Macromol. Symp. 2010, 291–292, 193–201 DOI: 10.1002/masy.201050523

Jamming in Filled Polymer Systems

Sven Richter, Marina Saphiannikova, Klaus Werner Stöckelhuber, Gert Heinrich*

Summary: After an introduction into the general characteristics of the jamming behavior, two filler flocculation experiments on a polycarbonate melt filled with multi-walled carbon nanotubes and on a silica-filled ethylene propylene diene monomer elastomer are presented. We propose that these experiments can be regarded as jamming phenomena. The experimental data are successfully modeled using the power saturation equation. Further insights into the physics of such jamming processes have been obtained with the help of X-ray photon correlation spectroscopy experiments.

Keywords: elastomers; fillers; melt; nanocomposites; rheology

Introduction

Growth and Evolution

We encounter growth and evolution processes both in the microcosmos and the macrocosmos, in all time scales and ranges. Growth and evolution are present everywhere and are the most astonishing and impressive phenomena in our world.[1]

Growth processes are frequently based on an inner program. Self-organization and structure-accumulation processes for which such inner program either does not exist or has only a small influence are called evolutionary processes, like the origin of life.[2,3]

The idea of evolution is as old as mankind. All philosophical systems of the past had to formulate a specific point of view in considering evolution. In the natural sciences, essential progress in understanding evolution is connected with the names of Darwin[4] in biology and of Prigogine[5,6] with his concept of dissipative structures in irreversible thermodynamics (see e.g.[7–10]); Eigen[11] as well as Haken[12] in physical and chemical evolution or self-organization.

There is no doubt that the term ''evolution'' designates phenomena of high complexity, in which some dialectic polarities play an important role like statics/dynamics, continuous/discontinuous, whole/part, randomness/necessity, and structure/function.

The growth dynamics of some species is a source of structure-building, but on the other hand, growth in its dynamics is only possible given the background of special structures. Therefore, the connection between growth and structure-building is an essential aspect of the dialectics of structure/function.[1] In the light of such general contemplations, we would like to examine more closely the so-called jamming phenomenon, which can be considered as an example of growth process with an inner program mainly determined by interaction forces.

The Jamming Phenomenon

Why does mayonnaise act both like a liquid and a solid? What causes shaving cream to flow differently from toothpaste? These types of questions are at the heart of soft condensed matter, the study of materials with both fluid and solid properties (often called complex fluids). Moreover, the mechanical properties and ability to flow are in fact the defining features of soft materials, and represent a key to their practical utility. The answers to these questions relate the mesoscopic structure of a complex material to its macroscopic properties (such as its viscoelastic modu-

Leibniz Institute of Polymer Research Dresden, Hohe Str. 6, D-01069 Dresden, Germany
Fax: (+49) 351-4658-362;
E-mail: richter-sven@ipfdd.de

lus). With the wide variety of mesoscopic structures for different materials, it might be expected that the answers would depend strongly on the details of each material, and that the study of such systems would be the study of many special cases. However, a recently proposed idea of jamming suggests the possibility of universal behavior of complex fluids under stress, and, in particular, that such systems may behave like granular media.[13] In each case, the material behaves in many ways like a solid. The macroscopic picture of jamming depends on the microscopic behavior of such systems. Yet, there is little experimental evidence to support the idea of macroscopic similarities between these systems.

One can start by summarizing the solid-like states of the complex fluids, and the relevant parameters which control the transitions into the solid-like state,[13] see Table 1.

The idea of jamming is that perhaps all of these amorphous solids are solid-like for the same reason; that there is a universal jammed state, and by understanding it, we understand all of these materials simultaneously. Moreover, in each case there are control parameters that allow the system to be changed from the unjammed state to the jammed state.

Perhaps, there is a universal jamming transition that describes how a material changes from an unjammed to a jammed one. The glass transition, then, is a specific case of the more general jamming transition. More precisely, a jammed material can be defined as a microscopically disordered structure that can support a finite stress up to a critical one without plastic deformation or flow.

