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Viscoelastic properties of composite materials with random structure

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A model for the structure of filled polymeric composites has been developed. To simulate filler-filler and filler-matrix interaction on a meso level, the Voronoi polyhedron representation of smallest structural elements (filler particles) is used while fractal concepts are applied for the description of more coarse-grained structures. An iterative method based on the ideas of renormalization group transformations is presented to calculate viscoelastic properties such as the storage and loss modulus of the composite. The influence of frequency as well as the properties of filler and matrix on the effective viscoelastic properties of polystyrene melt filled with glass spheres has been elucidated in a wide concentration range. The calculations and the experiments are in good agreement. Moreover, model calculations coincide with results of percolation theory.

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I. INTRODUCTION

The influence of filling on the rheological properties of composites is well-known from the experimental and theoretical point of view in the range of small concentrations [1]. For higher concentrations, the straightforward solution of hydrodynamic equations is difficult and only approximate solutions or numerical results are available. For the highest concentrations, where direct contacts between the particles dominate deformation behavior, the theoretical description is mainly based on empirical models [1]. In general, models based on realistic structural ideas, describing the rheological properties of filled polymers in a wide range of concentrations are missing so far. In the following, we suggest a structural model and a method for the calculation of viscoelastic properties of filled polymers for the case of known properties of the constituents.

Prior to the theoretical analysis for the viscoelastic properties of filled polymeric compounds, we pay attention to one important principle simplifying the analysis, namely the correspondence principle [2,3]. It states that the solution of an elastic problem can be transformed to the solution of a viscoelastic problem under steady state oscillatory conditions by replacing the elastic modulus μ with the corresponding complex modulus $\mu^*(i\omega)=\mu'(\omega)+i\mu''(\omega)$. Therefore models applied to describe elastic materials can also be used for viscoelastic materials on the basis of the correspondence principle. This is the reason why we do not differentiate between both approaches.

The general theory for the effective physical properties of heterogeneous media including elastic ones is presented in papers [4–11]. Relying on publications which are dedicated to the theoretical and experimental study of physical properties of heterogeneous media with random structure, one can conclude that the prediction of elastic properties of these materials in a restricted concentration range is possible in two cases [11–21].

(a) The ratios of the properties of phases z_k (these might be the ratio of the shear moduli, $z_1=\mu'_m(\omega)/\mu'_f(\omega)$ and the ratio of viscosities $z_2=\eta_m(\omega)/\eta_f(\omega)$, with $\mu''(\omega)=\omega\eta(\omega)$ where subscript m corresponds to the polymer matrix and f corresponds to the filler phase) vanish: $z_k\rightarrow 0$.

(b) The properties of phases differ by not more than two orders of magnitude: $10^{-2}<z_k<1$.

In the first case, the prognosis relies on results from the percolation theory [14–21] while in the second case methods from the "effective media theory" are used [6,7,21].

Results from the percolation theory can be presented in the following way:

$$\mu \sim (p-p_c)^{\tau}, \quad p>p_c, \quad 3<\tau<4, \tag{1.1}$$

$$\mu \sim (p_c-p)^{-s}, \quad p<p_c, \quad 0.5<s<1. \tag{1.2}$$

The equations describe in general the change in the effective shear modulus μ in dependence on the particle bulk concentration, p, and, in particular, the abrupt change of properties at the percolation concentration, p_c, which is the result of clustering processes for the dispersed phase components.

In compliance with the effective media theory, the shear modulus can be presented, for example, by the Kerner equation (see, e.g., [7]):

$$\mu=\mu_m\{(1-p)\mu_m+(\alpha+p)\mu_f\}/\{(1+\alpha p)\mu_m+\alpha(1-p)\mu_f\}, \tag{1.3}$$

$$\alpha=2(4-5\nu_m)/(7-5\nu_m), \tag{1.4}$$

where ν_m is the Poisson ratio of matrix.

Using the correspondence principle, $\mu_k\rightarrow\mu_k^*(i\omega)$, and relying on Kerners results, Christensen [22] gave the next formula for the effective complex shear modulus of a viscoelastic material:

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$$\mu^*(i\omega) = \mu_m^*(i\omega)\frac{(1-p)\mu_m^*(i\omega) + (\alpha+p)\mu_f^*(i\omega)}{(1+\alpha p)\mu_m^*(i\omega) + \alpha(1-p)\mu_f^*(i\omega)}. \tag{1.5}$$

In various papers [23–36] the comparison of experimental results with calculations from the Palierne model [32] (an even more generalized rheological constitutive equation for heterogeneous materials) was performed and significant differences were observed. Thus, e.g., Palierne's equation transforms into the following equation under the condition $z_k \to 0$

$$\mu^*(i\omega) = \mu_m^*(i\omega)\left(\frac{1+1.5p}{1-p}\right), \tag{1.6}$$

which agrees neither with Eq. (1.1) nor with Eq. (1.2). Moreover, from Eq. (1.6) it follows that $\mu^*(i\omega)\to\infty$ tends to infinity if the concentration tends to unity; the latter differs significantly from the true result $\mu^*(i\omega)\to\mu_f^*(i\omega)$.

