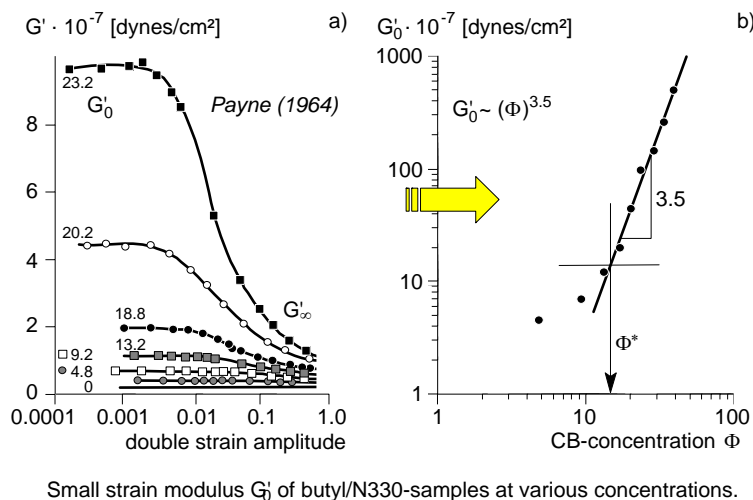


Structural kinetics in filled elastomers and polyethylene/layered double hydroxide composites

Anhand von verschiedenen dynamisch-mechanischen und rheologischen Experimenten an gefüllten Elastomeren bzw. Low-density-Polyethylen-Hybrid-Nanokompositen wurden Spezifika und Gemeinsamkeiten der strukturellen Reorganisation der jeweiligen Füllstoffüberstrukturen diskutiert. Im Fall der Elastomere konnte die Füllstoffkinetik anhand der dynamischen Modulerholung bei Amplitudensweeps mit zeitabhängiger Amplitudenvariation studiert werden. Im Falle der gefüllten Polyethylenschmelzen wurde die Zeitabhängigkeit der Füllstoffstrukturen insbesondere anhand von nicht-linearen Scherexperimenten untersucht. Für den Fall der Modulerholung wurde ein einfaches Modell der Cluster-Cluster-Kinetik vorgeschlagen. Es konnte gezeigt werden, dass die Flokkulationskinetik von Füllstoffstrukturen in Polymeren in den allgemeinen Kontext einer kooperativen Aggregation in komplexen Systemen eingeordnet werden kann.

Filler structures in elastomers and their kinetics

The effect of amplitude dependence of the dynamic-mechanical properties of filler reinforced rubbers was brought into clear focus by the work of Payne in the 1960s. He (and later, G. Kraus 1984 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 [1, 2] 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 (Figures 1 and 2).



Keywords

filled elastomers
nanofiller/thermoplastic composites
filler cluster kinetics
rheology
complex systems

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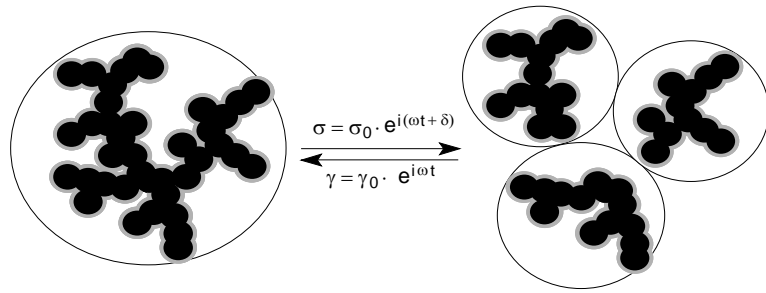
G. Heinrich
F.R. Costa
M. Abdel-Goad
U. Wagenknecht
B. Lauke
M. Saphiannikova

Kooperation

Prof. Dr. Volker Härtel,
Dr. Jürgen Tschimmel,
Continental AG, Hannover
Dr. Manfred Klüppel,
Deutsches Institut für Kautschuk-
technologie e. V., Hannover
Dr. A.L. Svistkov, I. A. Morozov
Institute of Continuous Media
Mechanics, Perm, Russia