It is certainly possible that all of the materials listed in Table 1 are solid-like for unrelated reasons. Another possibility is that there are several different jamming transitions. Some materials may share a common transition, but perhaps it will be found that there are distinct categories of these transitions, with sharp differences between categories. Why, then, has jamming become a very popular idea? The hope is that by comparing and contrasting these different systems, we may learn more about each of them. Findings about one type of material may provide insights about the behavior of another material. Individually each of these amorphous solids provide many puzzles, but perhaps considering them as a group, we may collect a number of clues that will eventually lead to better understanding. One important idea of jamming is that the control parameters for the materials mentioned in the table can be unified by one ‘‘phase diagram.’’

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 their dynamics, 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.

Indeed, deformation in jammed particle filled systems, and in other jammed athermal systems such as foams, appears to act as the temperature in typical glass-forming

Table 1.
Systems which undergo the jamming transition.[13]

Molecular glass	Formed by decreasing T or increasing P (thus increasing density ρ)
Colloidal glass Granular material	Formed by increasing particle volume fraction ϕ
Emulsion glass	Formed by increasing droplet volume fraction ϕ
Colloidal gel	Formed by increasing volume fraction ϕ , or increasing attractive energy U
Polymer gel	Formed by increasing polymer concentration c, or by cross-linking polymers
Foam	Solid-like when bubble volume fraction ϕ is increased
Thermosensitive hydrogels	Volume phase transition, when changing T[14]

liquids. The notion of ''effective temperature'' has been proposed for these complex materials where solid-to-liquid transitions are driven by the applied stress, strain, or vibration.

Based on the view of jammed particles and glasses as related materials, Liu and Nagel[15,16] proposed a jamming phase diagram with axes of temperature, load (stress), and $1/\rho$, where ρ is the density of particles in the system. Indeed, such a phase diagram was demonstrated experimentally for attractive particles by Trappe et al.[17] The density of particles was varied via the volume fraction of filler, ϕ, in the suspending fluid in the study by Trappe et al.[17]

The disordered fluid-like structure remains essentially unchanged at the transition. The jammed solid can be refluidized by thermalization, through temperature or vibration, or by an applied stress. The generality of the jamming transition led to the proposal of a unifying description, based on a jamming phase diagram. It was further postulated that attractive interactions might have the same effect in jamming the system as a confining pressure, and they could, therefore, be incorporated into the generalized description. Trappe et al.[17] studied experimentally the fluid-to-solid transition of weakly attractive colloidal particles, which undergo markedly similar gelation behavior with increasing concentration and decreasing thermalization or stress. One can support the concept of a jamming phase diagram for attractive colloidal particles, providing a unifying link between glass transition, gelation and aggregation.[17]

It is a strong indication that the jamming transition may really be a phase transition - although of a new kind, because no growing static long-range order is detected. Only dynamical correlations are found to increase approaching the transition.[18]

Keyes et al.[19] fitted the growth of the time- and length-scales in a granular material (air-driven granular beads) using laws that were introduced for glass-forming liquids: the Vogel-Fulcher-Tammann (VFT) law and power-laws. Remarkably, the VFT fit gives a transition value, which is very close to the one independently determined for the jamming transition. It is a mark of the value of this study that it raises at least as many questions as it resolves. Indeed, the fits presented by the authors, although not conclusive, are very suggestive. Could it be that explanations of the glass transition work for the jamming transition? More generally, if jamming is indeed a critical phenomenon, what is the nature of the underlying phase transition?[18] Or could the divergence of length- and time-scales be instead related to a thermodynamic transition towards a static amorphous long-range order, as proposed for the glass transition and for hard sphere systems? These and many other questions remain. But the experimental study of the critical properties of the jamming transition, initiated in the work of Keys et al.,[19] offers a promising route to answering at least some of them.[18] In summary, features defining characteristics of the jammed state are: (i) microscopic disorder, (ii) elastic response, (iii) non-ergodicity (out of equilibrium, the microscopic configurations of the material are unreachable), (iv) dynamical heterogeneity and (v) aging.[20]

Filled Polymer Systems as Jammed Materials

Polymer networks are important materials for contemporary technology, with many applications in the car industry, and an increasing number of applications in medicine and biotechnology. There are remarkable similarities between dynamic strain-induced non-linearity in the modulus of filled rubbers 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 even filler networks. The agglomeration and network formation of filler in elastomeric matrix are typical jamming processes, and, correspondingly, de-agglomeration and recovery are de-jamming processes. It is now reasonable to assume that different routes, through strain, volume fraction, and temperature changes, can effectively lead filled rubbers to the same jammed state.[21]

The effect of amplitude dependence on the dynamic-mechanical properties of filler reinforced rubbers was brought into clear focus by the work of Payne in the 1960s. 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 reforming 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.[22–24] and references therein). At large strains, this filler network is broken down and the modulus is then determined only by polymer-polymer cross-links, elastically effective filler-polymer couplings and hydrodynamic filler effects, see Figure 1.

