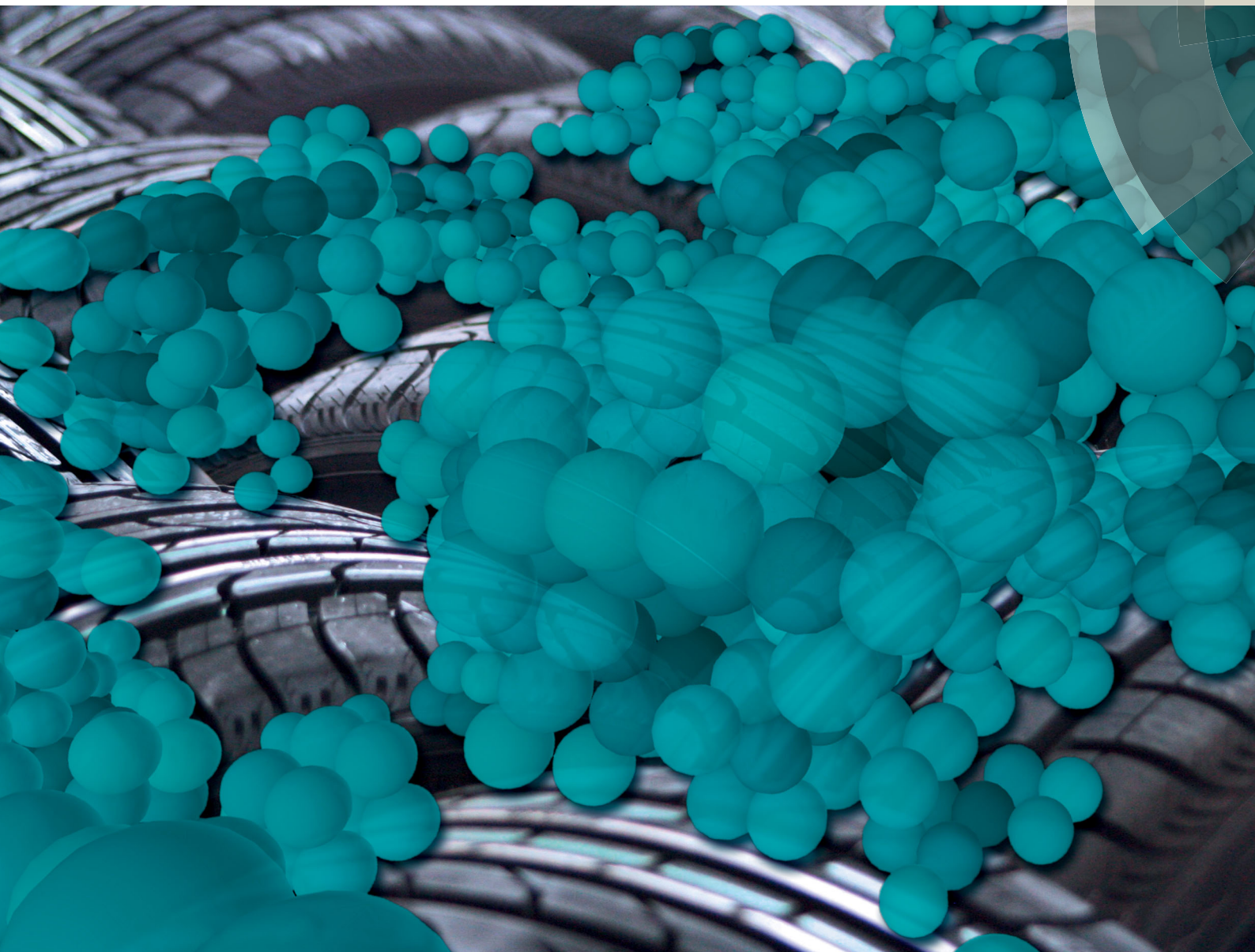


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## Filler flocculation in polymers – a simplified model derived from thermodynamics and game theory

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The performance of elastomeric materials, *i.e.* in car tires, is substantially determined by the used reinforcing filler system. In particular, the flocculation tendency of filler particles to form clusters and even network-like structures significantly determines the mechanical properties of these elastomer materials and enhances especially their energy dissipation under periodic mechanical deformations. In a simplified thermodynamic model, inspired by a segregation model from game theory, we describe fundamental mechanisms of filler structure formation. As the final goal of this paper we want to demonstrate how similar structures in society, nature or materials like rubbers emerge when supposing obvious cardinal mechanisms of structure formation in complex systems.

### Introduction

Elastomer materials need to be reinforced by filler particles to obtain properties necessary for dynamically strained products, *i.e.* car tires. During the mixing of rubber, these particles, consisting of agglomerates (clusters) of spherical particles with a diameter in the length scale of 10 nm, get finely dispersed in the polymer matrix down to aggregates, which are mechanically not further destructible in the prevailing shear fields during the rubber mixing processes. If the rubber composition is heated again, *e.g.* during the early part of the vulcanization process before the polymer network is fully established, these finely dispersed filler particles or their aggregates tend to re-agglomerate, due to a process called “filler flocculation”.<sup>1–3</sup> The filler flocculation mostly leads to the formation of a filler network, which has a drastic influence on the dynamic mechanical behavior of the elastomer material. For instance, this filler network is responsible for the non-linear amplitude dependency of the elastic and viscose moduli of the elastomer, the so-called Payne-effect.<sup>4–7</sup> The economic implications of the higher energy dissipation due to this effect can be considered as the main part of fuel consumption due to the rolling resistance of vehicle tires. This Payne-effect has recently been discussed already in a more general and ample context of a “jamming transition”.<sup>8</sup> With increasing strain amplitude under periodic mechanical deformation the disruption of the filler network resp. of finite filler cluster configurations leads to dejamming observed as softening of the rubber. As a theoretical approach we

mapped this problem on the Ising model which is well-known in solid state physics and as a paradigm for many physical problems. Furthermore, several other aspects of filler flocculation have been very recently investigated by simultaneous rheological and dielectric studies of carbon black filled rubbers and are well described by a superimposed cluster-cluster aggregation process (CCA).<sup>9,10</sup> When developing a self-consistent field theory of the polymer-mediated interactions, the filler flocculation stability ratio for practically important fillers and rubber materials can be calculated.<sup>11</sup>