The effective media theory was also used for the calculation of rheological properties of liquid-liquid heterogeneous materials (emulsion models, see, e.g., [31–33]). Calculations presented in these (and other) papers are based on the concept of homogeneous distributions of the heterogeneities. These models are not able to account for aggregation or cluster formation of inclusions and, consequently, their results differ from those obtained by percolation theories.

In the paper of Wu *et al.* [29] the rheological properties of polymeric composites were investigated in the concentration range $p\to p_c$ and the Nielsen equation, which is a generalization of the Kerner equation, has been used for some comparisons with theory. But the Nielsen equation does not describe percolation effects either.

Efforts to describe percolation phenomena in filled rubbery materials were presented by Klüppel *et al.* Their results can be used if $z_k\to\mathbf{0}$, whereas if z_k is finite they can hardly be used.

Rheological properties of filled polymeric materials are heavily influenced by interfacial phenomena such as the formation of an interfacial layer (IL) at the phase boundaries [1]. An analysis of the IL's properties on the viscoelastic properties of filled polymers was given by Vignaux-Nassiet *et al.* [30]. The authors introduced a finite size interfacial layer into the Palierne model, with properties different from the matrix. Doing so, they were able to describe their experimental results satisfactorily.

Huber and Vilgis [24] performed a theoretical study on how the aggregation of particles having interfacial layers of different sizes influences the effective viscoelastic properties of composites. Doing so, they generalize the well-known Einstein-Smallwood equation. The calculations yield no quantitative but a qualitative agreement with experiments in the concentration range where aggregation of particles strongly influences the viscoelastic properties of the composites.

In general, a sufficient theory which accounts for effects of aggregation and interfacial effects does not exist so far for the case of viscoelastic properties for the constituents of composites being in the range $0<z_k<10^{-2}$ and if the amount of filler is changing in a wide concentration range. In the following we will present a method which allows one to calculate the viscoelastic properties of filled polymeric materials with random structure of fillers taking into account the above-mentioned requirements. Doing so, we assume that the viscoelastic properties of the constituent phases are known. We will show that our results agree very well with the results of percolation theories as well as effective media theories.

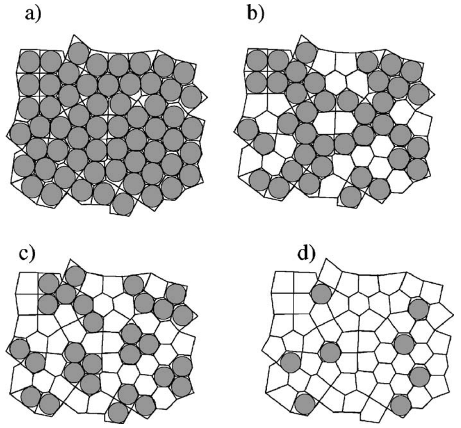

FIG. 1. Schema of structural changes with concentration of Voronoi polyhedra, x: (a) $x=1$, (b) $x<1$ and $x>x_c$ (x_c is the critical concentration of VP, which is defined in Appendix B), (c) $x<1$ and $x<x_c$, and (d) $x\ll 1$.

II. STRUCTURAL MODEL

Defining structural properties of a composite material with random structure is a rather complicated task. That is why we will introduce some simplifying assumptions. First of all, we assume that the filler particles are spherical in shape and uniform in size having the radius R. Second, although we know that in reality particles are heterogeneous in nature due to the formation of an interfacial layer or due to grafted polymers to its surface, we assume that the particle is homogeneous.