Experimental Part

Oscillatory shear experiments on a polycarbonate melt filled with 5 wt-% multi-walled carbon nanotubes (CNTs) were conducted on a controlled strain rate rheometer (ARES rheometer, Rheometrics Scientific) using a plate-plate geometry (diameter of 25 mm, gap between the plates 1–2 mm) in a nitrogen environment. Flocculation studies were performed at 230 °C, at a frequency $\omega = 1$ rad s^{-1} and with a strain of 0.5%. All test specimens were cut from injection molded plates.

For the flocculation study, an elastomer composite of un-crosslinked ethylene propylene diene monomer rubber (EPDM, Buna EP G 6850, Lanxess, Leverkusen, Germany) with 40 g pyrogenic silica (Aerosil 200, Degussa, Hanau) per 100 g of rubber (phr) was compounded on a two roll mill (Servitec Polymix 110 L, Wustermark, Germany). Measurements of the flocculation kinetics were carried out with the help of a moving die rheometer (Scarabaeus SIS V-50, Langgöns, Germany) at 160 °C. For this study, sinusoidal strains of different values (0.3%–25%) at a frequency $\omega = 1.67$ Hz were applied.

Results and Discussion

Within a physical approach, a dynamic flocculation model of rubber reinforcement has been introduced which is based on the kinetic cluster-cluster aggregation (CCA) model of filler networking in elastomers.[25]

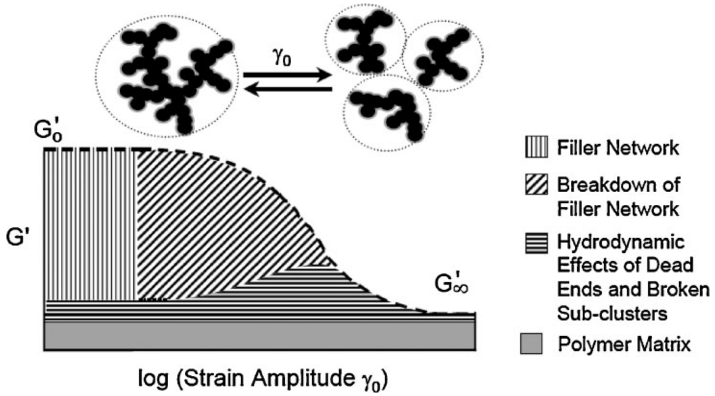

Figure 1.
Interpretation of the Payne effect, visualization of filler cluster de- and re-agglomeration. The drop of the storage modulus G' with increasing strain amplitude γ_0 corresponds to a gel-sol-like transition of the filler network at moderate strain and a breakdown of the remaining sub-clusters at large strain.[25]

According to this approach, a filler network consists of a space-filling configuration of clusters with a characteristic mass fractal dimension.[25] The elastic modulus of such filler network at small strain amplitude depends on the fractal connectivity of the clusters. The modulus can be evaluated by referring to the model of flexible chain aggregates. In this model, the main contribution of the elastically stored energy in the strained filler clusters results from the bending-twisting deformation of filler-filler bonds. The predicted power-law behavior of the small strain modulus of filler reinforced rubbers is confirmed by a variety of experimental data, including carbon black and silica filled rubbers as well as composites with microgels as model fillers.[22,23]

Despite the technological significance of the Payne effect (which reflects a jamming-unjamming process[26]) in rubber applications, this strain-induced softening phenomenon is often regarded as a special area of physics specific to filled elastomers. However, dynamic strain-induced nonlinearity in the modulus of filled rubbers shows a striking similarity to what is known about the glass transition of solid materials and the jamming transition of granular materials. This analogy stems from the fact that shear strain in dynamic mechanical measurements introduces fluctuations in a filler network by forcing the system to explore different configurations. Such fluctuations can be described by an "effective temperature" that has many attributes of a true temperature, and, in particular, it is proportional to the strain amplitude. That a critical mechanical energy is necessary to break up a jammed structure may be related to the notion of a critical effective temperature.[21] Thus, filled rubbers with respect to strain will display many unusual phenomena that are usually observed in glass-forming materials and glass-like kinetic transitions,[21,26] but are now demonstrated also in filled melts.

