = 1.147$, $\chi_0 = 0.4164$, $\gamma = 0.3470$,
$C = 2.5$, $\rho_{\mathrm{filler}}/\rho_{\mathrm{rubber}} = 2$

phr DCP	1.08	1.35	1.62	1.89
λ_m	10.41	9.97	9.49	9.13

Table 2. Chemical composition

OTMS	$(CH_3O)_3 - Si(CH_{217} - CH_3$
DEG	$HO - (CH_2)_2O(CH_2)_2 - OH$

quasi-static monolayers around each filler particle. Individual properties of the contacts do not enter into the description. How the filled rubber is reinforced is expressed by the defined reduction of the mean effective chain length within the rubbery matrix, whereby this reduction is proportional to the density of the chemical junctions.

Swelling equilibrium in filler loaded rubbers

The equilibrium degree of swelling of filler loaded rubbers can be computed with the aid of Eqs. (2) and (8). $\lambda_{m,v}$ has to replace λ_m. With the same fundamental network parameters as in the unfilled network (M_u, λ_m and a) the experiments are fairly well described. This is seen by evidence from Fig. 1 [2, 14].

It is deduced from x-ray investigations [23, 24] that there should only exist monolayers around each primary filler particle [22, 25]. The Einstein–Smallwood parameter is always equal to $C_0 = 2.5$. The primary filler particles operate as solid spheres with quasi-permanent matrix contacts not showing a measurable influence of the presence of clusters [1, 2, 26]. In this approach many particle interactions are neglected. This is justified because filler particles practically do not fluctuate. *A direct energy or momentum transfer between filler particles across rubbery bridges is not likely to occur.* This differs from conclusions put forth in the literature [3, 27–30].

At room temperature the filler-to-matrix contacts are quasi-permanent and do not allow for any solvent molecule to replace polymer segments at the filler surface. On simple extension, on the other hand, slipping of adhesional contacts is observed [2]. Chain segments are not permanently bound to the surface. Contact dynamics [4–9, 22] and the thermodynamic factors of adsorption guarantee that the contact density is strain invariant. Adsorption and desorption processes should match each other so as to yield to a unique and constant density of the contacting elements. This indirectly evidences the existence of rapid adsorption-desorption processes.

Modified silica

To prove the above ideas the surface properties of the filler should be modified so as to change the density of polymer contacts. Wolff [10] investigated swelling equilibrium in silica loaded rubbers where oligomer silanes have been bound to the surface. This modification was done in situ: Silica (*Ultrasil VN2*) and octadecyltrimethoxy silane (*OTMS*) (Table 2) were simultaneously mixed with the rubber. The chemical reaction then runs during the whole mixing process. Wolff noticed that the trialkoxysilyl group of the silane reacts with the silanol group at the silica surface. A well-defined number of surface sites is occupied by *elastically inactive oligomer strands.* The fraction

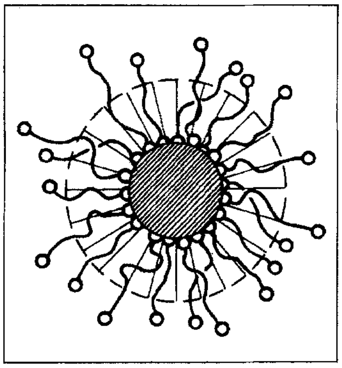

Fig. 2. Sketch of a single silica particle. The surface is totally modified with silane

of silanes was changed so as to modify the relative number of oligomers anchored to the surface of the silica particles. At the end of the mixing process the compound was crosslinked with dicumylperoxide (*DCP*). It was possible to keep the density of junctions constant, independent of the degree of surface modification. The sketch in Fig. 2 shows a totally modified silica particle which is fully covered by a monomolecular of the silanes, each one anchored to the surface. The oligomer shell behaves in the outest layer like a liquid. According to its dynamics, adhesional equilibrium is now made by a weak liquid-to-liquid layer interaction. If the density of silanes is reduced the surface cannot be fully covered any more. The question is how the oligomer silanes then are distributed over the surface of the silica particles. This should determine how many "network active" filler-polymer contacts can be built up.