To describe the structural properties of random media composed of a matrix and particles with mentioned properties, the Voronoi polyhedron (VP) [37] and its modifications are used. For example, the Voronoi polyhedron was used to describe the structure of quickly cooled liquids, metallic glasses, and noncrystalline systems [38–40]. The VP is a convex polyhedron circumscribed around a particle. To construct a VP, we emanate from particle configuration at the limiting filler concentration, p_0. In this situation [see Fig. 1(a)] at the contact points of all the particles, we build planes tangent to the particle surfaces and perpendicular to the radii connecting the particle centers. The polyhedron whose volume is limited by these planes and which comprises the volume of the particle itself (which might include the volume of an interfacial layer) and some matrix material is a VP. Voronoi polyhedra (VPa) connected by such planes fill the whole volume of a random medium without any gap in the case of limiting filler concentration.

Now, we will examine the structure of a maximally filled polymeric material in more detail (see Fig. 1). Around each of the particles we will form a VP. As a result, the whole volume of the composite will be filled with VPa. The number of faces in each polyhedron is equal to the average coordination number, N. We will designate the VP bulk concentration as x. The relationship between the filler particle bulk concentration p and the Voronoi polyhedron bulk concentration is determined as $x=p/p_0$, where p_0 is the limiting bulk concentration of particles, which in the case of random packing of spheres amounts to $p_0 \cong 0,6$ [41,42]. At the VP concentration $x=1$ $(p=p_0)$ the whole volume is filled with Voronoi polyhedra.

When the particle bulk concentration (and, correspondingly, the Voronoi polyhedron bulk concentration) decreases, the structural change of the composite can be represented as in Fig. 1 (for details also see Appendix B).

At $0<x<1$, the filled polymeric composite can be represented as a random mixture of two sorts of polyhedra: the ones with and without filler particles (see Fig. 1). The results of the theory of percolation [16,17] are applicable to such a mixture of polyhedra. According to this theory, at $x<x_c$ isolated clusters are formed from VP; at $x>x_c$ the infinite cluster is formed from VP, where x_c is the percolation threshold. Knowing that for three-dimensional systems $(d=3)$, the percolation threshold $x_c \cong 0,2$, we can define the critical concentration of filler particles, p_c, at which the infinite cluster is formed, in the following way:

$$p_c = p_0 x_c. \tag{2.1}$$

In general, the limit filling, p_0, depends on the form of particles as well as on the way of packing and it can change within the limits

$$0 < p_0 \leqslant 0.74. \tag{2.2}$$

The maximum value $p_0 \cong 0,6$ corresponds to the limiting filling of the volume with randomly distributed spheres. Thus, taking $x_c=0.2$, we obtain

$$0 < p_c \leqslant 0.12. \tag{2.3}$$

The estimations of p_c show that percolation transition in polymeric composites can occur at filler particle bulk concentration $p<0.12$. Thus the critical concentration, p_c, is not a universal characteristic of a composite, in contrast to the percolation threshold x_c.

The determination of the effective properties of filled polymeric composites is further divided into two stages. At the first stage of the calculations, the elastic properties of Voronoi polyhedra are determined, and at the second stage, the two-component system, which consists of VPa occupied by filler particles and those occupied by a matrix polymer, is examined. While for the former, effective properties have to be determined, for the latter the effective properties are those of the matrix.

III. STRESS TRANSFER

A. The Voronoi polyhedron's shear modulus

The estimation of the Voronoi polyhedron shear modulus μ_V is a rather difficult task. The analytical dependence of the VP effective shear modulus on its parameters can be approximately estimated using the method of integral sections [43–46].

The Voronoi polyhedron complex shear modulus $\mu_V^*(i\omega)$ was obtained as (see Appendix B)

$$\begin{aligned}\mu_V^*(i\omega) = {} & 2\frac{\mu_m^*(i\omega)\mu_f^*(i\omega)}{[\mu_f^*(i\omega)-\mu_m^*(i\omega)]^2\pi_1} \times \Bigg[[\mu_f^*(i\omega)-\mu_m^*(i\omega)]\pi_1 \\ & + \mu_f^*(i\omega)\log_{10}\left(\frac{\mu_f^*(i\omega)}{\mu_f^*(i\omega)-[\mu_f^*(i\omega)-\mu_m^*(i\omega)]\pi_1}\right)\Bigg] \\ & + (1-\pi_1)\mu_m^*,\end{aligned} \tag{3.1}$$

where

$$\pi_1 = c\left(\frac{3(1-q_V)}{4\pi}\right)^{1/3} \text{ and } c = 1.912 \text{ in the case of } p_0 = 0.6.$$

The dependence of the polymer bulk concentration in a Voronoi polyhedron $q_V=1-p_V$ (p_V is the volumetric concentration of a filler particle in a VP) on the particle bulk concentration p was defined as (see Appendix B)

$$q_V = 0.73 - 0.54p \quad (p_c < p \leqslant p_0,\ ) \tag{3.2}$$

for the case $p_0=0.6$.