Figure 2 shows the flocculation kinetics of silica nanoparticles in the EPDM elastomer sample. After a sudden breakdown of the filler network caused by an application of 24% strain (the first step which is not shown here), the storage modulus *G*' is found to slowly increase with time. After around 70 min, *G*' recovers

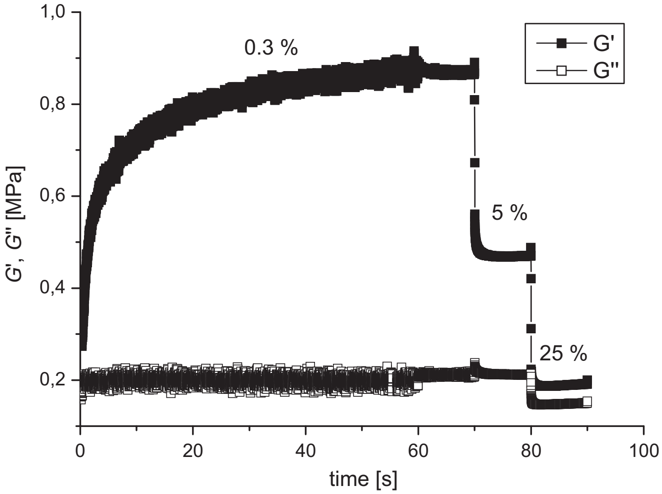

Figure 2.
Flocculation kinetics (jamming experiment) of the silica filled EPDM elastomer sample. First step (not shown here): Destruction of the filler network by an application of 24% strain. Second step: Monitoring of the flocculation kinetics (formation of a filler network) at 0.3% strain. Third step: Breakdown of the filler network by application of 5% as well as 25% strain.

its initial equilibrium value. We denote this recovery process as a filler flocculation process. At the second step of the jamming experiment, the sample is subjected to oscillatory shearing with a strain of 0.3%. It is chosen to be so low that the sample at this stage can be considered to be in a quasi-quiescent state. The slight oscillatory perturbation is only necessary to detect the changes in G' and G'' with time. Thus, at the second stage, one is able to follow in-situ the re-agglomeration of the filler clusters destroyed previously. When the stationary state is attained, the sample is subjected to shearing with high strain amplitude at which the filler clusters are effectively destroyed. Here, we chose a two-step shear-induced breakage of the filler structure, first at 5% and then at 25% strain.

The similar experiment carried out with a polycarbonate melt filled with 5 wt-% CNT is shown in Figure 3. Let us first consider the sample behavior in the quasi-quiescent state (0.5% strain). It can be seen that both moduli considerably increase with time: G' approximately three times and G'' approximately on 25% compared to the initial values. Furthermore, one observes at least two relaxation processes. The first process is relatively fast with the relaxation time of about 50 s and can be very likely associated with the agglomeration of CNTs into a viscoelastic network-like structure. Simple Brownian motion cannot be responsible for this agglomeration process as diffusion of non-interacting filler particles is estimated to be too slow to be taken into account in the explanation of this effect. Rather, strong attractive interactions between the dispersed CNTs and thermodynamic incompatibility between the particle and the polymer phases facilitate such fast diffusion of the CNTs within a highly viscous medium. The second relaxation process is very slow without a sign of saturation even after two hours and can be presumably associated with the extremely slow reorganization of the filler network structure.

Recent dielectric measurements[24] on carbon black filled elastomers also revealed the two-step recovery in which one observed first the fast formation of cluster particles, followed by a slower reaggregation of the filler particles.