Experiments

The equilibrium volume fraction of the polymer φ_p of swollen silica loaded NR-networks is shown in Fig. 3 for four different modifications. At constant volume fraction of the silica, the polymer volume fraction decreases rapidly when the surface modification is increased. If the surface is fully covered the intrinsic equilibrium degree of swelling in the matrix is the same as in the unfilled rubber provided that the density of chemical junctions is the same. In this limit, the equilibrium swelling does not depend on the degree of loading.

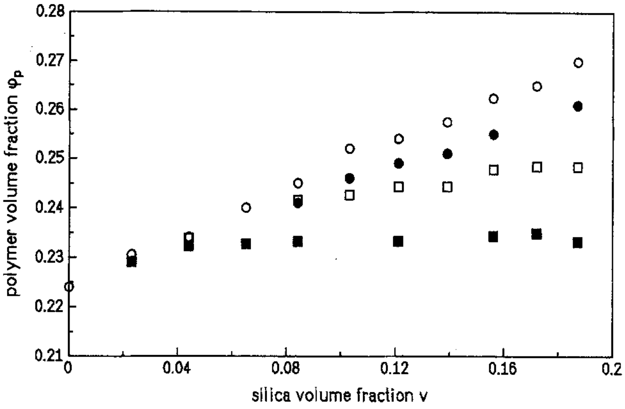

Fig. 3. Equilibrium swelling of NR filled with modified silica in benzene (2.03 phr DCP) at T = 293 K. The silica surface is covered with silane (○ 0%, ● 20%, □ 30%, ■ 100%) [17]

There are no direct filler-to-matrix contacts any more. Interaction with the outer regions of the layer is very weak, showing liquidlike segmental mobilities so that the filler particles move like myryapods with cooperative dynamics of a spherical brush constituted by more or less flexible $C_{18}CH_{37}$ -arms.

Explanation

To interpret this observation, we assume that adsorption equilibrium is established. The oligomer silanes should be partitioned according to the Langmuir adsorption law [31]. This allows a full description of our experiments (Fig. 4).

To understand this, let us consider the theoretical situation. A Langmuir adsorption isotherm describes the adsorbed mass from the gas phase at a defined pressure. A kinetic treatment of the absorption equilibrium [32] of electrically neutral particles deposited on a solid surface leads to the *Langmuir type of adsorption*. The following conditions should be fulfilled :

- a monomolecular layer is formed;
- each molecule contacts a defined surface area (*adsorption sites*);
- the energy of contacts should not be changed during the adsorption process;
- the solid surface should show an invariant density of adsorption sites;

- absorption and desorption is kinetically stationary;
- the desorption rate should not be depend on whether neighboring sites are occupied or not.

Under these conditions, the Langmuir adsorption isotherm is described by

$$\Gamma = \Gamma_0 \frac{p}{p + b^*} ; \tag{10}$$

Γ is the concentration of the adsorbent at the surface, Γ_0 gives the maximum mass of the monolayer, p is the equilibrium pressure, and b^* is the ratio of the velocity constants of desorption and adsorption [33].

It is now crucial to determine how to use this model for describing adsorption of molecules or polymer segments in the swollen rubbery matrix. Adsorption competition should occur, controlled by the size of the adhesive energies of the adsorbent, the solvent molecules, and polymer chain segments. The adsorbent should have the largest contact energy, followed by that of the polymer segments. The solvent, on the other hand, should not make any direct contact with filler particles.

We now treat the mixture in the rubbery matrix as an ideal solution. The adsorbent and solvent behave analog, like molecules in a gas. In these limits, the "partial pressures" of the components do not depend on each other. The silanes with the highest contact energy (larger than the one of the polymer segments and the solvent) are deposited first. The rest sites in the surface should then be contacted with polymer segments.