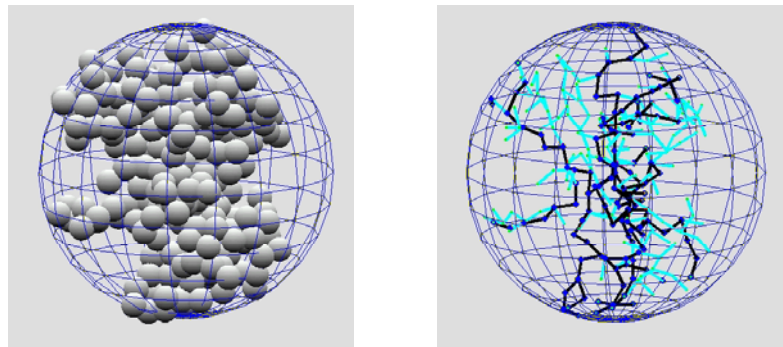
Fig. 1:
Visualization of the Payne effect
(a). Figure (b) shows the power-law
dependence of the small-strain
modulus on filler loading.

Fig. 2:
Visualization of filler cluster de- and re-agglomeration



Within a physical approach a dynamic flocculation model of rubber reinforcement is introduced which is founded on the kinetic cluster-cluster aggregation (CCA) approach of filler networking in elastomers. Accordingly, filler networks consist of a space-filling configuration of CCA clusters with characteristic mass fractal dimensions (Figures 3). The elastic modulus of such filler networks at small strain amplitude depends on the fractal connectivity of the CCA clusters. It can be evaluated by referring to the model of flexible chain aggregates [3]. 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 behaviour 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 [1, 2, 4].

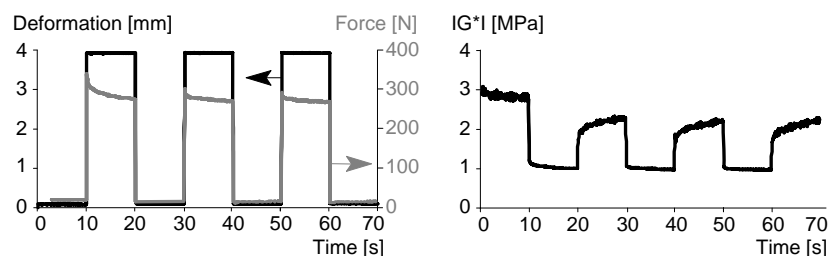
Fig. 3:
Modelling of filler cluster geometry assuming a (mass) fractal dimension $d_f = 1.8$ corresponding to CCA. The right figure shows the connectivity of the cluster.



Very recently, we studied the kinetics of the modulus recovery with experimental set-ups where the stiffness response on repeated amplitude steps was measured [5]. Figure 4 shows the stiffness response on repeated amplitude steps (frequency 10 Hz, room temperature).

The rate of contacts (say N) contributing to filler-filler interactions after the sudden breakdown due to a step-like increase ($\Delta\varepsilon$) of deformation amplitude is assumed to be proportional to the square of concentration of units. These units correspond to filler aggregates forming successively new agglomerates, respectively the (infinite) filler network.

Fig. 4:
Stiffness response on repeated amplitude steps during DMA of carbon black filled rubber



Then,

$$\frac{dN}{dt} = kN^2 \quad (1)$$

where k is a rate constant. This type of growth is described as a second-order reaction of type I. The final state would be reached as $N = N_\infty$ at $t \rightarrow \infty$. We assume that the corresponding excess modulus $G \equiv |G^*|$ ($\approx G'$) is proportional to the increase of new contacts, where for $t = t_0$: $N = N_0$ and for $t \rightarrow \infty$: $N = N_\infty$. Here, N_0 is the remaining number of filler/filler contacts just after the breakdown where the amplitude increases stepwise from ε_0 to $\varepsilon_0 + \Delta\varepsilon$. Therefore, this number N_0 can be regarded as the starting level of the recovery process. The number of contacts after total recovery is N_∞ corresponding to small (nearly zero) deformation amplitude. We note that the description of recovery effects by a second order kinetics in rubber systems is not unusual. Very recently, the filler/filler interactions were attributed to the formation of 'rubber-like junctions' within the glassy layer between two neighbouring aggregates forming larger clusters [11]. This layer formation itself can be connected with studying the formation of bound rubber on filler particles. Recently, the formation of bound (PDMS) rubber on silica was investigated and a second-order kinetic process was also found [12].