Filler network reformation kinetics can also be observed in crosslinked rubbers,<sup>12</sup> containing reinforcing fillers. In these systems, relative movements of particles and portions of polymer chains are very small. Nonetheless, the network recovery behavior, after the initial shear-induced network break-down, is rather similar to the filler flocculation for filled uncrosslinked rubbers.<sup>13</sup>

The industrial and economic impact of the above discussed re-agglomeration of dispersed filler particles grew drastically when the tire industry introduced the so-called “green tire technology” 20 years ago, *i.e.* the filler system in the tread compounds for high-performance passenger car tires was changed from carbon black to silica.<sup>14</sup> The driving force of the filler flocculation process – the difference in surface energies of the filler and the polymer – for silica filled rubber is much more pronounced than in the traditional carbon black systems. To overcome this problem, a surface modification of the silica particles by sulfur containing silanes was introduced in rubber resp. tire industries, which makes the silica surface more compatible to the rubber matrix, leading to better filler dispersion during the mixing process, and couples the filler during the curing process to the polymer.<sup>15,16</sup> However, still a strong tendency to filler flocculation can be observed, even in modern tire tread mixtures based on a silica/silane system.<sup>2,17,18</sup>

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But, how does game theory come into play here?

As mentioned above, the surface energies of fillers and polymers play a crucial role in the flocculation process. The filler particles move and segregate from the polymer matrix due to their different surface characteristics. In 1971 Thomas Schelling (Nobel Memorial Prize in Economic Sciences, 2005) studied the ways that people who differ conspicuously settle in binary groups (*e.g.* skin color, religion *etc.*) by modeling this spatial “segregation”<sup>19</sup> in a simple checkerboard model<sup>20</sup> and was pioneering thereby a field of study that later became known as “agent-based computational modeling.”

In our paper we will point out that some of the basic principles of filler flocculation – a segregation of filler and polymer phase – can be investigated using the same tools as, for example, in demographic research.

In his book “Micromotives and Macrobehavior”,<sup>21</sup> Thomas Schelling introduces “A Self-Forming Neighborhood Model”. Hereby, the motivation of racial segregation is the wish of an individual, not to be a minority in the surrounding of the other group. Schelling played originally with 2 kinds of coins (Pennies and Dimes) on a ruled paper, and found that a randomly mixed arrangement showed after a few moves already a pattern formation and segregation. Today powerful computer software for agent based modelling is available, where such problems can be easily programmed and visualized (Fig. 1).

In the following we show if and how such simple segregation processes could be applied to filler flocculation in polymers and thus gain general insights into the underlying processes of this important effect. Therefore, the model is kept as simple as possible, only the surface energy of the particles is considered, all other parameters, which have an influence on filler flocculation, *e.g.* the viscosity of the polymer *etc.* are considered as constant and will be neglected as influencing factors in the model.

This means that large objects (here filler clusters and filler networks) are the products of very general principles of organization and of collective behavior and cannot in any meaningful sense be reduced to the behavior of only elementary constituents. Large objects are often more constrained by those principles than by what the principles act upon.<sup>24</sup>

The aim of this paper is not to include a multitude of possible specific filler properties and interactions into this very

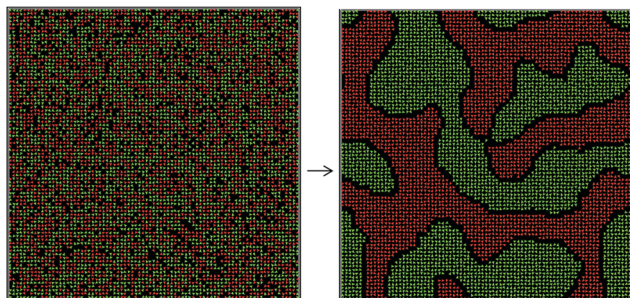


Fig. 1 Segregation model: Wilensky<sup>22</sup> according to Schelling from NetLogo Agent based modelling software.<sup>23</sup> Left: Randomly mixed initial state; right: segregation between red and green agents due to the wish not being minority in their surrounding.

simplified model. In contradiction, our intention is to show that a very easy model adapted from social sciences is able to explain a multitude of effects of filler flocculation in polymers.

### Thermodynamic modelling of filler flocculation

The driving force for filler flocculation – which we can use as an analogy of “people’s happiness” in Schelling’s segregation model – is the difference in the work of adhesion  $\Delta W_a$  between the state of a dispersed filler particle in contact with a polymer and the flocculated state, where the filler particles are in contact with each other.<sup>25–28</sup>

$$\Delta W_a = W_a(\text{FF}) + W_a(\text{PP}) - 2W_a(\text{FP}) \quad (1)$$

Hereby,  $W_a(\text{FF})$  means the work of adhesion of two filler particles and  $W_a(\text{PP})$  and  $W_a(\text{FP})$  between the polymers and fillers and polymers, respectively.

The work of adhesion between two phases 1 and 2 is defined by the Dupré equation:<sup>29</sup>

$$W_a(12) = \gamma_1 + \gamma_2 - \gamma_{12}, \quad (2)$$

where  $\gamma_1$  and  $\gamma_2$  are the surface tensions of phases 1 and 2 and  $\gamma_{12}$  is the interfacial tension between the two phases. This work of adhesion is the work which must be done to separate two adjacent phases 1 and 2 of a liquid–liquid or liquid–solid phase boundary from one another in a thought experiment. We note here that, indeed, details of the interactions between filler particles amongst each other and the polymer matrix cannot be captured completely in terms of work of adhesion. However, the specific components of the free surface energies of the constituents of the filled polymer system, which determine the work of adhesion, are known and can be used to derive much information about the system, *e.g.* the strength of filler–polymer interactions, the state of dispersion *etc.*

Due to the fact that the interfacial tension  $\gamma_{12}$  is not experimentally accessible in liquid/solid systems, the work of adhesion can be calculated from the polar and dispersive parts of the surface tensions:<sup>30</sup>

$$W_a(12) = 2\sqrt{\gamma_1^D \gamma_2^D} + 2\sqrt{\gamma_1^P \gamma_2^P} \quad (3)$$

The superscripts D and P denote the disperse and the polar part of the surface tensions, respectively.

