Studies of the So-Called Jamming Phenomenon in Filled Rubbers Using Dynamical-Mechanical Experiments

Sven Richter,[1] Hermann Kreyenschulte,[1] Marina Saphiannikova,[1] Thomas Götze,[1] Gert Heinrich*[1,2]

Summary: In the past, several models have been proposed to describe the so-called jamming on filled rubbers. We carefully repeated such experiments on carbon black filled EPDM systems and found that the interpretation given in the literature is not transferable to our systems. Therefore, one has to be very careful in using these universal criteria to describe such dynamic-mechanical transitions on filled polymer systems.

Furthermore, we present an improved multi-stage agglomeration model to describe the flocculation process in filled elastomer systems.

Keywords: filled elastomers; filler flocculation; jamming; non-linear rheology

Introduction

Jamming processes, which exhibit non-equilibrium transitions from a fluid-like to a solid-like state, and which are characterized solely by the sudden arrest of particle dynamics,[1] can occur in a variety of systems of diverse characteristic length scales, e. g. molecular structures, colloidal suspensions, polymer-filler composites, granular materials, and even automobile traffic. Jamming and glass-formation processes appear to have interrelated physics. More examples about the general jamming phenomenon are given in one of our previous publications.[2] The agglomeration of filler particles in an elastomer matrix is claimed to be a typical jamming process.[3]

Filled Polymer Systems as Jammed Material: Strain Induced Nonlinearity

Polymer networks in general are a class of relatively soft inherently stable materials which find many applications in contemporary technologies, e. g. automotive industry, medicine, biotechnology etc. Interestingly, in the case of particle filled rubbery networks recent discussions were dedicated to remarkable similarities between the dynamic strain-induced non-linearity of the modulus and the physics of the glass transition of glass-forming materials, as well as the jamming transition of vibrated granular materials. This has important implications with regard to the understanding of the strain-induced non-linearity of filled rubbers. The similarity stems from the fact that filler particles in the rubber matrix agglomerate and tend to form filler networks. The agglomeration and network formation of filler in elastomeric matrices are thought by some scientists to be typical jamming processes, and correspondingly de-agglomeration and recovery to be de-jamming processes. Further it is assumed that different routes, through strain, volume fraction, and temperature changes, can effectively lead filled rubbers to the same jammed state.[3]

The effect of amplitude dependence on the dynamic-mechanical properties of filler reinforced rubbers was brought into clear

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[1] Leibniz-Institut für Polymerforschung Dresden e. V., Hohe Strasse 6, D-010169 Dresden, Germany
Fax: (+49) 351-4658-362;
E-mail: richter-sven@ipfdd.de

[2] Technische Universität Dresden, Institut für Werkstoffwissenschaft, D-01069 Dresden, Germany

focus by the work of Payne. He (and later Kraus in a first quantitative model) interpreted the sigmoidal decline from a 'zero–amplitude' value of the storage modulus, G'_0, to a high–amplitude plateau G'_∞ as the result of a breakage and rebuilding of physical (van der Waals) bonds between filler aggregates that were assumed to build an energetically elastic filler network within the soft rubber matrix (for reviews, see refs.[4–7] and references therein). At large strains, this filler network is broken down and the modulus is then determined only by polymer–polymer cross-links, elastical effective filler–polymer couplings and hydrodynamic filler effects.

In some recent reports several criteria (isoenergetic character; exponent in the power spectra after a FFT analysis of the fluctuations in G') have been proposed by the group of Robertson et al. [3,8,9] for the jamming transition in filled rubbers. First of all, the authors found when plotting the normalized storage modulus G'/G'_0 (or loss modulus $G''/G''_{\max}$) against the variation of the mechanical energy, that all experimental data appear to collapse approximately on the same curve. Of most importance is that the critical mechanical energy after the transition is constant.