Experimentally, after a certain time $\Delta t^* = t_1 - t_0$ the deformation amplitude again increases step-like from ε_0 to $\varepsilon_0 + \Delta\varepsilon$. As a consequence, the value N_∞ will not be reached totally. According to the assumptions of second-order reaction type (Eq. 1) and the direct relation between number of contacts and modulus contribution, the following equation for $G \equiv |G^*|$ immediately follows:

$$dG(\xi) / d\xi = k \left(\frac{G_\infty - G(\xi)}{G_\infty} \right)^2 \quad (2)$$

Equation (2) yields the solution for the modulus recovery

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

where C [Pa] is a constant of integration. The rate constant k [$\text{Pa}\cdot\text{s}^{-1}$] depends on filler type, temperature and filler loading. Eq. 1 is the 'power saturation'-case of the hyperlogistic differential equation which is of relevance for aggregated growth in soft systems [6]. 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 plays the role of complexity measures. The more this exponent deviates from 1, the higher is the cooperativity within the considered system.

Rheological characterization of polymer nano-composites based on LDPE and Mg/Al based layered double hydroxide

Other interesting systems for studying features of structural kinetics are nano-composites of hybrid material of a thermoplastic melt and nano-fillers [7]. In our case, the melt-state linear and non-linear shear rheology properties of hybrid materials of nano-composites based on polyethylene (PE) and Mg-Al layered double hydroxide (LDH) were studied. Mg and Al based LHD shall be used as flame-retardant. These LDHs are anionic clays with

stacked layers of hydroxides of Mg and Al, were exfoliated in polymer matrix to obtain their fine dispersion. The idea behind using LDH materials as flame-retardant is to exploit the possibility of exfoliation of the layers present in their structure in PE matrix. Due to high charge density of the metal hydroxide layers in LDH it is almost impossible to perform direct intercalation of the polymer chains in the inter layer spaces. Besides, the non-polar nature of PE is also an obstruction against such intercalation. Therefore, some pre-treatment of LDH materials before compounding them with polymers has been performed using different anionic surfactants [7].

The melt flow behaviors of polymer composites containing particulate suspension are strongly influenced by the nature of particle aggregation and the particle-particle and particle-polymer interactions. Rheological analysis is a very efficient means to investigate such influences and it has become, in combination with other analytical techniques, an inevitable method for characterization of polymer nano-composites. The conventional way of carrying out rheological analysis of such materials is to investigate their viscoelastic response in the linear flow regime that means under very low shear strain or strain rate. The purpose is to study the flow behaviors of the melts without destroying the particle-particle interactions or any network structure that may form among them. The flow behaviors are then related, mostly qualitatively or at least semi-quantitatively, with the state of dispersion of the particles in the matrix. The response of viscoelastic fluid to non-linear shearing (so called flow reversal experiment) has also been reported in literature [8-10] to study the structure formation among the dispersed particles. In such an analysis, polymer melt is first subjected to a steady shear followed by a certain rest period (shearing is stopped) followed by shearing in reverse direction. It has been observed that formation of any network structure is manifested in the stress shoot up in flow reversal step. The time necessary to attain the stress-shoot-up peak and its magnitude depends on duration of the rest period, shear rate and also the state of the particle dispersion in the melt.

The melt rheological properties of our material were determined using an ARES-Rheometer (Rheometrics Scientific, USA). The measurements were performed in the dynamic mode and 25 mm parallel plates geometry with gap settings about 2 mm under nitrogen atmosphere. The strain amplitude was kept 2% in the whole frequency range to ensure viscoelastic linearity. The temperature was varied from 160 to 240 °C as a function of the angular frequency, ω . The frequency is varied between 100 and 0.056 $\text{radian}\cdot\text{s}^{-1}$.

The non-linear shear experiment was carried out in the same rheometer with cone and plate geometry having 25 mm plate diameter and 0.1 radian cone angle. The gap between the blunt face of cone and the plate surface was set 56 μm , which was the distance at which the theoretical tip of the cone touches the plate surface.

Linear viscoelastic behavior

The presented data were measured at 240 °C only as to display the effects of incorporation of LDH into low-density polyethylene (LDPE). We found similar results for all the measured temperatures (160 to 240 °C). Shifting the data into a master curve at reference temperatures was possible, but the comparison among the composites was somewhat inaccurate due to the variation in the shifting accuracy for the composites.

Therefore, the master curves are excluded in this presentation.