Hereby, the dispersive part represents the interactions due to London’s dispersion forces; the polar part subsumes the interactions, which are evoked by polar functional groups, *i.e.* hydroxy, carboxyl or amino moieties. The dispersive and the polar part add up to the total surface energy.<sup>27</sup>

After inserting the terms for the work of adhesion according to eqn (3), we derive after some rearrangement the relation:<sup>25,27,31</sup>

$$\Delta W_a = 2\left(\sqrt{\gamma_F^D} - \sqrt{\gamma_P^D}\right)^2 + 2\left(\sqrt{\gamma_F^P} - \sqrt{\gamma_P^P}\right)^2 \quad (4)$$

Here, the indices F and P stand for the filler and the polymer. From eqn (4) it can be derived that the  $\Delta W_a$  values for phases with the same surface tension is zero, which also implies that filler particles, having the same surface energy and polarity as the polymer do not



flocculate. Values for the polar and dispersive parts of the surface energies of some common filler systems and rubber polymers can be found in ref. 28 and 31.

In the agent-based programming language and integrated modeling environment NetLogo3D,<sup>23</sup> a software was programmed, which provides according to Schelling's segregation model a 3D simulation of a very simplified filler flocculation process. Hereby, firstly a number  $N$  of filler particles are distributed randomly in a scalable cube on orthogonal lattice sites. The remaining space of the grid is supposed to be filled by the polymer. To avoid boundary effects, particles, which leave the cube on one side, enter it from the other side, so that the play field is correctly expressed as a torus.

To model the filler flocculation process in 3 dimensions on an orthogonal grid, every lattice site has 26 ( $=3^3 - 1$ ) direct neighbors. Therefore, the energy of one individual filler particle  $E_p$  depends on the number of equal immediate neighbors:

$$E_p = \sum_0^{26} \Delta W_a \quad (5)$$

The difference of work of adhesion  $\Delta W_a$  can be taken hereby as a unit of energy (Fig. 2).

The agent based software calculates the energy of any of the individual filler particles  $E_p$ , the total energy of the system  $E_{tot}$ , which is the sum of  $E_p$  of all particles, and the degree of flocculation  $F$ , which is defined as

$$F = (26 - E_{tot}/N)/26 \times 100\%. \quad (6)$$

where  $F$  is equal to 0% for a set of all individual particles not in contact with each other and 100% for the (not achievable) case that all particles would have 26 particles as closest neighbors.

To follow the sociological segregation model of Schelling, we now have to define a number of equal neighbors, which is the threshold, if particles are "happy" with their actual position, or if they would have the driving force to move to a place which is energetically more favorable. From another point of view, we can equate this value with "thermal energy"  $E$ , which opposes the agglomeration tendency of the particles (also in units of 0 to 26  $\Delta W_a$ ). A particle, whose individual energy  $E_p$  is lower than this threshold will stay in its environment, whereas a particle, whose individual energy is higher than this value will break apart a particle cluster and move to a different position. The movement of these particles was realized in the model just by a random walk on a vacant neighbor position. Fig. 3 shows the flowchart of this very simplified flocculation model.

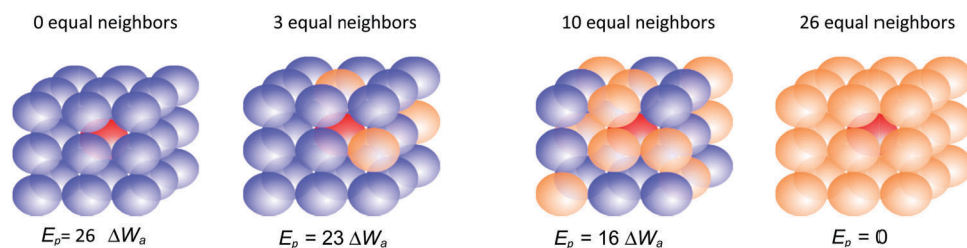


Fig. 2 The energy of an individual filler particle (red)  $E_p$  as a function of the number of equal neighbors in units of the difference of  $\Delta W_a$ .

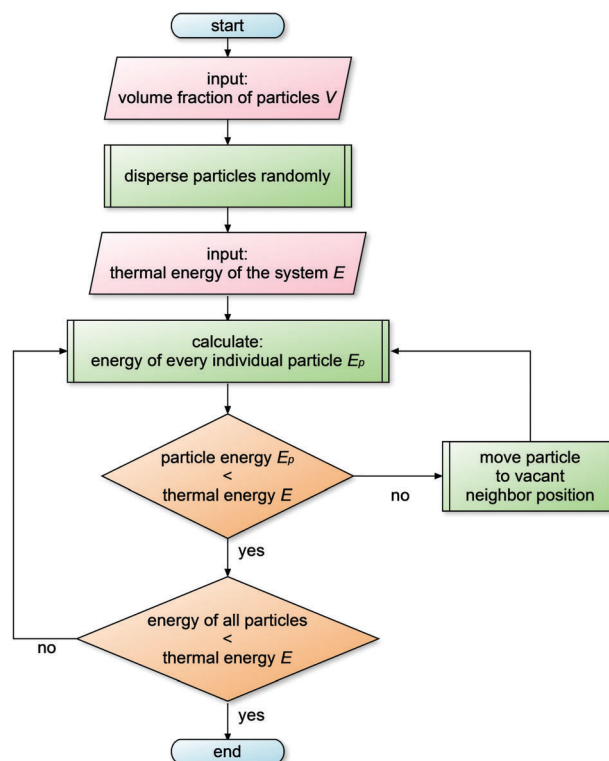


Fig. 3 Flowchart of a simple flocculation model.  $V$ : volume fraction of particles;  $E$ : thermal energy of the system (= energy threshold for moving)  $E_p$ : energy of individual particle (depending on the number of neighbors); energy unit = 1  $\Delta W_a$ .