After application of the oscillatory shearing with 5% strain, the storage modulus drops immediately, staying, how-

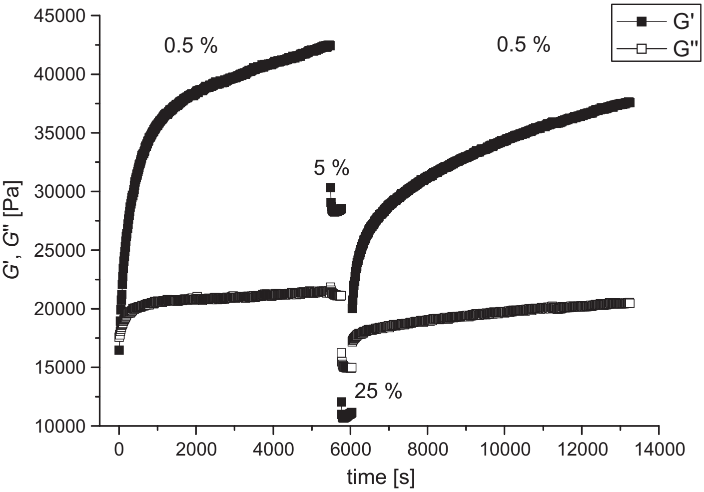

Figure 3.
Flocculation kinetics (jamming experiment) of the polycarbonate melt filled with 5 wt-% CNTs at 230 °C at different strain amplitudes. First step (not shown here): Destruction of the filler network in the process of injection molding. The second and third steps are similar to those in Figure 2. Fourth step: Monitoring of the jamming process with 0.5% oscillatory strain.

ever, higher than its initial value measured in the beginning of the jamming experiment. The loss modulus stays unchanged. The fast drop in G' is caused solely by the rapid destruction of the CNT clusters as we can certainly exclude the orientation of tubes at this step. The next shearing step with 25% is done and leads now to a higher value of G''compared to G'(Figure 3). Interestingly, both moduli drop below their initial values measured in the beginning of jamming experiment. As one can see from Figure 3, this destruction is very rapid and takes place at very small shearing rates. This together means that the CNT clusters are very soft and, they, therefore, can be easily damaged at shear rates $\dot{\gamma}_0 \geq 1\ \mathrm{s}^{-1}$. Taking into account extremely high shear rates (10^3–$10^4\ \mathrm{s}^{-1}$) at the injection molding process, we assume a total breakage of clusters in the as-received samples.

The same experimental conditions were carried out on the un-filled matrix polymer samples (not shown here). No significant influence of the applied different strains on the moduli values was found. The viscous properties of the matrix polymer were always dominating.

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 2: step 1, destruction of the filler network by an application of 24% strain) due to a step – like increase of deformation amplitude is proportional to the square of the concentration of the units. These units correspond to filler aggregates which form successively new agglomerates in the (infinite) filler network. Then

$$\frac{dN}{dt} = k(N - N_0)^2 \qquad (1)$$

where k is a rate constant. This type of growth is described as a second-order reaction. We note that eq. (1) 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 $\mathrm{G} \equiv |G^*|$ ($\approx G$') 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 eq. (1) for the modulus recovery yields[25]

$$G(\Delta t) = G_\infty\left(1 - \frac{G_\infty}{k\Delta t + C}\right) \qquad (2)$$

where C [Pa] is the constant of integration. The rate constant k [Pa s^{-1}] depends on the filler type, the temperature and the filler loading. Eq. (1) is the ‘‘power-saturation’’ case of the hyperlogistic differential Equation which is of relevance for aggregated growth in soft systems.[1] Within this very general background, the exponent ‘‘2’’ in eq. (1) characterizes the autonomous (but forced by restrictions) saturation in the aggregated growth process and is a measure of the complexity. The more this exponent deviates from 1, the higher the cooperativity within the considered system.[25] The results of the fit according to eq. (2) on the two systems are presented in Figure 4.

Throughout the literature, there are two other systems known to show the same asymmetric behavior when the thermodynamic properties approach equilibrium differently depending on the initial state. One is the structural relaxation process in glassy materials, most notably the relaxation and recovery of enthalpy and volume.