B. Stress transfer between Voronoi polyhedra

Connecting the Voronoi polyhedra centers at $x=1$ $(p=p_0,)$ we obtain the network presented in Fig. 1. Each link between knots (contact point between two spheres or a sphere with the matrix) may be replaced by elastic springs (or resistors in the case of electrical analogy) of two sorts (see Fig. 2). One has the elastic properties of VP as defined by Eq. (3.1), and the other has the elastic properties of the matrix, $\mu_m^*(i\omega)$. Generally, these links form a network of the two sorts of springs and are distributed randomly. We will assume that the link distribution of the network is uncorrelated, in other words, a link in a certain position will not affect any neighboring links (a case when the links are correlated might be explored later). Thus the mechanical response of a polymeric material to an impact may be modeled by a network with randomly distributed springs of the two types.

IV. MODULI OF THE COMPOSITE

The effective shear modulus of the filled polymeric material is calculated on the basis of an iterative method of averaging over different particle configurations. To illustrate this method we consider a random distribution of filler particles in volume V [Fig. 3(a)]. Let $x^{(0)}$ be the bulk concentration of Voronoi polyhedra in volume V and let us divide volume V into minimal volumes $V_i^{(0)}$ $[V_i^{(0)}\ (l^{(0)})^3]$, $(i=1,2\ldots,n)$ [Fig. 3(b)]. At $x^{(0)}<1$, it is possible to identify two main configurations of the particles in $V_i^{(0)}$. In the first one, a connecting

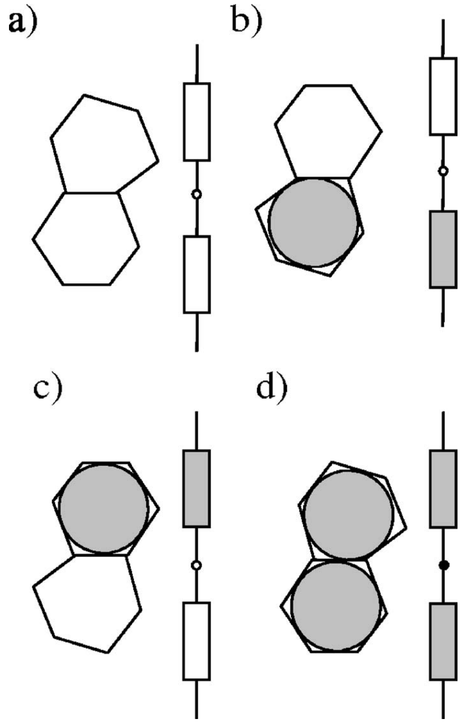

FIG. 2. Definition of two sorts of connections between Voronoi polyhedra.

set (CS) of particles is formed, in the second a nonconnecting set (NCS). We will call the particles in volumes, $V_i^{(0)}$, in which they form a CS, the sort one particles of the first level, and the particles in volumes, $V_i^{(0)}$, where they form a NCS, the sort two particles of the first level.

The probability of forming a CS from the sort one particles of the first level, $R(x^{(1)})$ is equal to the ratio of the number of the sort one particles of the first level to the number of all the particles of the first level.

In the next step we divide volume V into minimal volumes $V_i^{(1)}$ $[V_i^{(1)}\ (l^{(1)})^3]$. We characterize volumes $V_i^{(1)}$ only by two signs: whether CSs are formed in $V_i^{(1)}$ from the sort one particles of the first level, or whether NCSs are formed. The probability of forming CSs from the sort one particles of the second level $R(x^{(1)})$ is equal to the ratio of the number of the sort one particles of the second level to all the particles of the second level.

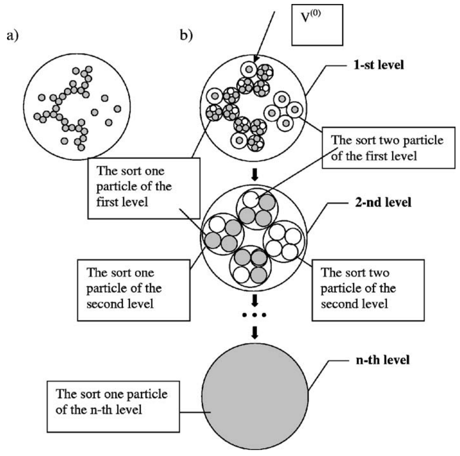

FIG. 3. Illustration of the iterative method of averaging: (a) typical particle configuration corresponding to $x^{(0)}$ (the VPa are not shown); and (b) successive coarsening of particle configuration by averaging.