## Results from filler flocculation modelling

### Influence of the "thermal energy" – or accordingly "the desired number of neighbors"

Using the NetLogo model for filler flocculation described above, some simulations were done; as parameters for the model 1546 particles in 9261 cells (a cube with 21 cells side length) were chosen, which corresponds to a volume fraction of 16.7%. This is equivalent to a volume fraction of 40 phr of the filler (density appr. 2 g  $\text{cm}^{-3}$ , i.e. carbon black) in rubber (density ca. 1 g  $\text{cm}^{-3}$ ). The modeling was done with different thermal energies  $E$  from 0 to 13  $\Delta W_a$ , which corresponds to "the desire to have 0 to 13 equal neighbors". In Fig. 4 the results of the 3D simulation are shown. For low thermal energies  $E$  – or from another point of view – at a small difference in the surface

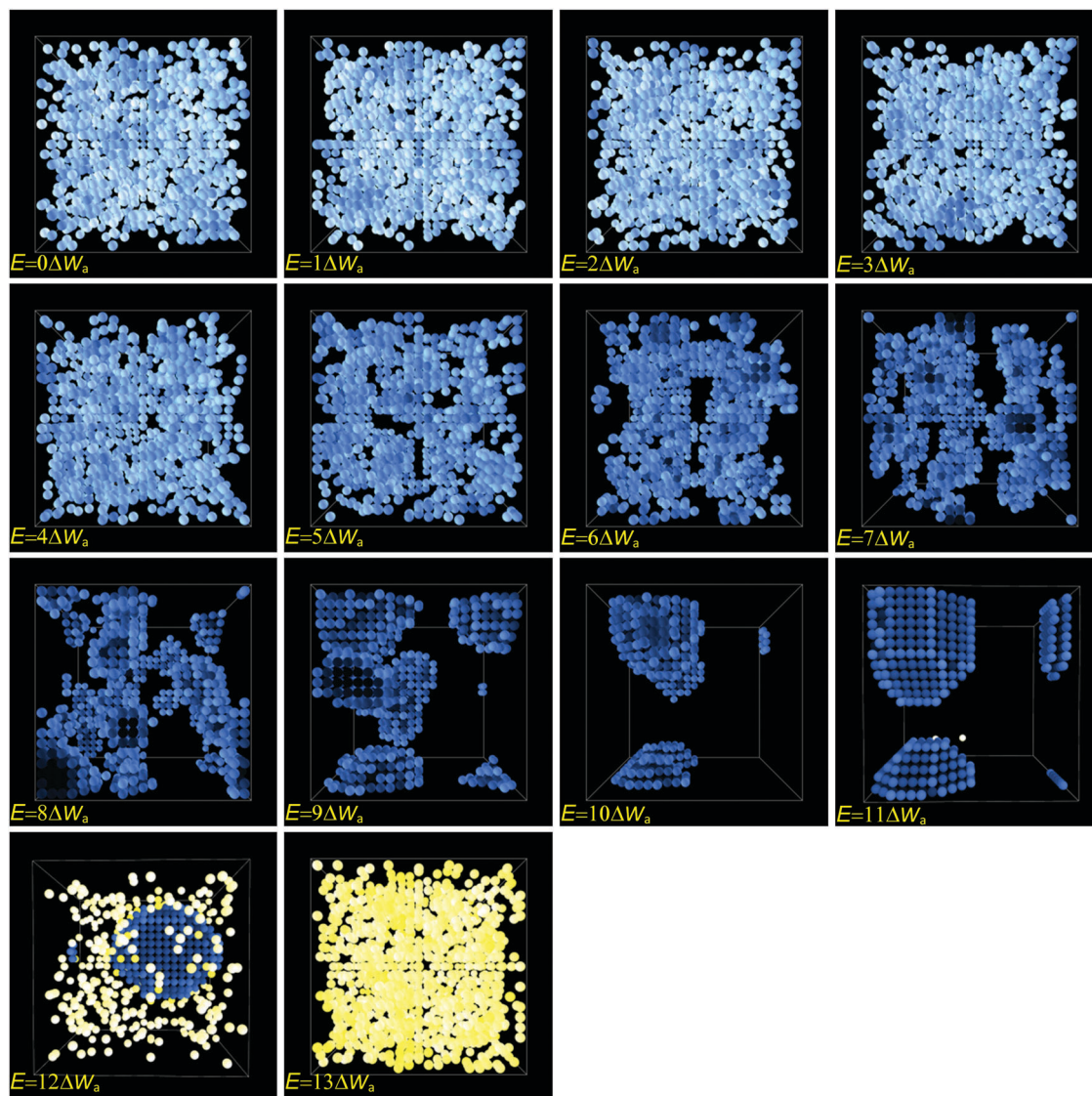


Fig. 4 Filler flocculation simulation for different thermal energies ( $=$  desired number of equal neighbors) in a 3D model with 1546 filler particles in 9261 cells ( $21 \times 21 \times 21$  cube). Blue particles have reached the status of the desired number of neighbors (the darker a particle, the lower is its individual energy  $E_p$ ); yellow particles have not reached  $E$  within 2000 iteration steps.

energies of filler and polymer – no flocculation effect can be observed; the particles stay more or less at their randomly determined places. If the value of  $E$  exceeds 3 to  $4 \Delta W_a$  the formation of a filler particle network can be observed. If the thermal energy exceeds a value of  $7 \Delta W_a$  the picture is changed: now big more or less round shaped particle aggregates are formed in a mechanism, which reminds us of a homogeneous nucleation process. If we increase the value of  $E$  further, the process slows down and the particles hardly find places where the condition of similar neighbors can be fulfilled. At a value of  $12 \Delta W_a$  the formation of one big round-shaped cluster of particles could be observed after a long initial phase; at greater values no condensation of the particles takes place, the particles keep on moving.