In this case, the specific volume of a glass after abrupt cooling to a temperature T is known to approach equilibrium faster than a glass heated to the same temperature. The reason is that the cooled sample arrives at temperature T with a larger free volume than the heated glass. Another situation with asymmetric relaxation behavior is the density fluctuation in a vibrated granular material. In this case, the granular material is in its jamming state. Once a void large enough to contain a grain is created, it will be quickly filled by a new particle. The rate of density settling from above or below equilibrium depends on the rate of void creation and the initial density of the material. Nevertheless, in both cases, the

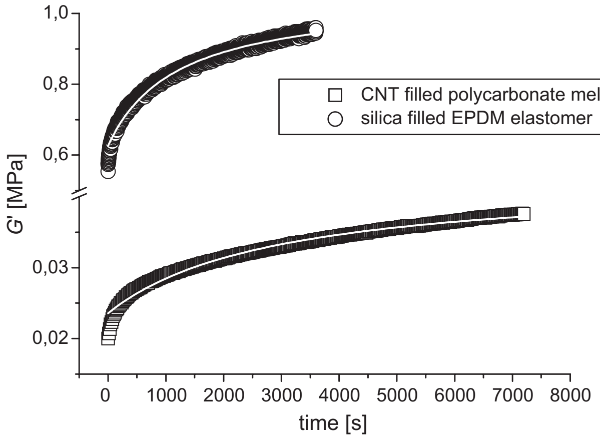

Figure 4.
Fits with the power saturation function (solid white line) of the storage modulus G' during the recovery process (filler agglomeration, dejamming) of the two filled systems (second step in Figure 2 and fourth step in Figure 3).

free volume plays a crucial role in determining the rate of approaching equilibrium. Obviously, these two cases share a common ground of physics.

Despite a very large amount of work performed since more than 50 years, the non-linearity in viscoelastic properties of filled rubbers is still poorly understood. Various explanations have been proposed, among others filler de-agglomeration under strain and re-agglomeration during recovery.[22] To investigate this assumption, first SAXS measurements on elastomers filled with carbon black and silica (hydrophilic or hydrophobic aerosil 200) were performed.[27] This work allowed us to observe the appearance of an anisotropy in the low-q domain above an elongation corresponding to the maximum in the stress-strain curve, in systems that display such a feature. The dynamics of filled elastomers during aging after elongation was followed by time-resolved x-ray photon correlation spectroscopy (XPCS) measurements at beamline 8-ID at the Advanced Photon Source (APS, Argonne, USA). For the detection, heterodyne detection (HD-XPCS) in addition to the classic homodyne one was used for the first time. This experiment allowed the determination of the velocity of the filler particles which was found to decrease with the aging of the sample. It also led to two important observations: (i) the relaxation time τ scales as q^{-1}; and (ii) the intensity correlation functions g_2 are better fitted by a compressed exponential function $g_2 = 1 + \beta \exp[-2(\tau/\tau_0)^{\mu}]$ with $\mu = 1.5$ than by a usual exponential function. The same features were found for jammed systems[20] which allows us to conclude that there is an intrinsic similarity between them and filled elastomers.[28,29]

Conclusion

Oscillatory shear rheological experiments on two filled polymer systems have been carried out. We pointed out that these experiments can be regarded as the so-called jamming phenomenon. The flocculation experiments (jamming kinetics) on both systems can be described by using the same power saturation model.

As a summary, one can point out: (i) Flocculation ("jamming") phenomena can be followed in filled elastomers as well as in filled polymer melts by using shear rheology. (ii) Control parameters for the filler (de)agglomeration are in our cases: $G'(t)$, $G''(t)$, shear rate, temperature. (iii) The universality of the jamming hypothesis has not yet been tested on such systems. (iv)

There is a need for other control parameters answering the following points: What will happen inside various filled polymer systems under application of mechanical stress? Can this filler flocculation process be unified to a new kind of phase transition called jamming?

(v) Outlook: Can XPCS provide another control parameter such as the scaling of the relaxation time τ versus the scattering vector q, such as $\tau \propto q^{-n}$?

There are still several questions that can be asked about jamming: (i) What is the nature of the jammed state? (ii) How does a system get into the jammed state? (iii) Are there any similarities between the jamming in driven, athermal systems and the jamming in quiescent thermal systems (such as glass transitions in molecular liquids). (iv) Is there any control parameter for filled polymer systems, like the effective temperature? (v) Can jamming be regarded as a new kind of phase transition?[18]

Acknowledgements: This work was carried out with the support of the BMBF Project "CarboNet". Dr. Michael Bierdel (Bayer Technology Services GmbH, Leverkusen, Germany) is gratefully acknowledged for providing the CNT filled polycarbonate samples for rheological measurements. Furthermore, we thank Mr. René Jurk (IPF Dresden) for carrying out the experiments on the silica filled EPDM sample.