Secondly, filler clusters in elastomeric matrices are not in the equilibrium state because the filler particles cannot freely access all of their possible configurations. Under shear, the filler particles in the matrix are forced to explore different configurations in the system. In particular, forcing two large filler clusters to pass through each other should result in jamming, detectable when analyzing the fluctuations in G'.[8]

In our present work we will check these criteria on EPDM rubber samples loaded with different carbon blacks, and we will propose an improved model to describe the filler agglomeration process after non-linear dynamic-mechanical shear treatment.

Experimental Part

The oscillatory shear experiments for measuring the shear modulus G' were conducted on an Ares G2 Rheometer (TA Instruments) using a plate-plate-geometry. To prevent slippage at high strain amplitudes the samples were glued to the plates using a cyanoacrylate superglue (Pattex, Henkel). A master batch was formulated with 100 parts per hundert rubber (phr) ethylene propylene diene rubber (EPDM, Buna EP G3440, Lanxess) with varied (10 to 80 phr) of carbon black (N660) or constant (50 phr) (HS 45 and LS 18), 2 phr stearic acid, 5 phr zinc oxide and 2 phr polyethylene glycol (Lipoxol 4000). Mixing was performed with a Rheomix 600p using a mixing speed of 80 rpm at 70 °C for 5 min (first step). The curatives used were: 1 phr Vulkacit Mercapto C, 1.2 phr Perkacit TBZTD-PDR, 2 phr Rheocure TP/S and 0.75 phr sulfur 80/90. The curatives were added to the first mixture and mixed afterwards at 70 °C with 50 rpm for 2 min. The dilution process was carried out by using a two-roll mill at 50 °C for 5 min with a gap size of 0.5 mm. The prepared samples were finally cured in molds at 170 °C for t_{95} +5 min. The vulcanization times have been characterized using a SIS V50 rubber process analyzer (Scarabaeus).

The three carbon black grades (N 660, HS 45 and LS 18; Evonik Carbon Black GmbH) differ in the specific surface area (characterized by nitrogen adsorption (statistical thickness surface area (STSA); STSA values of N 660: 34 m^2/g, HS 45: 39 m^2/g and LS 18: 19 m^2/g) and structure (given by the oil adsorption number (OAN); OAN values of N 660: 90 ml/100g, HS 45: 121 ml/100g and LS 18: 73 ml/100g). The uncrosslinked specimens (diameter of 25 mm) which did not contain the vulcanizing system were cut from pressed plates of approximately 4 mm thickness. The crosslinked specimen had a diameter of 8 mm and a height of 12 mm. All mechanical tests at Ares G2 were performed at 100 °C under nitrogen environment and at a frequency of 1 Hz. First, a strain amplitude of 10% was applied for 1.5 hours to destroy possible filler-filler-networks, then the samples were allowed to

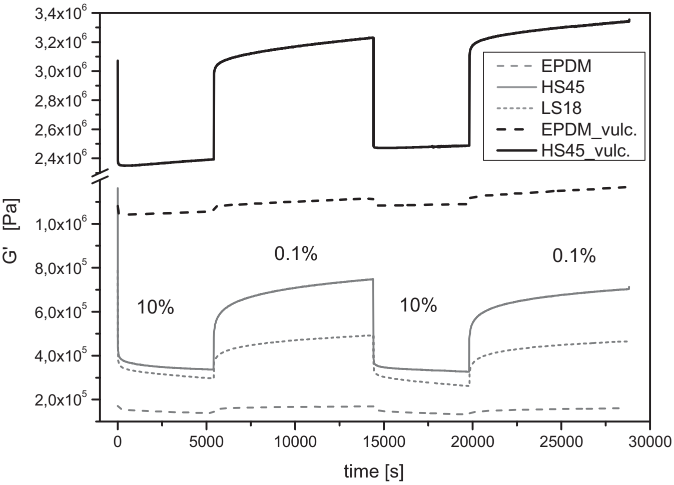

Figure 1.
Shear storage modulus G' as a function of strain (10% and 0.1%) and time for the EPDM matrix (cross-linked as well as uncross-linked), the carbon black filled systems (50 phr HS 45 & LS 18) (cross-linked) for HS45 as well as uncross-linked for both filled systems).

recover at 0.1% strain for 2.5 hours. This procedure was repeated twice to identify irreversible effects (see Figure 1).