Fig. 5 shows the time-dependent degree of flocculation  $F$  of the simulation displayed above: as expected, for low values of  $\Delta W_a$  of 0 to 2 no driving force for flocculation exists, the system remains

in the state of the randomly dispersed start state; for thermal energies from 3 to  $7 \Delta W_a$  flocculation curves with a similar initial gradient result, also showing a steady increase of the final flocculation degree  $F$ . For values of  $E$  from 8 to  $11 \Delta W_a$  we find different kinetics with a slower initial flocculation degree, but with continuously increasing final flocculation values. For  $E = 12 \Delta W_a$ , a very noisy slow flocculation curve is observed, whereas for values of  $E = 13 \Delta W_a$  or higher no flocculation takes place at all.

As already mentioned, the network formation of filler particles, which is predicted by the model at lower thermal energies, is a well-known phenomenon in real elastomers and is considered as the main reason for non-linear (strain dependent) mechanic-dynamic behavior (Payne effect). However, this nucleation like formation of nearly spherical clusters is unknown in rubbers and has never been described in the literature on filler flocculation in rubbers. We assume the following reasons: (i) in rubber the necessary

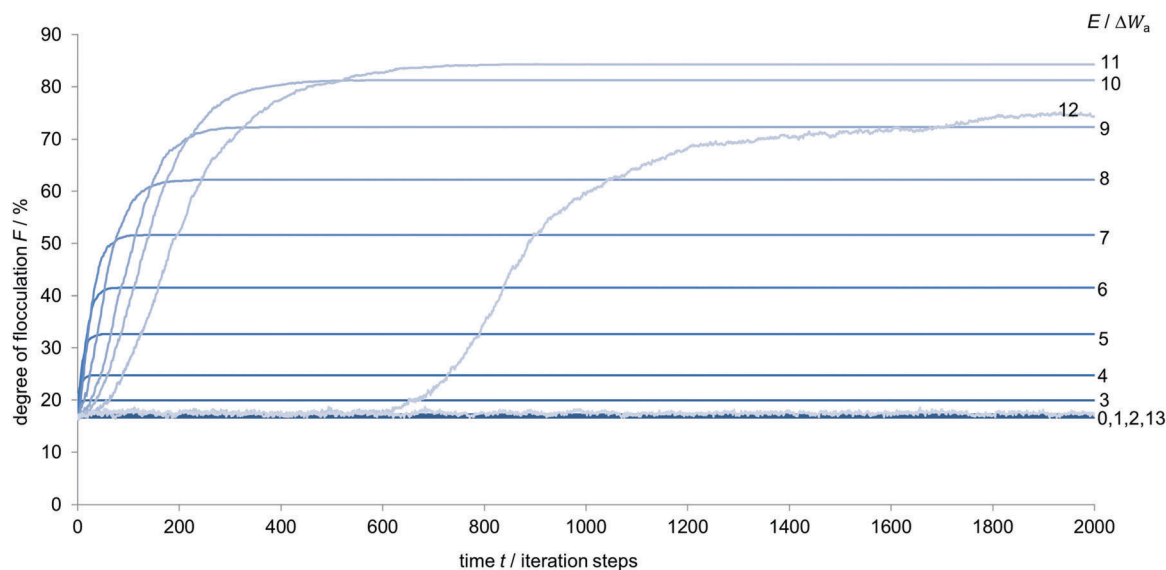


Fig. 5 Flocculation degree for different thermal energies  $\Delta W_a$  (= desired number of equal neighbors) in a 3D model with 1546 filler particles in 9261 cells ( $21 \times 21 \times 21$  cube).

temperatures for this process will not be reached, and (ii) the mobility of the filler particles in the highly viscous rubber matrix is too low. The viscosity of the polymer matrix is hereby a function of the molecular weight of the polymer, which has therefore also a direct influence on flocculation;<sup>1,32</sup> also physical jamming may arrest further movements of the filler particles as well.<sup>3,33,34</sup>

Recently, the formation of dendritic or “raspberry-like” filler structures in a dilute aqueous natural rubber/silica mixture as a function of the silica particle size has been observed.<sup>35</sup> This could also be referring to a transition from a network-forming process to nucleation. Another reason could be that big clusters of fillers in a rubber material would be rather considered a consequence of an incomplete dispersion of the filler particles during mixing than as a consequence of filler flocculation.

### Filler flocculation kinetics of the model

The flocculation kinetics can be fitted by several models. For the obtained simulation data, it became apparent that the so-called logistic saturation equation delivered the best results:

$$F(t) = \frac{F_0 F_\infty e^{F_\infty k t}}{F_\infty - F_0 (1 - e^{F_\infty k t})} \quad (7)$$

with the rate constant  $k$  and  $F_0$  and  $F_\infty$  as flocculation states at the beginning and at the end of the simulation. This function is a solution of the so-called hyperlogistic differential equation, which is of great importance for the modeling of natural growth processes, not only from the point of view of a good fit, but also from that of “its relevance for aggregated growth in soft systems”.<sup>34,36</sup> In this logistic saturation model, the rate constant  $k$  characterizes the autonomous growth in the intensive phase, whereas  $F_\infty - F_0$  is the saturation value or the steady state. In Fig. 6, the rate constant  $k$  and the saturation plateau  $F_\infty - F_0$  are shown as a function of thermal energy  $E$ . The exponent  $k$  constantly decreases with the thermal energy  $E$ , and the plateau value  $F_\infty - F_0$  increases with the thermal energy.

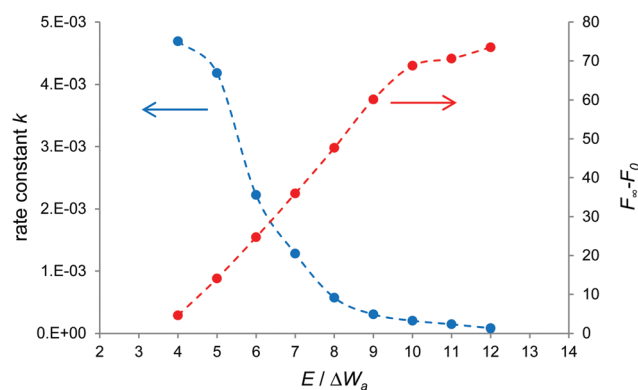


Fig. 6 Rate constant  $k$  and an increase in the degree of flocculation from a fit of the data in Fig. 5 by means of logistic saturation eqn (7).