[1] M. Peschel, W. Mende, "*The Predator-Prey Model: Do We Live in a Volterra World?*", Akademie-Verlag, Berlin 1986.

[2] A. I. Oparin, "*Die Entstehung des Lebens auf der Erde*", Deutscher Verlag der Wissenschaften, Berlin 1957.

[3] W. Ebeling, R. Feistel, "*Chaos und Kosmos. Prinzipien der Evolution*", Spektrum Akademischer Verlag, Heidelberg 1994.

[4] C. Darwin, "*Die Entstehung der Arten durch natürliche Zuchtwahl*", Reclam, Leipzig 1984.

[5] G. Nicolis, I. Prigogine, "*Die Erforschung des Komplexen*", Piper, München 1987.

[6] I. Prigogine, "*Die Gesetze des Chaos*", Insel, Frankfurt/Main 1998.

[7] I. R. Epstein, J. A. Pojman, "*An Introduction to Nonlinear Chemical Dynamics*", Oxford University Press, New York 1998.

[8] F. W. Schneider, A. F. Münster, "*Nichtlineare Dynamik in der Chemie*", Spektrum Akademischer Verlag, Heidelberg 1996.

[9] W. Ebeling, "*Strukturbildung bei irreversiblen Prozessen*", Teubner, Leipzig 1976.

[10] H.-W. Kammer, K. Schwabe, "*Thermodynamik irreversibler Prozesse*", Akademie-Verlag, Berlin 1985.

[11] M. Eigen, *Naturwissenschaften* **1971**, *58*, 465.

[12] H. Haken, "*Synergetik - Eine Einführung*", Springer-Verlag, Berlin 1983.

[13] E. R. Weeks, "*Soft Jammed Materials*", in: "*Statistical Physics of Complex Fluids*", S. Maruyama, M. Tokuyama, Eds., Tohoku University Press, *Sendai, Japan*, **2007**. pp. 2-1–2-87.

[14] E. Geissler, K. Kosik, A. Fluerasu, A. Moussaïd, K. Laszlo, *Macromol. Symp.* **2007**, *256*, 73.

[15] A. J. Liu, S. R. Nagel, *Nature* **1998**, *396*, 21.

[16] A. J. Liu, S. R. Nagel, "*Jamming and Rheology: Constrained Dynamics on Microscopic and Macroscopic Scales*", Taylor and Francis, London, New York 2001.

[17] V. Trappe, V. Prasad, L. Cipelletti, P. N. Segre, D. A. Weitz, *Nature* **2001**, *411*, 772.

[18] G. Biroli, *Nature Physics* **2007**, *3*, 222.

[19] A. S. Keys, A. R. Abate, S. C. Glotzer, D. J. Durian, *Nature Physics* **2007**, *3*, 260.

[20] L. Cipelletti, L. Ramos, S. Manley, E. Pitard, D. A. Weitz, E. E. Pashkovski, M. Johansson, *Faraday Discuss.* **2003**, *123*, 237.

[21] X. Wang, C. G. Robertson, *Phys. Rev. E* **2005**, *72*, 031406.

[22] G. Heinrich, M. Klüppel, *Adv. Polym. Sci.* **2002**, *160*, 1.

[23] M. Klüppel, *Adv. Polym. Sci.* **2003**, *164*, 1.

[24] J. G. Meier, M. Klüppel, *Macromol. Mater. Eng.* **2008**, *293*, 12.

[25] G. Heinrich, V. Härtel, J. Tschimmel, M. Klüppel, F. R. Costa, M. Abdel-Goad, U. Wagenknecht, A. L. Svistkov, B. Lauke, *Kautschuk Gummi Kunststoffe* **2005**, *58*, 163.

[26] C. G. Robertson, X. Wang, *Phys. Rev. Lett.* **2005**, *95*, 075703.

[27] F. Ehrburger-Dolle, F. Bley, E. Geissler, F. Livet, I. Morfin, C. Rochas, *Macromol. Symp.* **2003**, *200*, 57.

[28] F. Livet, F. Bley, F. Ehrburger-Dolle, I. Morfin, E. Geissler, M. Sutton, *J. Appl. Cryst.* **2007**, *40*, s38.

[29] F. Livet, F. Bley, F. Ehrburger-Dolle, I. Morfin, E. Geissler, M. Sutton, *J. Synchrotron Rad.* **2006**, *13*, 453.