Dynamic mechanical analysis for determining E' and E'' were performed with an Eplexor2000N dynamic measurement system (Gabo Qualimeter® Testanlagen) using a constant frequency of 10 Hz at a temperature of 20 °C. The samples were analyzed in the tension mode. For measurements of the complex tensile modulus, E^*, a static load of 1 N was applied, and then the samples were oscillated to a dynamic load in a range between 0.1–40% strain.

Results and Discussion

First of all, in Figure 1 the results of the filler flocculation process are presented. It is clearly to be seen, that higher values in the STSA and OAN numbers of the carbon black HS45 lead to better mechanical properties in comparison to the sample filled with carbon black LS18. Furthermore, as expected one can observe that cross-linking leads to higher storage moduli values G' (EPDM_vulc. and HS45_vulc.), too. Additionally, for the filled and cross-linked sample (HS45_vulc.) the long-time relaxation behavior is similar to that of the sample HS45.

Strain Induced Nonlinearity of the Carbon Black (N660) Filled Rubber System and the Isoenergetic Jamming Criterion

In Figure 2 the strain dependency of the storage tensile modulus E' is presented for different filler contents of carbon black (N 660). Independent of the strain amplitude the storage modulus is increasing with increasing filler content. At filler contents

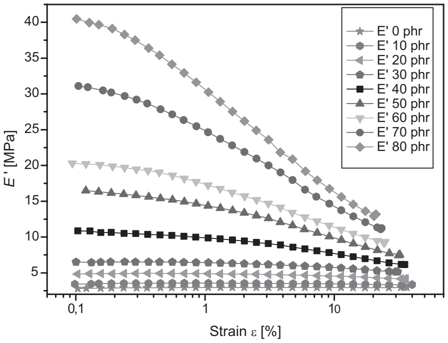

Figure 2.
Strain dependency of the storage tensile modulus E' as a function of carbon black content.

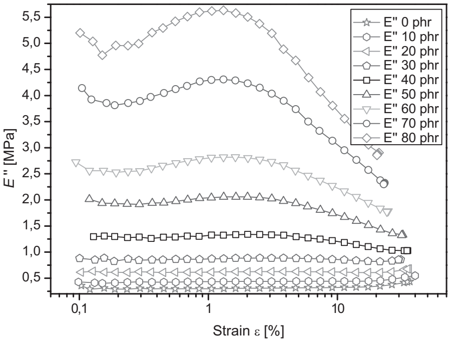

Figure 3.
Strain dependency of the loss tensile modulus E'' as a function of the filler content. The maximum in E'' denotes the value of the critical strain ε_c.

higher than the percolation threshold (i.e. ≥40 phr, see Figure 4) the storage modulus decreases with increasing strain amplitude. This effect is well known as Payne-Effect[7] and is more pronounced at higher filler contents. At low filler contents (<40 phr) no significant strain dependency can be observed.

Figure 3 shows the strain dependency of the loss tensile modulus E'' as a function of the filler content. Similar to the storage modulus presented in Figure 2, the loss modulus is increasing with increasing filler content but contrary to the storage modulus the loss modulus shows a maximum at intermediate strain amplitudes. This maximum is more pronounced at higher filler contents and disappears at filler contents smaller than 40 phr.

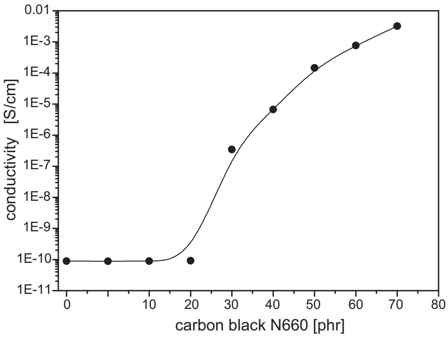

Figure 4.
Electrical conductivity of the filled rubber sample as a function of carbon black (N 660) content.