### Influence of the history of the system

Not only the value of  $E$  determines the final flocculation state of the simulated system, but also the thermal history of the system is important. When the thermal energy  $E$  in the simulation is slowly increased step by step, a filler network is formed soon; upon a further increase of  $E$ , the particles, which are at grid places with too fewer equal neighbors, search for a new, more energetically favorable position. As a result a strong network is formed (as in Fig. 7, left side). Fig. 8 shows the corresponding flocculation behavior of the model: up to a thermal energy  $E$  of  $10 \Delta W_a$ , the degree of flocculation grows continuously and a network-like flocculation structure is formed (as seen in Fig. 7, left); a further stepwise increase of  $E$  leads to disintegration of the already formed filler network structure, followed by a random distribution of the particles like in the initial state (see Fig. 7, middle).

In contrast, if the thermal energy  $E$  (or desired number of equal numbers) is set directly to a high value, a nucleation process starts, and after a rather long induction period, a nearly spherical cluster

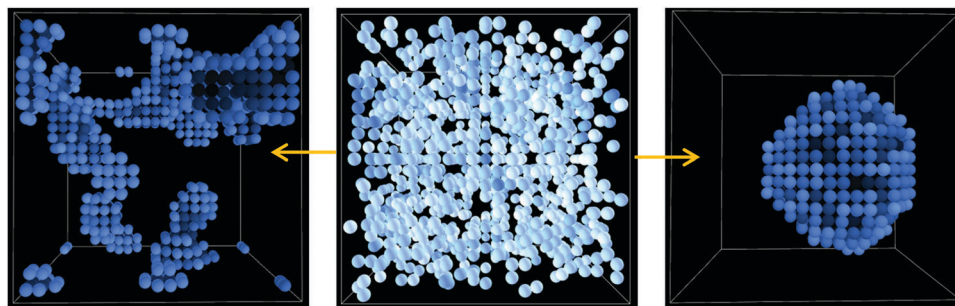


Fig. 7 Dependence of the structure formation of the particles on the history of the system: from a randomly dispersed state (middle), by a stepwise increase of thermal energy  $E$  from 0 to  $10 \Delta W_a$  a network structure is formed (left); a direct simulation at  $E = 10 \Delta W_a$  yields a spherical cluster of particles (right); filler volume fraction was 12.7%.

of particles (Fig. 7 right side) is formed, such as a condensation droplet with a minimized surface due to its surface tension.

It would be an interesting task to find out, if in real rubbers this effect could be reproduced, and if the filler flocculation and consequently the Payne effect could be influenced by an adjusted temperature management during processing and storage of uncured rubber mixtures.

#### Effect of filler volume fraction and “thermal energy” – “phase diagram of flocculation”

The model was tested not only for different thermal energies  $E$ , but also for different volume fractions of filler particles. In order to avoid too long computing times, simulation was done for each combination of thermal energy and volume fraction for a maximum of 500 iterations. The mean energy difference in this time or equilibrium of one particle was taken as a measure for flocculation efficiency. Fig. 9 shows the result of these simulations.

In Fig. 9 several different regions can be observed: for low  $E$ -values, as well as for high  $E$ -values, no increase of the individual mean energy of a particle can be noticed; in-between these two regions, an area with increasing energy values is located. With increasing thermal energy, for every volume fraction of particles, the mean energy of a particle increases, firstly in a rather linear manner, which changes to a somehow chaotic pattern for higher thermal energies.

If we look on the corresponding flocculation structures (Fig. 10 left), we can identify four different regimes of structural arrangements.

(1) At low thermal energies, which correspond to the “wish” of particles to have only 1 or two equal neighbors, the particles do not feel the driving force to move to energetic places. The system is “frozen”.

(2) With increasing values of  $E$ , a network-like structure, as known from TEM-micrographs of filled rubbers, is formed.

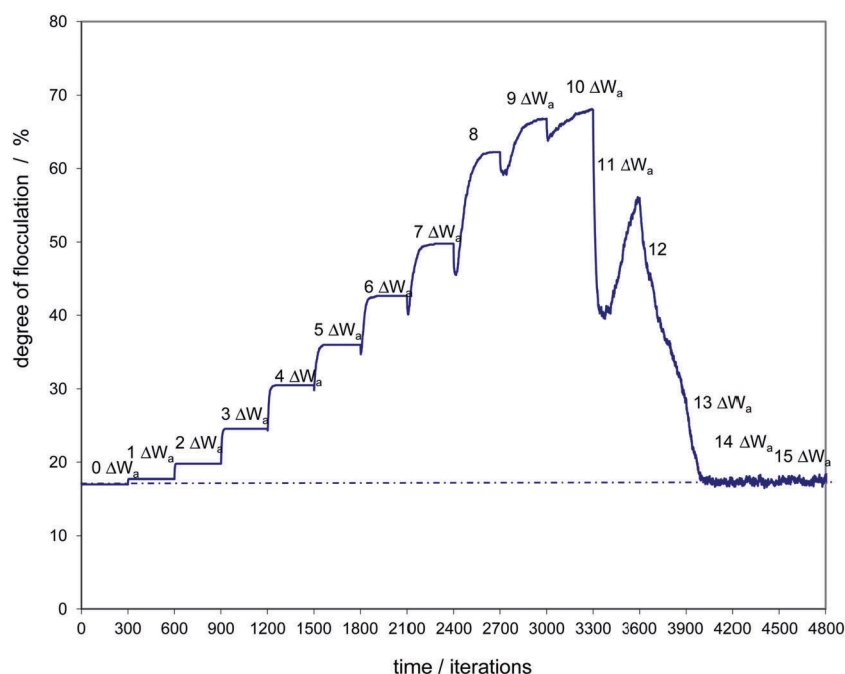


Fig. 8 Flocculation upon a stepwise increase of thermal energy  $E$  from 0 to  $15 \Delta W_a$  at 12.7% volume fraction – corresponding to Fig. 7 (left).



