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LETTER TO THE EDITOR

Universal properties in the dynamical deformation of filled rubbers

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Abstract. Starting from the observation that the filler particles in filled rubbers form fractal clusters which are connected to each other, a theoretical model is developed which establishes a connection between the amplitude dependence of the elastic deformation of filled rubbers and the structural properties of the filler. It is assumed that the elastic modulus is dominated by the rigid filler network at very low strain, whereas at higher strain the rubber matrix provides the main contribution because of cluster break-up. Within this model the exponent arising in an empirical description of the amplitude dependence is derived from the connectivity of the filler clusters.

Filled rubbers are used in a wide range of applications, the most important being the production of automotive tyres, where the performance characteristics are strongly affected by the filler properties. The basic achievement of filling relatively soft networks, i.e. crosslinked polymer chains, is to reach a significant reinforcement of the mechanical properties. It has been shown that the modulus of a filled rubber network is indeed significantly higher, when compared to the 'bare' modulus of the unfilled network. The latter is of the order of Nk_BT, where N is the number of chains and k_BT the thermal energy [1].

Moreover, fillers like carbon black (cb) or silica are active fillers, i.e. the elastic properties of the rubber are modified more than by means of a mere addition of hard randomly dispersed particles to a soft polymer matrix. Such a random dispersion would lead only to a hydrodynamic reinforcement [2]. The additional reinforcement is essentially caused by the complex structure of the active fillers (see, e.g., [3] and references therein). For example, carbon black consists of spherical particles with a rough and energetically disordered surface [4, 5], forming rigid aggregates in the 100 nm range with a fractal structure. Agglomeration of the aggregates on a larger scale forms filler clusters and even a filler network at high enough cb concentrations, which leads to additional processes [6]. Thus at filling fractions larger than a certain threshold the clusters form an irregular network that is fractal on some scales. The main point is that the filler network has the property that it is not stable, but breaks up into smaller units with increasing mechanical strain.

It is now widely accepted [4] that the filler networking is responsible for the typical nonlinear viscoelastic behaviour of filled rubbers, i.e. the characteristic amplitude dependence of the elastic moduli with periodical strain $\varepsilon(t) = a\sin(\omega t)$ with amplitude a. For constant temperature and frequency the stress is given by $\sigma(t) = G^*(a)\,\varepsilon(t)$ where $G^* = G' + \mathrm{i}G''$ is the complex elastic modulus, and G' is called the storage modulus, and G'' the loss modulus.

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Experimentally, with increasing strain amplitude a decrease of the storage modulus G' from G'_0 to a plateau value G'_∞ is found. This peculiar behaviour is known as the Payne effect and is present in most filled rubber systems. Payne [7] interpreted the decline of the storage modulus as a result of a dynamical break-up of the filler network described above: (van der Waals) bonds between cb aggregates are continuously broken and reformed, so at low deformations the energetic elastic contribution of the rigid filler network is dominant, whereas at high deformations the filler has only a small remaining effect, which is hydrodynamic and caused by the rubber–cb interaction [8]. In spite of the fundamental significance for the reinforcing of filled rubbers, a full knowledge of the influence which the structure of the filler network has on the mechanical properties is still lacking.

Kraus [9] developed a phenomenological model which quantifies the Payne effect and has often been successfully applied for the fitting of experimental data. The model is based on the assumption that the filler network breaks and recombines with various rates, which depend on amplitude (deformation) and on some rate constants. The result says that the decline of the storage modulus G' with growing strain amplitude has the characteristic functional form

$$\frac{G' - G'_\infty}{G'_0 - G'_\infty} = \frac{1}{1 + (a/a_c)^{2m}} \tag{1}$$

where a_c is a constant. It was shown by [9, 10, 11] that the form exponent $m \approx 0.6$ is universal, i.e. it is to a large extent independent of temperature, frequency, cb content and the type of carbon black and rubber mixture used. Unfortunately within the Kraus model the exponent m is a purely empirical (input) parameter, the reasons for the universality remaining unclear. Moreover the constant a_c is determined by quantities—such as rate constants for the breaking and recombination process—which cannot be measured by experiments. It has to be realized that a_c and m are fitting parameters without obvious physical relevance to the structural properties of the cluster network.

In the following it is shown that the phenomenological result from equation (1) can indeed be derived from a physical model, that uses a realistic model for the cluster network. The present new model is based essentially on the assumption that the clusters forming the filler network have a self-similar, i.e. fractal structure, which can be described by correlations similar to those that appear in the percolation model. This is not totally correct, inasmuch as the cluster growth for cb concentrations above the gel point of the filler network is governed rather by a kinetic cluster than by the cluster aggregation process [6]. Therefore the model presented here is restricted to filler concentrations near the gel point, which is the case in most systems under application. At lower concentrations a crossover to the pure rubber behaviour is expected. This will be discussed in more detail in a longer publication.