Figure 4 presents the electrical conductivity of the filled rubbers as a function of carbon black load. As the load passes through a threshold (between 30–40 phr), there is an abrupt increase in electrical flow with increasing carbon black load. The transition is analogous to the general critical phenomena in terms of percolation.

Figure 3 shows that the magnitude of the critical strain ε_c (σ is the stress amplitude with $\sigma = E'\varepsilon$) at the mechanical transition (Payne effect) decreases with increasing filler load. Remarkably, when the normalized storage modulus E'/E'_0 (not shown here) and loss modulus E''/E''_{max} (in particular it is really difficult to locate the maximum in E'' below filler concentrations of 30 phr, because there is no distinct maximum at all) are plotted against the variation of the mechanical energy $\sigma\varepsilon$, experimental data appear to collapse approximately together only at about 40 J/m^3, see Figure 5. Our observation is completely different from that done in the work of Wang and Robertson[3] (on polybutadiene rubber filled with carbon black N343), where practically one mastercurve was presented.

Summarizing these results presented in Figure 3, 4 and 5 we can conclude the following. The Payne effect (a jamming-dejamming transition in filled rubbers according to Wang and Robertson[3]) can

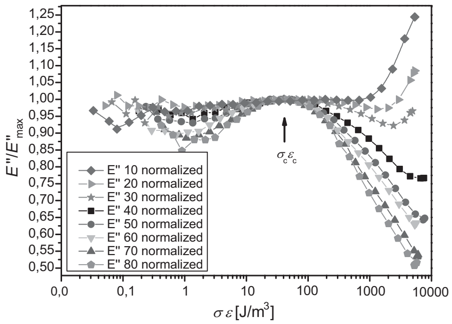

Figure 5.
Normalized loss tensile moduli E''/E''_{max} of the filled rubber system with indicated filler volume concentrations (10-80 phr) plotted versus $\sigma\varepsilon$. The E'' data are vertically scaled by E''_{max}, the peak value of E'' (compare Figure 3).

be detected by a strain sweep. The Payne effect and the electrical percolation threshold occur at approximately the same concentration of carbon black (between 30–40 phr). Hence, this study also reveals that the flocculation effects and electrical percolating of fillers in rubber composite share the same physical origin.

An isoenergetic character at transition as an indication for the jamming phenomenon could not be observed. We found that there was no shift in the maximum of $\sigma_c\ \varepsilon_c$. Furthermore, no distinct maximum of $\sigma_c\ \varepsilon_c$ is detectable at lower carbon black contents. So, we conclude, that this isoenergetic feature cannot be a universal criterion for the so-called jamming transition (Payne effect). We only observe, that the shape of the curves behave different at the Payne effect transition. So, we have to look at other rheological criteria to describe filler flocculation/jamming phenomena.

Fluctuations of Storage Modulus as an Indicator for Jammed Systems

Wang and Rackaitis[8] claimed to find jamming-specific fluctuations of the storage modulus of rheological long term measurements on filled, vulcanized rubbers. A fast Fourier transformation (FFT) of this data lead to the power spectrum $P(f)$ which is defined as

$$P(f) = \lim_{\Delta f \to 0} \frac{A^2(f, \Delta f)}{\Delta f} \qquad (1)$$

where A is the signal power (or the sum of FFT amplitudes) in the frequency band from f to $f + \Delta f$. The power spectra are found to obey a power law behavior $P(f) \sim 1/f^{\beta}$ with an exponent $\beta = 2$ over a wide frequency range which is proposed to be a hint for a jamming – dejamming transition when big agglomerates are forced to pass one along another.[8] This second jamming criterion stems from investigations of Albert et al. on jamming in granular materials.[10] The authors measured the force needed to drag a rod through a cylinder filled with glass spheres. The fluctuations of the force signal could neither be explained by ordinary stick slip processes nor by the motion of a frictional plate on top of granular medium and were therefore supposed to be characteristic for the failure of the jammed state. Analyses of the fluctuations of the storage modulus G' at the end of the second high and low strain sequence were analyzed using FFT and lead to the power law dependence in the power spectrum. We checked this criterion with one of our systems.