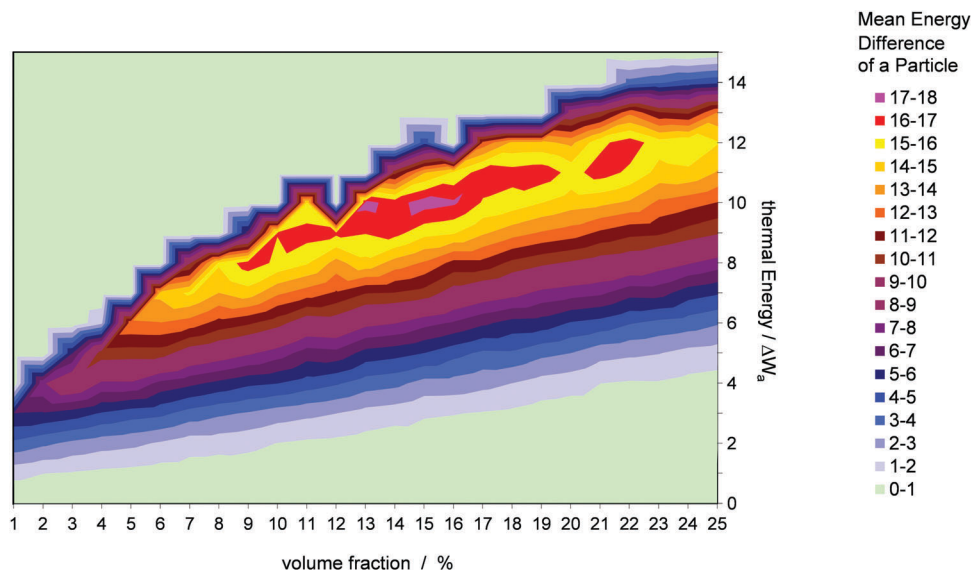


Fig. 9 Mean energy difference of a particle in the simulation in equilibrium or after 500 iteration steps as a function of thermal energy  $E$  and volume fraction.

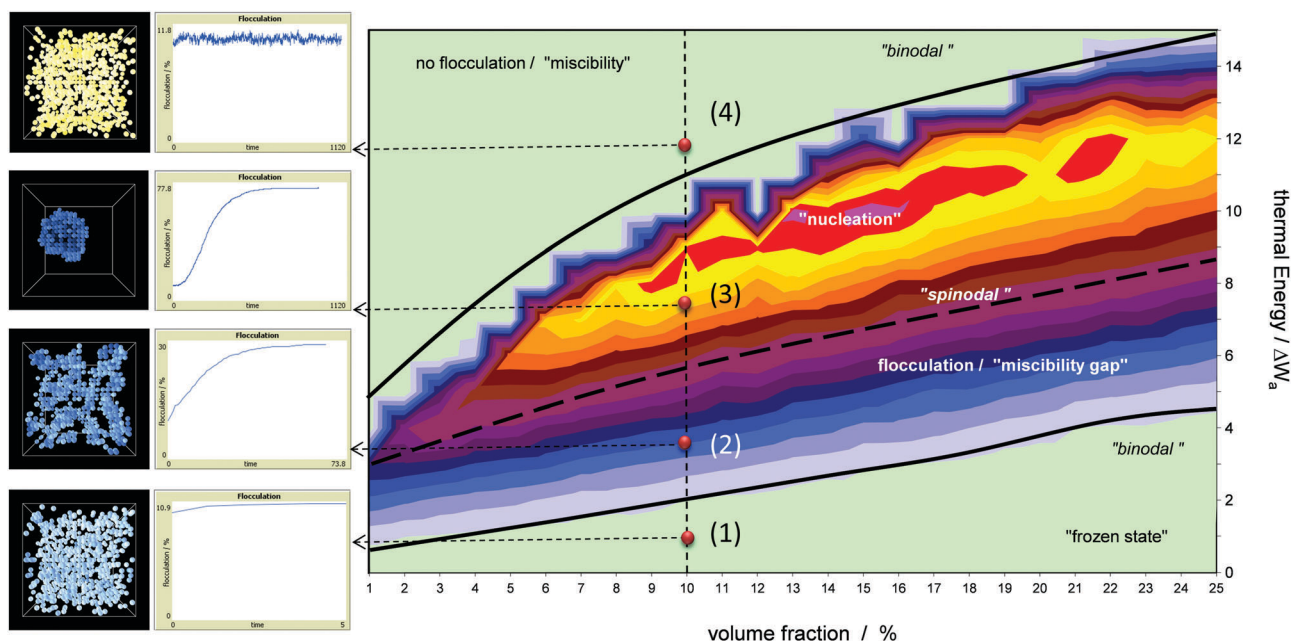


Fig. 10 "Phase diagram"-like interpretation of the flocculation behavior of the model. On the left side the particle the structures of the particle system is shown for an example of 10% volume fraction.

This flocculation process also could be denoted as "spinodal decomposition" of the polymer/filler – system.

(3) With a further increase of thermal energy, the formed filler structures change to spherical aggregates, in a "nucleation"-like process. In contrast to the previous process, this structure formation is characterized by a rather long induction time until the nucleation starts.

(4) A further increase of the thermal energy  $E$  leads to a state, where no structure formation takes place; all particles are in movement continuously.

From these observations, we can interpret the flocculation behavior of this simple model as an analogue of a phase diagram. The state of low thermal energy  $E$  (1) can be interpreted as the "frozen state" followed by a "miscibility gap" of fillers and the matrix, where "spinodal decomposition" of both phases takes place (2). After crossing the limit of local stability ("spinodal"), the system turns into a state, where nucleation takes place (3). At even higher thermal energies, no particle flocculation occurs, which could be understood as a "miscibility" of the two phases, fillers and the polymer matrix.