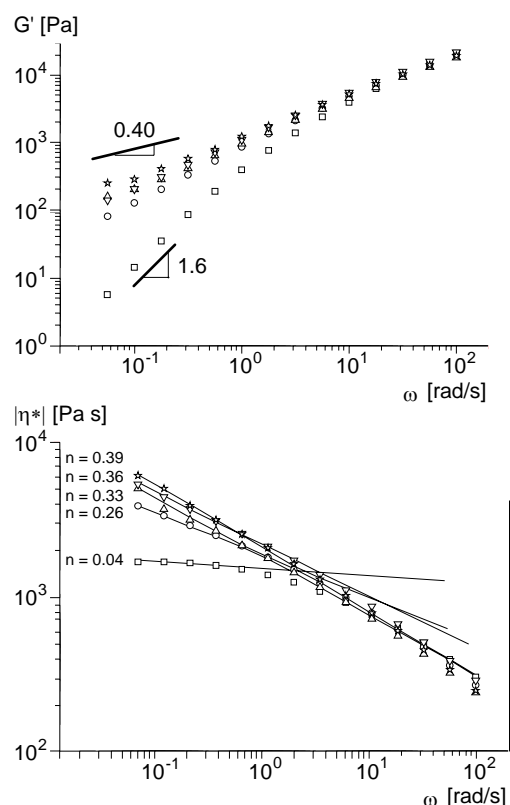


Fig. 5:
Comparison of the storage modulus (G') of the LDPE/LDH composites and LDPE at 240 °C. As the LDH loading increases the plot approaches plateau behavior at low frequency.
□ LDPE;
○ LDPE + 2 phr LDH;
△ LDPE + 3 phr LDH;
▽ LDPE + 5 phr LDH;
☆ LDPE + 10 phr LDH

Fig. 6:
Comparison of complex viscosity of the LDPE/LDH composites and pure LDPE at 240 °C. The low frequency data are fitted to straight line to obtain shear thinning exponent n from the slope.
□ LDPE;
○ LDPE + 2 phr LDH;
△ LDPE + 3 phr LDH;
▽ LDPE + 5 phr LDH;
☆ LDPE + 10 phr LDH

Storage modulus G' and complex viscosity $|\eta^*|$ of LDPE and LDPE/LDH composites are logarithmically plotted at 240 °C as a function of angular frequency in Figures 5 and 6. The dynamic spectrum of shear modulus with respect to frequency contains information regarding the manner in which a sample responds to small magnitude deformation applied over varying time scale. The storage moduli of the composites are higher than the one of LDPE, in particular at low frequencies; the difference is significant and their values are found to increase, within the experiments range, with increasing LDH loadings. In the low frequencies regimes of the log G' versus log ω plots, the liquid-like behavior of the polymer melt is evident in case of LDPE, which changes to a liquid/solid-like transition behavior by the addition of LDH. This is reflected in the plateau regions at low frequencies in case of composites in Fig. 5. Here, the relaxation exponent n ($G' \sim \omega^n$) changes from about 1.6 for LDPE to about 0.4 for the LDPE/LDH composites. This transition shows similar features like a sol-gel transition during chemical network formation. However, in our case it is related to the formation of physical cross-links due to the interaction between the LDPE chains and LDH layers leading to a network-like structure and resulting in an increase of the dynamic moduli. In addition to that, the incorporation of a high modulus material, like clay, into a relatively low modulus material, like LDPE, increases the modulus due to hydrodynamic reinforcement.

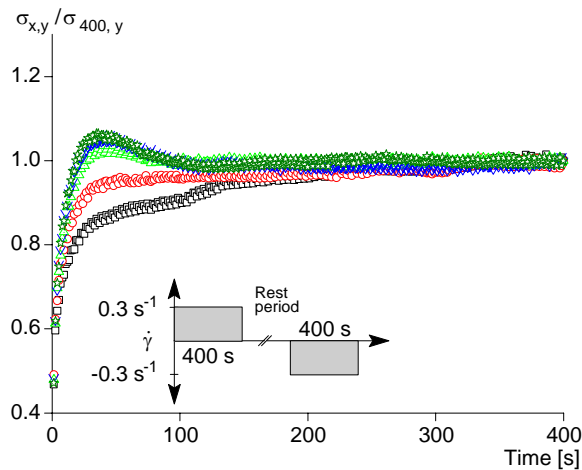
The complex viscosity, $|\eta^*|$, at 240 °C is plotted logarithmically versus ω in Fig. 6. It is seen that $|\eta^*|$ decreases monotonically with increasing ω . At low frequencies, $|\eta^*|$ approaches the zero-shear viscosity (at which the viscosity is nearly independent of the frequency) in the case of LDPE. The deviation in $|\eta^*|$ of LDPE/LDH composites from this Newtonian-plateau at very low frequency is a sign of the exfoliation (as confirmed also in Fig. 5).