According to this model the "partial pressure" p of the absorbent should obey the simple equation $p = cRT$, where c is the concentration of the absorbent molecules. Any thermodynamic generalization of this approach suggests itself. In our idealizing approximation Eq. (10) is then rewritten as

$$\Gamma = \Gamma_0 \frac{c}{c + b}; \quad b = \frac{b_{00}}{RT} . \tag{11}$$

The concentration of the modifier c is identical with its volume fraction v_M.

$$c = \frac{V_M}{V_M + V_R} \equiv v_M ; \tag{12}$$

V_M and V_R are the volume of the modifier and the rubber, respectively. b_{00} characterizes stationary adsorption. In our experiments the volume of the modifier and the volume of the filler V_F were related according to

$$V_M = \alpha \cdot V_F; \quad \alpha = \text{const} . \tag{13}$$

The concentration c may thus be rewritten as

$$c = \frac{\alpha}{\alpha + \frac{1 - v_M}{v_M}} . \tag{14}$$

The mass of the absorbed modifier increases with the degree of loading. Polymer *FM*-contacts decrease accordingly, systematically reducing reinforcement.

A modified Einstein Smallwood relation

The Einstein–Smallwood modification of the modulus results from a continuums treatment of the boundary value problem formulated for large particles in an elastic matrix. Contacts must not be specified. It should, on average, be guaranteed that the matrix is quasi-permanently adhered to the surface within a "macroscopic" time scale. The crucial question is then of how to describe the reinforcement if the filler surfact is only partly covered by the adsorbent.

In our model, we expect that all of the filler particles are equivalent. The concentration of occupied sites is on average the same for each particle. If there is no lateral interaction the silanes should randomly be anchored to the particles surface. Polymer segments then contact the well-defined number of sites where no silanes are bound to; the solvent does not make any contact with the filler.

Quasi-permanent adhesion in the sense of Einstein Smallwood guaranteed the density of reinforcing *FM*-contacts is reduced within the monolayers when the concentration of silanes is increased. Reinforcement is diminished correspondingly. This leads to the new Einstein Smallwood relationship.

$$G_v = G_0(1 + \xi C_0 v) , \tag{15}$$

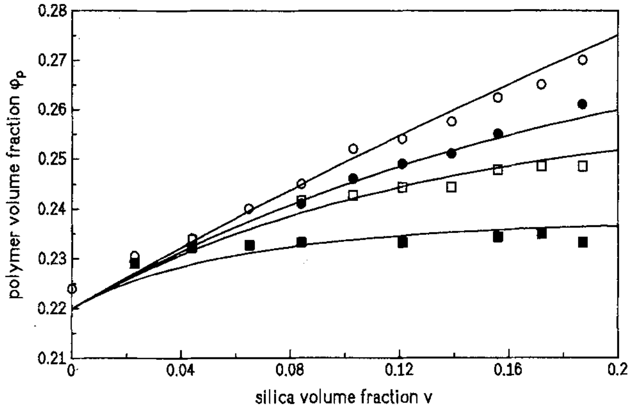

Fig. 4. Volume fraction of NR-networks (2.03 phr DCP) swollen in benzene as a function of the volume fraction of the silane-modified silica (α: ○ 0, ● 0.056, □ 0.110, ■ 0.368) [17]. The solid lines are calculated with the help of the Langmuir adsorption (parameters in Table 3)

Table 3. NR with silane-modified silica in benzene

$a = 0.27, \lambda_m = 8.90$
$M_1 = 78\ \mathrm{gmol}^{-1}, y_1 = 1.147, \chi_0 = 0.4255, \gamma = 0.3020$
$C = 2.5, b = 0.0319$

where ξ measures the fraction of polymer contacts. With the aid of the relationship in Eq. (11), we deduce

$$\xi = 1 - \frac{\Gamma}{\Gamma_0} = \frac{b}{c + b}\,; \qquad (16)$$

ξ is zero if the whole surface is covered ($\Gamma/\Gamma_0 = 1$), while it approaches its maximum value equal to one with decreasing surface concentrations of silanes.