In Figure 6 the power spectra of the fluctuations of the last 128 points of the high strain (10%) sequence are presented. All power spectra show a decay proportional to f^{-2}. The line with a slope of -2 is drawn to guide the eye. There is no significant difference between the spectra of filled and unfilled samples regardless whether the samples are vulcanized or not. The power spectra of the fluctuations of the last 128 points of the low strain (0.1%) sequence show similar behavior (see Figure 7). One has also to note, that in our experimental studies we used carbon black particles, which have completely different interactions than the glass spheres used in the experiment of Albert et al.[10] on jamming in granular materials mentioned above. Therefore, one cannot correlate this achieved exponent of -2 of such experiments and analysis on carbon black filled rubbery systems.

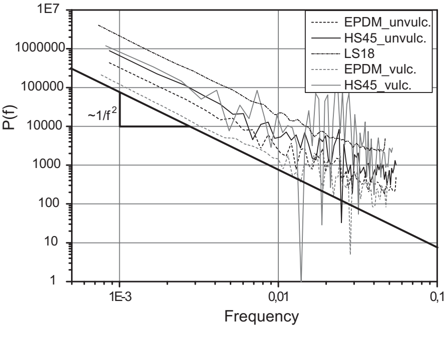

Figure 6.
Power spectra $P(f)$ as a function of frequency f for all investigated samples (compare Figure 1) of the second cycle (G' fluctuations during destruction of the carbon black filled network) at 10% strain. The solid line has a slope of -2.

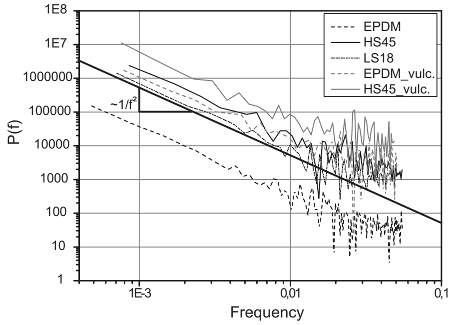

Figure 7.
Power spectra *P*(*f*) as a function of frequency *f* for all investigated samples (compare Figure 1) of the second cycle (G' fluctuations during recovery of the carbon black filled network) at 0.1% strain. The solid line has the slope of -2.

Describing the First Filler Flocculation Recovery Process at 0.1% Strain

In a very simple and naive approach, we may assume that the rate of change of contact number (say N) contributing to filler-filler interactions after the sudden breakdown (see Figure 1: step 1, destruction of the filler network by application of 10% strain amplitude) due to a step – like increase of deformation amplitude is proportional to the square of the concentration of units. These units correspond to filler aggregates which form successively new agglomerates in the (infinite) filler network. Then

$$\frac{dN}{dt} = k(N - N_\infty)^2 \tag{2}$$

where k is a rate constant. This type of growth is described as a second-order reaction. We note that Equation (2) does not describe the modulus behavior under shear deformation but the recovery process. The final state would be reached when $N = N_\infty$ at $t \to \infty$. We assume that the shear modulus $G \equiv |G^*|$ ($\approx G'$) is proportional to the increase of new contacts, where for $t = t_o$: $N = N_0$ and for $t \to \infty$: $N = N_\infty$. Here, N_0 is the residual number of filler-filler contacts just after the breakdown where the amplitude increases stepwise.

The solution of Equation (2) for the modulus recovery yields[11]

$$G(\Delta t) = G_\infty \left(1 - \frac{G_\infty}{k\Delta t + C}\right) \tag{3}$$

where C is a constant of integration. The rate constant k depends on the filler type, temperature and filler loading. We will denote Equation (3) as the power-law saturation equation. Within this very general background, the exponent "2" in Equation (2) characterizes the autonomous (but forced by restrictions) saturation in the aggregated growth process and is a measure of complexity. The more this exponent deviates from 1, the higher is the cooperativity within the considered system.[11] The results of the fit according to Equation (3) on two filled rubbers systems are presented in Figure 8.

