Elasticity of Fractal Filler Networks in Elastomers

Manfred Klüppel

Deutsches Institut für Kautschuktechnologie e. V., Eupener Straße 33
D - 30519 Hannover, Germany
E-mail: Manfred.Klueppel@DIKautschuk.de

Summary: The role of filler networking in the elastic properties of elastomer composites is investigated by means of a fractal approach to filler aggregation in high viscosity media and a linear elastic model of flexible chains of filler particles. The filler netwok is described by a space-filling configuration of fractal filler clusters, resulting from a kinetic cluster-cluster aggregation (CCA) process. The elastic modulus of the filler network is shown to fulfil a scaling relation with respect to filler concentration. The universal value 3.5 of the elasticity exponent reflects the fractal nature of the filler network. Experimental results on various elastomer composites with conventional- and model fillers (microgels) demonstrate that a corresponding scaling prediction for the small strain modulus is well fulfilled.

1. Introduction

Two fundamental micro-mechanical concepts of filler networking and non-linear viscoelasticity of reinforced rubbers are provided by the (L-N-B) model [1] and the cluster-cluster-aggregation (CCA) model [2-5]. They consider the arrangement of filler particles in clusters with well defined fractal structures and the elasticity or fracture of such clusters under external strain. These two models refer to different geometrical arrangements of sub-units in particular filler network structures, resulting from percolation or kinetical cluster-cluster aggregation, respectively.

2. The CCA model of filler networking in elastomers

We will focus here on the kinetic cluster-cluster-aggregation (CCA) model of filler particles in elastomers. It is based upon the assumption that the particles are allowed to fluctuate around their mean position in a rubber matrix. Upon contact of neighbouring particles or clusters they stick together, irreversibly. This refers to the fact that the thermal energy of colloidal particles is in general much smaller than their interaction

 CCC 1022-1360/00/$ 17,50+.50/0

energy. Dependent on the concentration of filler particles, this flocculation process leads to spatially separated filler clusters of solid fraction Φ_A or a filler network that can be considered as a space-filling configuration of fractal CCA-clusters. The different cases are shown schematically in Figure 1.

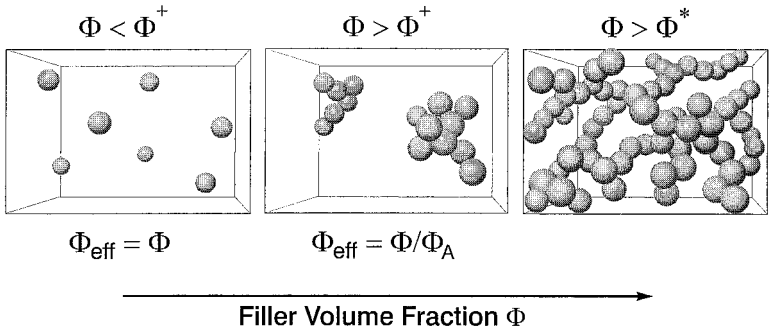

Figure 1: Schematic view of in-rubber filler morphology in three concentration regimes. For $\Phi < \Phi^*$ reinforcement is due to hydrodynamic amplification by particles ($\Phi < \Phi^+$) or clusters ($\Phi > \Phi^+$) with $\Phi_{eff} = \Phi$ or $\Phi_{eff} = \Phi/\Phi_A$, respectively. For $\Phi > \Phi^*$ reinforcement is due to the deformation of a flexible filler network (see below).

At sufficient high filler concentrations, above the gel point ($\Phi > \Phi^*$), diffusion limited cluster by cluster aggregation leads to a space-filling configuration of CCA-clusters, similar to colloid aggregation in low viscosity media [2-5]. Due to the characteristic self-similar structure of the CCA-clusters with fractal dimension $d_f \approx 1.8$ [6], the cluster growth as described by the solid fraction Φ_A of the clusters is given by a space-filling condition, stating that the local solid fraction equals the overall solid concentration:

$$\Phi_A(\Phi) = N_F^{-1}\,\Phi \quad \text{for} \quad \Phi > \Phi^* \tag{1}$$

The solid fraction of the fractal CCA-clusters fulfils the scaling law:

$$\Phi_A(\xi) \equiv \frac{N(\xi)\,d^3}{\xi^3} \cong \left(\frac{d}{\xi}\right)^{3-d_f} \tag{2}$$

Here, N is the number of particles of size d in clusters of size ξ and N_F in Eq. (1) is a generalized Flory-Number of order one ($N_F \cong 1$) that considers a possible interpenetrating of neighbouring clusters [3]. Eqs. (1) and (2) imply that the cluster size ξ decreases with increasing filler concentration Φ according to a power law. This reflects the fact that smaller clusters occupy less empty space than larger clusters (space-filling condition). It means that the size of the fractal heterogeneity of the filler network, i. e. the CCA-clusters, decreases with increasing filler concentration.