Modified silica filler

The equilibrium swelling of *NR* loaded with silane-modified silica (Fig. 3) is fairly well described as it is shown in Fig. 4 (parameters in Table 3). For the *NR / benzene* system χ_0 and γ were determined in [14] by describing swelling experiments reported by McKenna [34, 35] covering a wide range of degrees of crosslinking (1–10 *phr* DCP).

The Langmuir parameter *b* turns out to be constant. Each differently loaded sample displays, under varying degrees of modification, isothermal Langmuir behavior of adsorption whereby the adsorption-desorption dynamics is invariant. It follows that silanes should occupy on the silica surface single sites without lateral interactions. Desorption of the silanes can apparently thermally be activated. The adsorption equilibrium of the modifier seems to be an autonomous process not showing a measurable competition with the polymer or the solvent. The density of "*free*" surface sites is then well defined and constant. This part of the surface is contacted by polymer segments that are on average tightly enough bound so as to establish quasi-permanent contacts. Reinforcement then is calculable from the stoichiometry on the surface where the fraction of silanes is determined by the Langmuir equation.

Surface contamination by glycol

It is now interesting to modify the filler surface of the silica by small molecules with specified strong adhesional energies. This is achieved, for example, by hydrogen bonds at the silica particle surface [36]. Such contacts are strong enough to replace polymer segments. This is supported by the finding that the critical slip forces of *FM*-contacts of silica fillers as deduced from stress-strain experiments [2] are comparatively low.

Wolff examined the equilibrium swelling of *NR* filled with silica (*Utrasil VN*2) when different amounts of diethylene glycol (*DEG*: Diethylene glycol) were added (Table 2) [10]. Due to hydrogen bonds at the silica particles surface glycol is preferably deposited. A defined fraction of the surface of each silica particle should be covered by glycol molecules. Reinforcement should be reduced accordingly because the number of polymer contacts is diminished.

The experimental results and their description with the aid of the Langmuir adsorption law are shown in Fig. 5 (parameters in Table 4). In fact, the polymer volume fraction φ_p decreases at constant silica volume fraction *v* with increasing amounts of glycol. If the whole surface is covered by a monomolecular layer of glycol the intrinsic swelling of the matrix is as large as for the unfilled

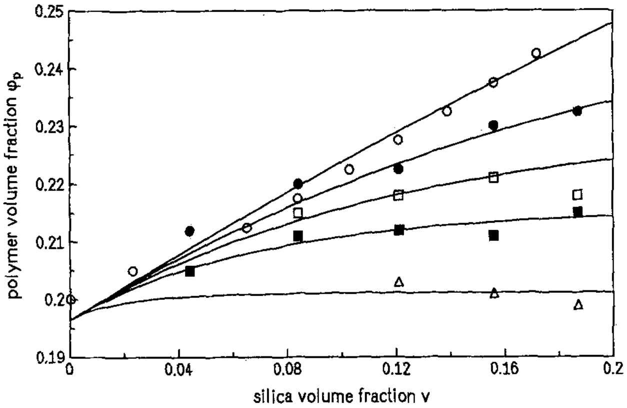

Fig. 5. Equilibrium swelling of NR-networks filled with silica in benzene (1.62 phr DCP) at T = 293 K. Five different amounts on glycol (α: ○ 0, ● 0.031, □ 0.061, ■ 0.092, △ 0.153) [17]. The solid lines are computed with the help of the Langmuir adsorption (parameters in Table 4)

Table 4. NR with silica and glycol in benzene

$a = 0.27$, $\lambda_m = 9.80$				
$M_1 = 78\ \text{gmol}^{-1}$, $y_1 = 1.147$, $\chi_0 = 0.4255$, $\gamma = 0.3020$				
$C = 2.5$				
loading α	0.031	0.061	0.092	0.153
b	0.0190	0.0154	0.0106	0.0033

rubber with the same density of junctions. No reinforcement is observed any more.