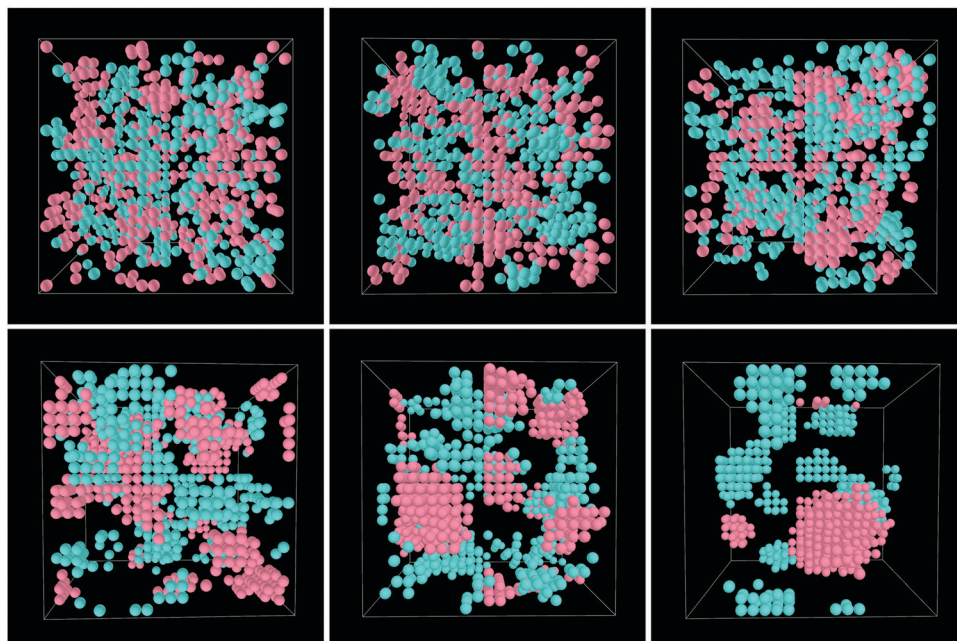


Fig. 11 Simulation of the flocculation behavior of a hybrid filler system consisting of a non-polar (carbon black, blue) and a polar filler (unmodified silica, red) in a non-polar rubber matrix (6 vol% each) at different thermal energies.

### More applied modeling – hybrid filler systems

The very simplified flocculation model can, if required, also be adapted to more applied scenarios, where real measured surface energies of fillers and polymers have to be used.

One example of such a model is the modelling of a polymer, containing two different filler types, for example, silica and carbon black. For this purpose, we have to take into account the dispersive and polar parts of surface energies of the two filler types and of the polymer. Every grid site of the simulation is occupied by one of the two filler types or of the polymer (not shown in the visualization for the sake of clarity). The individual energy of a particle  $E_p$  is then calculated by summation of the difference of work of adhesion  $\Delta W_a$  of its 26 closest neighbors according to eqn (4). An arbitrary adjustable threshold is in this approach acting as the thermal energy  $E$  (or to stay in terms of segregation theory the number of favorable similar neighbors).

As a concrete simulation example we have chosen a system with the physicochemical data of a non-polar rubber polymer ( $\gamma_P^D = 24.2 \text{ mJ m}^{-2}$ ;  $\gamma_P^P = 4.7 \text{ mJ m}^{-2}$ ) filled with a non-polar filler F1 ( $\gamma_{F1}^D = 27.0 \text{ mJ m}^{-2}$ ;  $\gamma_{F1}^P = 0 \text{ mJ m}^{-2}$ ) and a polar filler F2 ( $\gamma_{F2}^D = 19.4 \text{ mJ m}^{-2}$ ;  $\gamma_{F2}^P = 18.9 \text{ mJ m}^{-2}$ ). This corresponds to a mixture of carbon black (F1) and unmodified silica (F2) with a volume fraction of 6% each, in ethylene propylene diene rubber (EPDM); data are taken from ref. 27.

Fig. 11 shows the simulated flocculation behavior of such a hybrid system: it is obvious that – in particular for higher thermal energies – not only segregation between filler particles and the polymer matrix is observable, but also segregation between the two filler types, *i.e.* the polar and non-polar particles also segregate in different networks or clusters. Similar observations are made by Jinnai *et al.*<sup>37</sup> in the evaluation of

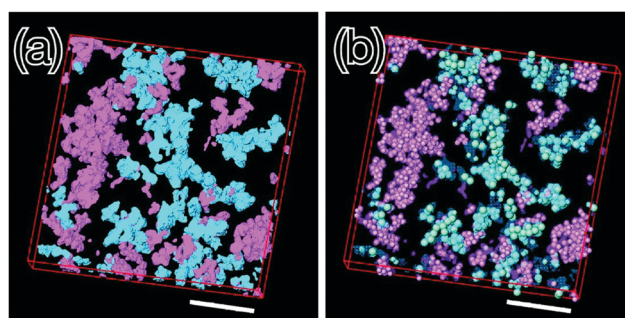


Fig. 12 (a) 3D transmission electron micrograph of a carbon black silica/rubber system. Blue and red regions consist of CB and Si nanoparticles, respectively (b) 3D reconstruction of the CB@Si/NRBR system after particle-packing analysis. The blue and red balls represent the CB and Si nanoparticles whose diameters are 25 and 20 nm, respectively. Bar shows 200 nm. Reprinted with permission from ref. 37. Copyright (2007) American Chemical Society.

3D-TEM studies of hybrid filler systems in rubber (see Fig. 12). They stated: “The nanoparticles were found to form aggregates in the matrix. It is intriguing that each aggregate was made of only one species; not a single aggregate contained both carbon black and silica nanoparticles.”

## Conclusion

In this contribution to the discussion of filler flocculation effects in polymers, it was shown that a very simplified simulation model, inspired by Schelling’s segregation model from game theory, can form similar structures, as are found in filled elastomers. Simply the surface energy, or more precisely, the difference of work of adhesion between filler particles and

polymers can explain the structure formation of fillers in the polymer matrix. The applied model reveals under certain conditions flocculated network-like filler structures, which in rubber science and technology are known from TEM micrographs of silica filled rubbers<sup>38</sup> and which are considered as the origin and explanation for the Payne-effect. If the segregation model demands a higher number of equal neighbors – corresponding to a higher thermal energy in flocculation – the simulation shows spherical filler clusters, which in the elastomer material are not observed as flocculation structures or are considered as a result of incomplete dispersion. Furthermore, the flocculation behavior of hybrid filler systems of non-polar and polar fillers can be explained by this simple flocculation model.

## Acknowledgements

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