The filler network formation seems to be based on the relative movement of the particles depending on the particle size, polymer-filler and filler-filler interaction. The apparent existence of a short, τ_1, and long, τ_2, relaxation time suggests that flocculation can be envisaged as a two-stage process. Intuitively, the fast process may be associated with the formation of clusters on smaller length scales, while the slow process may be linked with the cluster growth process on larger length scales. Meier and Klüppel[6] gave an alternative view on the slow process, obtained from the dielectric investigations, where nanoscopic

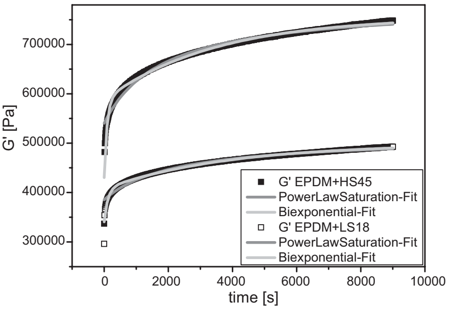

Figure 8.
Power law saturation fits (Equation (3)) as well as the biexponential fits (Equation (4)) of the data for the uncrosslinked EPDM samples filled with carbon black (LS 18 as well as HS 45).

gaps between adjacent carbon black particles are detected. These gaps are shown to decrease slowly in size during heat treatment on a time scale that is comparable to the long relaxation time τ_2. From a mechanical point of view this leads to a stiffening of filler-filler bonds and consequently to a slow increase of the modulus with annealing time.[5] The parameterization of the experimental data in Figure 8 required at least the sum of two exponential processes:

$$G'(t) = G'_1\left(1-e^{-\frac{t}{\tau_1}}\right) + G'_2\left(1-e^{-\frac{t}{\tau_2}}\right) \tag{4}$$

One can see that the initial state of the filler flocculation process cannot be described very well with the power law saturation equation. Furthermore, the biexponential fit is a more intuitively phenomenological model, and we think that this filler flocculation process is more complex by nature and so we developed a more detailed kinetic approach, describing the process in a more realistic way.

Multi-Stage Agglomeration Model

If the polymer matrix is filled with attractively interacting nanoparticles, its mechanical behaviour can be described in the framework of a superposition approach. In this approach the total stress tensor, σ, is represented by a sum of two stresses

$$\sigma = X\sigma_m + \sigma_f^{net} \tag{5}$$

where σ_m is the viscoelastic stress arising in the matrix due to stretching and orientation of polymer strands. To describe the polymer stress in this equation, one can probe any of appropriate constitutive models proposed for the elastomer matrix. The second component on the right side of Equation (5), σ_f^{net}, arises due to attractive interactions between the particles and will be described later.

Hydrodynamic reinforcement of the polymer matrix is taken into account by multiplying σ_m by the hydrodynamic amplification factor, X. In the case of hard spherical particles such as carbon black, X can be estimated using the Batchelor formula[12]

$$X = 1 + 2.5\phi + 6.2\phi^2 \tag{6}$$

where ϕ ($\phi = 0.183$ in our case at 50 phr carbon black) is the volume fraction of the filler particles. Analog to Equation (5) we can re-write the superposition for the case of oscillatory shearing at different strain amplitudes as follows

$$G' = XG'_m + G_f^{\prime net} \tag{7}$$

where G'_{m} is the storage modulus of the matrix as a function of time, which is taken as constant (compare Figure 1).

Time evolution of the pure elastic filler network can be described using the modified Hooke's model

$$\sigma_f^{Net} = G_f(1-f)\gamma \tag{8}$$

where G_f is the effective elastic modulus of the filler network and $0 \leq f \leq 1$ is a structural parameter that reflects the fraction of free particles, i.e. of particles that are not part of the filler network. This parameter can be calculated using Equation (9)

$$f = 1 - \left(\frac{G_f^{\prime net}}{G_{f,\max}^{\prime net}}\right) \tag{9}$$

where $G'_{f,\max}net$ is the maximal value of the storage modulus of the filler network.