A striking feature of the glycol adsorption is that b must be put to lower and lower values when the concentration of glycol is increased. The isothermally absorbed fraction of glycol grows rapidly towards the saturation value Γ_0. From the plot in Fig. 6 the empirical relation is easily deduced

$$b = b_0 - mc; \quad m = b_0 = \frac{V_M}{V_f}. \tag{17}$$

The ratio of desorption- to adsorption-rates is uniquely decreased. With Eq. (17), we arrive at the specified Langmuir relationship :

$$\Gamma = \Gamma_0 \frac{c}{c + b_0(1 - cV_f/V_M)} = \Gamma_0 \frac{c}{c + b_0\left(1 - \frac{c}{c_{\max}} \frac{1 - c_{\max}}{1 - c}\right)}. \tag{18}$$

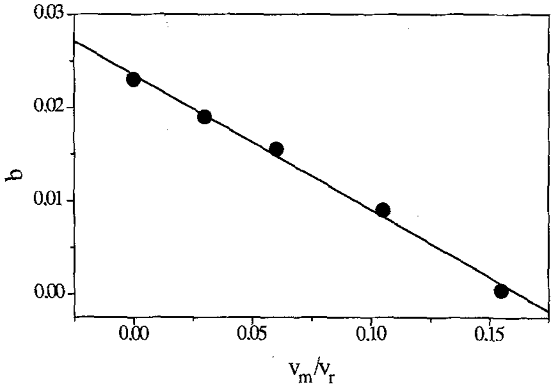

Fig. 6. The Langmuir parameter b against $\omega = V_f/V_{\text{rubber}}$

At smallest concentrations c, we should have single glycol molecules randomly deposited. We assume that adsorbed glycols can move laterally within the monolayers. If the density of the adsorbed glycol molecules increases, they then should be able to form clusters – as a kind of two-dimensional condensation. This is likely to happen due to additional hydrogen bonds formed between adsorbed glycols themselves. The ratio of adsorption-to-desorption-rate is continuously lowered therewith.

In this interpretation it is supposed that polymer segments are able to move laterally within a monolayer around a filler particle. This mobility should allow lateral *demixing* of adsorbent- and polymer-segments. This hypothesis is in accord with suggestions made recently according to which *FM*-contacts are anisotropic [37]. We found that strain-induced slip processes should depend on the symmetry of the mechanic field. The critical *FM*-adhesion energy seems to be determined by the component of the adhesional strengths in direction normal to the filler particles surface. Lateral movements are then likely to easily be activated.

An interesting conclusion

Langmuir isotherms characterize the equilibrium of adsorption. We have to justify that this can be achieved within a relatively short period of time. Let us prove this hypothesis by making a simple estimate. We assume that during the mixing process the modifiers are very rapidly

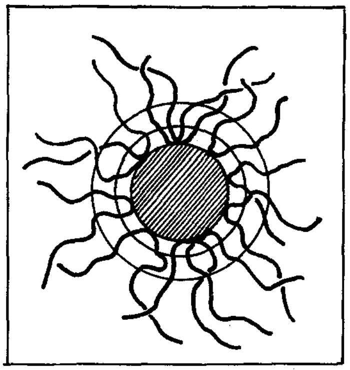

Fig. 7. Sketch of the surface of a filler particle

homogeneously distributed over the matrix. To establish adsorption equilibrium, diffusion steps across half of the mean distance between the filler particles are only necessary. The filler particles assumed to be randomly distributed over all directions for this distance ($\langle d \rangle$) is equal to

$$\langle d \rangle = R\frac{1 - v^{1/3}}{v^{1/3}} , \tag{19}$$

where R is the mean radius of the filler particles. Disregarding thermodynamic factors the diffusion length then can be estimated by calculating the distance arrived at by self-diffusion within the time t. According to Einstein, we have