A necessary condition for rubber reinforcement by filler clusters is the rigidity condition $G_A >> G_R$, where G_A is the elastic modulus of the clusters and G_R is that of the rubber. This is obvious because a structure that is weaker than the rubber cannot contribute to the stiffening of the polymer matrix. We will see below that the rigidity condition is not fulfilled in all cases, because the modulus G_A of the clusters decreases rapidly with increasing size of the clusters. It means that relatively small filler clusters of less than 100 particles can lead to reinforcement of the polymer matrix with $G_R \cong 0.1$ MPa. Here, only this case, necessary for reinforcement, is considered, i.e. the rigidity condition $G_A >> G_R$ is assumed to be fulfilled.

For filler concentrations above the gel point Φ^*, where a through-going filler network is formed, stress between the (closely packed) CCA-clusters is transmitted directly between the spanning arms of the clusters that bend substantially. In this case, the strain of the rubber is almost equal to the strain of the spanning arms of the clusters ($\gamma_R \approx \gamma_A$). It means that, due to the rigidity condition $G_A >> G_R$, the overwhelming part of the elastic energy is stored in the bending arms of the clusters and the contribution of the rubber to the elastic modulus G of the sample can be neglected, i.e. $G \approx G_A$. This indicates that the stored energy density (per unit strain) of highly filled elastomers can be approximated by that of the filler network that in turn equals the stored energy density of a single CCA-cluster. The last conclusion follows from the homogeneity of the filler network on length scales above the cluster size ξ.

3. Elasticity of flexible chains of filler particles

Since for highly filled elastomers the elastic modulus G can be well approximated by G_A, it is useful to consider the micro-mechanical background of the elastic modulus G_A of the CCA-clusters more closely. Therefore, we refer to Kantor and Webman's two dimensional, linear model of flexible chains that considers a vectorial Born-lattice model with a bending energy term between neighbouring bonds [7]. As outlined in Figure 2, the strain energy H of a chain composed of a set of N singly connected bonds $\{\boldsymbol{b}_i\}$ of length a under an applied force $\boldsymbol{F}$ at the two ends of the chain is:

$$H = \frac{F^2 N S_\perp^{\,2}}{2G} + \frac{aF^2 L_{//}}{2Q} \tag{3}$$

where

$$S_\perp^{\,2} = \frac{1}{F^2 N} \sum_{i=1}^{N} \left[(\boldsymbol{F} \times \boldsymbol{z})(\boldsymbol{R}_{i-1} - \boldsymbol{R}_N) \right]^2 \tag{4}$$

is the squared radius of gyration of the projection of the chain on a two dimensional plane and

$$L_{//} = \frac{1}{aF^2} \sum_{i=1}^{N} (\boldsymbol{F} \cdot \boldsymbol{b}_i)^2 \tag{5}$$

Here G and Q are local elastic constants corresponding to the changes of angles between singly connected bonds and longitudinal deformation of single bonds, respectively. The vector $\boldsymbol{z}$ is a unit vector perpendicular to the plane. For long chains the second term in Eq. (3) can be neglected and the major part of the strain energy H results from the first term, i. e. the bending term of the chain. Then, the force constant of the chain relating the elastic energy to the displacement squared of the end of the chain is given by:

$$k = G / (N S_\perp^{\,2}) \tag{6}$$

In the three-dimensional case (d = 3), the angular deformation is not limited to the on-plane bending, but also to the off-plane twisting. This can be taken into account in a simplified model, by accumulating the contributions from different kinds of angular deformation in the first term of Eq. (3), i. e. by replacing G through an averaged force constant of different kinds of angular deformations $\overline{G}$ [1]. The local elastic constant $\overline{G}$ is assumed to be controlled by the rubber phase around fillers, i.e. it is primary attributed to bound rubber. The elastic constant Q is controlled by van der Waals forces between fillers.

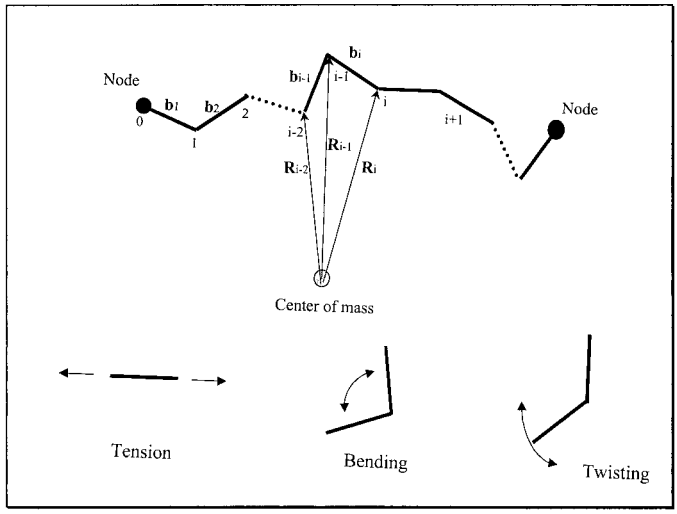

Figure 2: Illustration of Kantor and Webman's model of flexible chains with tension-, bending- and twisting energy terms.