In the absence of shear, time evolution of the structural parameter is usually described by a single kinetic equation

$$-\frac{d}{dt}f = kf_b^n \tag{10}$$

with the reaction constant k. The value of the exponent n defines what kind of cluster growth is expected during the recovery process: for example, $n = 1$ corresponds to the first-order kinetics and $n = 2$ to the second-order kinetics.

However, we found out that it is impossible to reproduce the decrease of the fraction of free particles in the recovery sequence, $\gamma = 0.1\%$, using a single kinetic Equation (10) with a constant value of the kinetic exponent, i.e. using a pure rate law. So, only the middle part of the recovery branch can be described using the second-order kinetics law, see Figure 8.

Initially, the growth of clusters is very fast obeying the kinetic law with $n = 3$, whereas it slows down considerably at the final stage of recovery process when n takes values around 1. Such complex behavior can be interpreted assuming different kinds of the agglomeration processes: first, in the very beginning, when a lot of single particles are provided, the multi-particle agglomeration, which gradually changes to the cluster-cluster agglomeration at the middle flocculation stages, followed by addition of the rest of particles to a well-formed network at the late stages (see Figure 9).

Therefore, time evolution of the structural parameter is not described by a single, but by three kinetic equations

$$-\frac{df}{dt} = k_n f^n \tag{11}$$

where n is the order of kinetics and k_n is the corresponding reaction constant. As the reaction is slowing down it is obvious that $k_3 > k_2 > k_1$.

Conclusion

Oscillatory shear as well as elongational rheological experiments on various carbon black filled polymer systems have been carried out. We have to conclude the following:

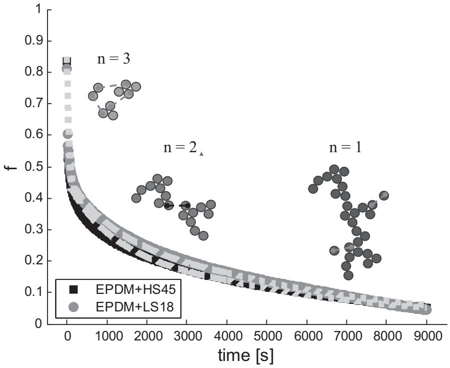

Figure 9.

Fits using Equation (11) of the data at several reaction orders and a scheme of the status of the filler network at several values of the order of kinetics n. f is equal to the fraction of free particles, which gives a structural parameter reflecting the state of the particle network, see Equation (9). The Equation (11) was solved numerically using Matlab.

(i) The so-called *jamming* phenomenon is still very controversial, when considering from *rheological* or *scattering* point of view. With *scattering*, we mean the X-ray photon correlation spectroscopy technique. Already several preliminary results have been proposed with this new method to get more insights in the dynamics of filled polymer materials.[13–15] In all these systems, the intensity correlation functions can usually be described by the Kohlrausch-Williams-Watts (KWW) compressed exponential form $\exp(-(\Gamma t)^n)$ where $n > 1$ and the relaxation rates Γ exhibit hyper-diffusive dispersion relationships $\Gamma \propto q^{\mathrm{p}}$, with $p = 1$ (ballistic motion) or, more generally, $p < 2$.[16]

(ii) Robertson's *''jamming criteria''* (isoenergetic character with a constant value of $\sigma_c\ \gamma_c$; FFT analysis of fluctuations in G') are not fulfilled in all of our given cases. So we think, that there is still a need of an unversial rheological *jamming* criterion for (especially filled) polymer systems.

(iii) We are convinced that the Payne effect (flocculation process) and percolation transition in the electrical conductivity of the filled rubber sample share the same physical origin.

(iv) Several models have been presented in the literature to describe the filler flocculation recovery process. The best fit to the G' data of the agglomeration process is not a pure kinetic rate law of second order. We rather assume a complex multi-stage agglomeration process and proposed a new approach here. And last but not least:

(v) Can jamming or flocculation be an example for emergence, self-organization in complex systems?

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