$$d_{\text{selfdiffusion}} = (6Dt)^{1/2} , \tag{20}$$

where D is the self-diffusion coefficient. For one second and $R = 20$ nm, we calculate with $D \approx 10^{-8} - 10^{-10}\,\text{cm}^2\text{s}^{-1}$ a distance of about $\langle d_{\text{selfdiffusion}} \rangle = 2.5\,10^3 - 2.5\,10^2$ nm. In a rubber loaded with a volume fraction of $v = 0.05$, filler particles with a radius of $R = 20$ nm are on average separated by about $\langle d \rangle = 33$ nm. Hence, adsorption equilibrium should very rapidly be establishable. This is the consequence of having subsystems with each showing, on average, the same structure. Their size depends on the degree of loading and they are relatively small in all the examples considered here (see $\langle d \rangle$ computed in the above example). The most important matter is that these subsystems are thermodynamically and kinetically equivalent. Rapid local adjustment of adsorption equilibrium identifies filler loaded rubbers as colloid systems.

Conclusions

In this paper the nature of contacts between solid filler particles and a rubbery matrix is identified indirectly. Within a sufficiently short time molecules or polymer segments are held fast to defined sites. To describe absorption equilibrium of modifiers with the Langmuir model a rapid dynamics of the contacts is necessary. Desorption apparently occurs in all the examples studied here. This should, of course, also hold true for polymer segments. Yet, it is difficult to detect the absorption- and desorption-dynamics of polymer segments from swelling experiments because even in presence of modifiers the concentration of segments is so large that according to the Langmuir equation all available sites should always be occupied.

A most important aspect is that each filler particle should on average show the same layer structure. The absorption equilibrium is always rapidly arrived at by local processes in a colloid system. The primary filler particles are autonomous, statistically and thermodynamically equivalent entities. This is the reason why the cluster structure does not matter at all.

Modifier, solvent, and polymer chains considered as ideal mixture in the Langmuir model can be used for describing adsorption from a diluted gel. Nearly independent competitive adhesion of modifier and polymer segments to the surface of the filler particles is observed. Adsorption runs, of course, at less than the usual rate for adsorption from gas phase. The adsorbent with the highest absorption energy seems to occupy, in an independent manner, as many sites as necessary to satisfy adsorption and desorption equilibrium. Polymer segments then are attached to the *free sites* without remarkably changing the absorption energies of the modifier.

This ideal situation seems to approximately hold true for the silanes. Surprising is that desorption of silanes is required to occur. In the opinion of most authors, silanes are believed to be fixed to the filler surface by chemical bonds. Glycol as low molecular solvent is also able to expel polymer segments from the surface of silica. Moreover, these molecules seem to be able to move in the lateral directions within a monolayer on the surface. They probably reduce their free enthalpy by forming clusters. Inter-glycol hydrogen bonds might favor this process of "*two-dimensional condensation*". This condensation should satisfy the thermodynamics of a two-dimensional phase transition in binary mixture. This would lead to a well-defined mass fraction of clusters in the monolayers. Adsorption and desorption rates are modified therewith. But they go, nevertheless, into stationary equilibrium and allow to formulate an extended version of the Langmuir equation. This elucidates universal features of this model. It seems always to be appropriate when adsorbed monolayers are formed.

Toluene as solvent shows adsorption energies so weak that these molecules cannot adhere to the surface at all. This explains why in swollen loaded rubbers the whole surface is always fully contaminated by only polymer segments.

The above results lead to a deeper understanding of the cooperation between filler and matrix in a loaded network without modifiers. It is only the thermodynamic factor of absorption that guarantees that the density of segmental contacts is strain invariant. The surface must, in any case, remain fully covered. This must also hold true in samples extended to large strains. Desorption of polymer segments is likely to be enhanced due to strain-induced activation. Extension of intra-cluster chains leads to selective slip processes. Yet, even during the deformation the adsorption and desorption rates are large enough to rapidly adjust stationary equilibrium. This is possible because these processes run on relatively local scales.

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