The shear thinning exponent, n ($|\eta^*| \sim \omega^n$) is altered from -0.04 in the case of LDPE to -0.26, -0.33, -0.36 and -0.39 by the incorporation of 2, 3, 5 and 10 phr (parts per hundred rubber) LDH into LDPE, respectively.

Response to non-linear shear flow

The results of the non-linear shear experiment for composite with 10 phr LDH are shown in Fig. 7. The behaviour is similar to the one observed in polypropylene/clay nano-composites [9, 10]. The stress shoot ups observed at the beginning of transient shearing in reverse direction are certainly the effects of the changes that the composite melt undergoes during the previous shearing step and the rest period. It is apparent from Fig. 6 that the evolution of structure is not an instant process. A sufficient rest period must be allowed to experience its effects within the resolution limit of the instrument. The stress shoot up indicates an increased resistance against melt flow and subsequent decay of the stress peak indicates the release of that resistance. The flow resistance is caused by the formation of network structure among the dispersed particles, which have a hierarchy of structures, such as domains of particulate agglomerates, tactoids composed of multiple platelets, etc. The driving force behind the development of network structures is the achievement of higher thermodynamic stability through attractive interaction among particulate species. The decay in the stress shoot up peak in flow reversal step indicates the breakdown of this network structure and orientation of the dispersed particles in the flow direction, which leads to a steady value of melt viscosity. In the first shearing step of the flow reversal experiment such structures are destroyed and during the rest period reformation takes place. We believe that with small rest period, reformation of these network structures is not complete and hence no stress shoot up is observed. The size of the particulate agglomerate plays an important role; the bigger agglomerates require longer time to flip from their ordered orientation to the thermodynamically more stable networked orientation.

Fig. 7:
Response to non-linear shear flow of the composite containing 10 phr LDH at 190 °C. The inset shows the shearing cycle. The time interval represents the duration of the annealing period at zero shear and constant temperature of 190 °C. Rest periods:
□ 4 min; ○ 10 min; △ 15 min;
▽ 20 min; ☆ 25 min



Discussions and Conclusion

In this article we demonstrated how filler structures in elastomers and thermoplastic nano-composites are broken as a result of specific dynamic-mechanical excitations of the polymer network or the melt, respectively. According to the specific time programs of loading further evolution of structural changes of the fillers can be detected. These structural changes are interpreted as a more or less complete reformation of the network-like filler structures. The simple approach in Eq. (1) can be viewed as a special case $m = 2$, $n = 0$ of (thermodynamically driven) non-linearities related to *regulation* in complex systems [13]:

$$\left(\frac{dN}{dt}\right)_{\text{reg}} \sim \frac{aN^m}{1 + bN^n} \quad (4)$$

This is more known from chemistry or biology where a substance may activate or inhibit the rate of its own production or of the production of another constituent, which in turn feeds back on the first substance. In chemistry two characteristic examples are autocatalysis and thermal feedbacks. In biology, regulation is intimately related to the peculiar structure and reactivity of the enzymes. In many cases it gives rise to non-polynomial non-linearities of the form Eq. (4) resulting in activation if $m \geq n$ and inhibition if $m < n$ [13].

Further investigations of the filler networking kinetics in elastomers are possible through monitoring of structural relaxation phenomena during heat treatment (annealing) of the uncross-linked as well as cross-linked rubber composites. This is achieved by studying the time development of the small-strain storage modulus and provides information about the flocculation dynamics, i. e. the flocculation of primary aggregates to form secondary aggregates (clusters) and finally a filler network [2].

In the case of elastomers investigations of structural evolution of fillers and of the corresponding kinetic time constants contribute to an improved predictive testing of tire tread related rubbers under complex dynamical modes of deformation which are, for example, typical under conditions of tire handling tests.

In the case of nano-composites of hybrid material of a thermoplastic melt and nano-fillers our investigations lead to an improved understanding of the processing influences on the properties of the final composites. We have demonstrated how results of measurements in the so-called non linear viscoelastic domain are essential for understanding and predicting morphology changes during processing [14]. Quantitative modeling of the evolution of the structure by corresponding kinetic equations is planned for the next future. Suitable approaches can be found, for example, in [15]. Several applications for the described filled polymeric systems (elastomers and thermoplastic nano-composites) can be found in [16 to 18].

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