4. Scaling behaviour of the elastic modulus of filled rubbers

From Eq. (6) one obtains the elastic modulus $G_A = k/\xi$ of the elastically effective CCA-cluster backbone, if $S_\perp$ is replaced by the cluster size ξ ($S_\perp \cong \xi$) and N is identified with the number N_B of particles in the cluster backbone. Thereby, we refer to an approximation of the CCA-cluster backbone as a single spanning arm, i. e. we consider it as the bending-twisting modulus of tender, curved rods [2-5]:

$$G_A \cong G_P \left(\frac{d}{\xi}\right)^3 N_B(\xi)^{-1} \cong G_P \left(\frac{d}{\xi}\right)^{3+d_{f,B}} \cong G_P \, \Phi_A^{(3+d_{f,B})/(3-d_f)} \qquad (7)$$

Here, $G_P := \overline{G}/d^3$ is the averaged elastic bending-twisting modulus of the different kinds of angular deformations of the flexible bonds between filler particles. In the second part of Eq. (7) the scaling behaviour $N_B \cong (\xi/d)^{d_{f,B}}$ of the particles in the cluster backbone is used, where $d_{f,B} \approx 1.3$ is the fractal dimension of the CCA-cluster backbone, here identified with that of a single spanning arm [6]. The third equality of Eq. (7) follows with Eq. (2).

Eq. (7) describes the modulus G_A of the clusters as a local elastic bending-twisting term G_P times a scaling function that involves the size and geometrical structure of the clusters. Consequently, the temperature- or frequency dependency of G_A is controlled by the front factor G_P or $\overline{G}$. As stated above, the local elastic constant $\overline{G}$ is governed by the bound rubber phase around the filler clusters. An essential part of the bound rubber consists of a layer of immobilised, glassy polymer, implying that the temperature- or frequency dependence of G_A is given by that of the glassy polymer. Since $G \approx G_A$, we expect an Arrhenius temperature behaviour for highly filled rubbers that is typically found for amorphous polymers in the glassy state. This is in agreement with experimental findings [8].

The dependency of the elastic modulus G of the compound on filler volume fraction Φ is obtained, if Eq. (7) is combined with Eq. (1):

$$G \cong G_P \Phi^{\frac{3+d_{f,B}}{3-d_f}} \qquad \text{for } \Phi > \Phi^* \qquad (8)$$

Eq. (8) predicts a power law behaviour $G \sim \Phi^{3.5}$ for the elastic modulus. Thereby, the exponent $(3+d_{f,B})/(3-d_f) \approx 3.5$ reflects the characteristic structure of the fractal heterogeneity of the filler network, i.e. the CCA-clusters. The predicted power law behaviour at higher filler concentrations is confirmed by the experimental results shown

in Figure 3, where the small strain storage modulus of a variety of filled rubbers is plotted against filler loading in a double logarithmic manner. The predicted scaling behaviour is also confirmed by viscoelastic data obtained for various other carbon black filled rubbers [3,4].

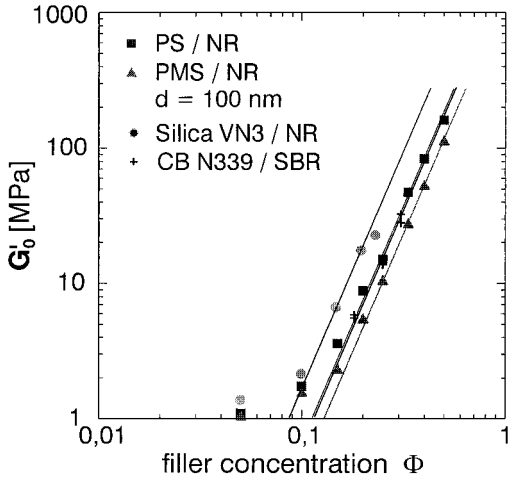

Figure 3: Double logarithmic plot of the small strain storage modulus vs. filler volume fraction for a variety of rubber composites as indicated. The solid lines with slope 3.5 correspond to the prediction of Eq. (8) (from Ref. 9).

1. C.-R. Lin, Y. D. Lee (1996) Macromol. Theory Simul. 5:1075; ibid. (1997) 6:339
2. T. A. Witten, M. Rubinstein, R. H. Colby (1993) J. Phys. II (France) 3:367
3. M. Klüppel, G. Heinrich (1995) Rubber Chem. Technol. 68:623
4. M. Klüppel, R. H. Schuster, G. Heinrich (1997) Rubber Chem. Technol. 70:243
5. R. H. Schuster, M. Klüppel, J. Schramm, G. Heinrich (May 1998) Paper No 56, ACS Rubber Division Meeting, Indianapolis, USA
6. P. Meakin (1990) Prog Solid State Chem 20:135; (1988) Adv. Colloid Interface Sci. 28:249
7. Y. Kantor, I. Webman (1984) Phys. Rev. Lett. 52:1891
8. R. Payne (1962) J. Appl. Polym. Sci. 6:57
9. M. Müller, R. H. Schuster, (Sept. 4-7,2000) Proceedings: German Rubber Conference 2000, Nürnberg, FRG