Presuming that a cluster consists of aggregates of size b, the relation between the number N of 'elastic active' aggregates in a cluster and the size ξ of the clusters is given by

$$N \cong (\xi/b)^C \tag{2}$$

with a connectivity exponent C. Here 'elastically active' means that in such irregular structures many structural elements (e.g. dangling and nonconnected parts) do not take part in the transmission of stress. In an ideal percolation cluster this exponent is to be identified with the fractal dimension of the elastic backbone, $C \approx 1.7$ [12].

In order to achieve a correct picture of a filled system, we first have to set up a relationship between stress and elongation of the filler clusters for uniaxial deformation. For this purpose we adopt the ideas proposed by Witten *et al* [13]. These authors derived a similar scaling behaviour for the elastic properties in the limit of large extensions, which we employ here with several modifications. In particular we assume that the filler clusters are

not stretched with growing strain but rather are broken up almost immediately into smaller and smaller units, the stress being supported by the rubber matrix.

The strong dependence of cluster size on the deformation leads to the assumption that ξ is inversely proportional to the external force. This is similar to the well known assumption in the original blob model of Pincus in polymer physics (see, e.g., [14]), when the deformation behaviour of excluded-volume chains is computed. The restriction there to large extensions does not apply here because of the different nature of the connectivity.

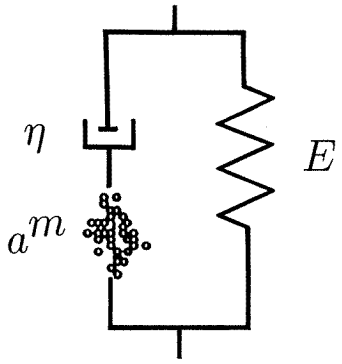

Figure 1. The Zener model with a nonlinear and a linear spring.

Following the lines of the work of Witten *et al* the total size R is the number of clusters $n = N_0/N$ (where N_0 is the total number of filler aggregates) times the cluster size ξ. Thus the elongation factor λ is given by

$$\lambda \cong \frac{R}{\xi_0} = \left(\frac{\xi_0}{\xi}\right)^{C-1} \tag{3}$$

where $\xi_0 \cong bN_0^{1/C}$ is the maximal cluster extension. The expression for the stress is $\sigma \cong (T/\xi_0)\lambda^{1/(C-1)}$, leading to the following nonlinear relation for the elastic modulus of the filler:

$$G(a) \propto \frac{T}{\xi_0}\ a^{-(C-2)/(C-1)} \tag{4}$$

where the amplitude a is proportional to the deformation. This has to be linked with the rubber matrix at dynamic deformation. In a first idealized *ansatz* we do this by using an elementary viscoelastic model, the so-called Zener model. As shown in figure 1 this is a Maxwell element with a nonlinear spring (representing the filler clusters) and viscosity η, combined in parallel with a further spring with spring constant E. In fact, this model is under current discussion [15] in different respects, and represents one of the most elementary models in the method of finite elements.

For periodic deformation the elastic moduli of the total system are easily calculated [16]. The result for the storage excess modulus is

$$\frac{G'(a) - E}{G'_0 - E} = \frac{1}{1 + (K/\omega\eta)^2 a^{-2(C-2)/(C-1)}} \tag{5}$$

where G'_0 is the storage modulus for $a \to 0$ and K is a constant containing the system parameters like temperature and material properties. Remarkably, this result can be compared to the result from the phenomenological model given by Kraus (equation (1)) and the parameters a_c and m can be identified. There two main points need some attention:

(i) The constant a_c (here $a_c = \omega\eta/K$) contains specific details of the model and thus all properties and constants from the Zener model are collected. Thus the critical amplitude a_c has no universal features.

(ii) The exponent m, however, is entirely determined by the structure of the filler network. We expect the exponent therefore to give universal features of the cluster network.

If the storage excess modulus (5) derived from the present model is compared to that for the Kraus model (1), it is found that $m = -(C-2)/(C-1)$. From the value $m \approx 0.6$ determined by fits to experimental data, a connectivity exponent $C_{\text{exp}} \approx 1.625$ is calculated. Hence the fractal dimension of the elastic backbone assumed above to be $C \approx 1.7$ is slightly too high. This value, however, corresponds to the 'ideal' percolation model. As mentioned above this is not the case in practice, as the aggregation process for filler clusters may fall in a different universality class of growth processes.

Of course the Zener model used in the derivation makes little claim to explain the influence of the rubber matrix in a proper way. This is why the parameters η and ω occurring in the model cannot be mapped onto experimentally obtained quantities the way the exponent C can. The next step is the inclusion of simple network models to describe the rubber behaviour. This will be shown in a forthcoming publication. Then it is expected that the nonuniversal constant a_c will be found to depend in detail on specific network properties, such as the typical mesh size, and relaxation times.

Nevertheless the present model shows the principles and the universal character of the Payne effect in filled rubbers. The characteristic form of the amplitude dependence of the dynamic elastic moduli was successfully derived from simple assumptions on the structure of the filler network.

The advantage of this simple model is that it already allows the characterization of realistic experiments, in the sense that the exponent used in the Kraus model does not depend on the nature of the filler particles. Hence we expect the same behaviour for all types of filler particle, independent of their special surface interactions, as long as they form clusters.

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