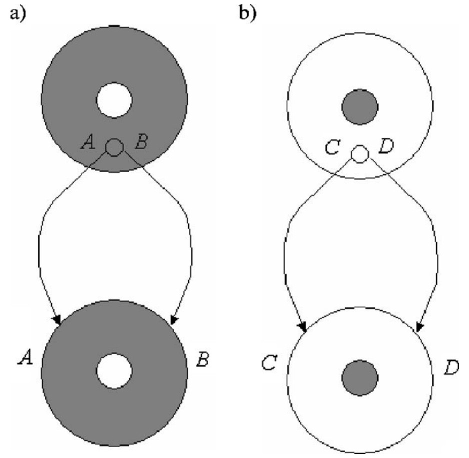

FIG. 4. Principle of modeling (a) the connected (CS) and (b) nonconnected sets (NCS) of Voronoi polyhedra.

The iteration process continues until we get an n-level particle of sort one or two. The effective shear modulus of the filled polymeric material is essentially influenced by two configurations: a connected set (CS) of springs possessing Voronoi polyhedron elastic properties allowing one to go from one side of a specimen to the other side only over these springs. In the case of a nonconnected set (NCS) of these springs there are no such links.

The CS is modeled as a continuous structure having Voronoi polyhedron properties with a polymer sphere inclusion and the NCS as a continuous structure of polymer with inclusion of a sphere having Voronoi polyhedron properties (see Fig. 4). The elastic properties of the corresponding sets we describe by the Hashin-Strikman formula [8,9], which has been applied successfully in similar cases [35]. This formula, which was obtained on the basis of the principle of an additional energy minimum by means of a variational method, allows one to determine the effective shear modulus of connected and not-connected sets. The formula for the CS has the following form in case of incompressibility of the material:

$$\mu_{CS}^*(i\omega) = \mu_V^*(i\omega) + \frac{(1-x)[\mu_m^*(i\omega) - \mu_V^*(i\omega)]}{1 + x b_V[\mu_m^*(i\omega) - \mu_V^*(i\omega)]}, \quad (4.1)$$

where $b_V = 2/5\mu_V^*$.

The formula for the NCS shear modulus can be obtained from Eq. (4.1) by changing the indices (v to p and vice versa) and the concentration correspondingly ($x \rightarrow 1-x$):

$$\mu_{NCS}^*(i\omega) = \mu_m^*(i\omega) + \frac{x[\mu_V^*(i\omega) - \mu_m^*(i\omega)]}{1 + (1-x) b_m[\mu_V^*(i\omega) - \mu_m^*(i\omega)]}, \quad (4.2)$$

where $b_m = 2/5\mu_m(i\omega)$.

Using the lowest possible number of two different springs connected linearly (see Fig. 2) the arrangements presented in Fig. 1(b) correspond to the CS and the arrangement in Figs. 1(c) and 1(d) to the NCS. Similarly to Hashin and Strikmann [8,9] we use a continuous analogon to these two sets as presented in Figs. 3(a) and 3(b) by the two upper circles with the corresponding inclusions. Equations (4.1) and (4.2) are used for the iterative calculation of viscoelastic properties for the filled polymers as presented in the following. The used iterative method was proposed in [35] to calculate the elastic properties of an inhomogeneous isotropic medium with random structure. Applying this method and the correspondence principle, the calculation of the properties for a polymeric composite can be made.

The calculation of moduli for the CS and NCS at the $k+1$ stage of iteration is performed in the following way:

$$\mu_{CS}^{*(k+1)}(i\omega) = \mu_{CS}^{*(k)}(i\omega) + \frac{(1-x^{(k)})[\mu_{NCS}^{*(k)}(i\omega) - \mu_{CS}^{*(k)}(i\omega)]}{1 + x^{(k)} b_{CS}^{(k)} [\mu_{NCS}^{*(k)}(i\omega) - \mu_{CS}^{*(k)}(i\omega)]}, \tag{4.3}$$

$$\mu_{NCS}^{*(k+1)}(i\omega) = \mu_{NCS}^{*(k)}(i\omega) + \frac{x^{(k)}[\mu_{CS}^{*(k)}(i\omega) - \mu_{NCS}^{*(k)}(i\omega)]}{1 + (1-x^{(k)}) b_{NCS}^{(k)} [\mu_{CS}^{*(k)}(i\omega) - \mu_{NCS}^{*(k)}(i\omega)]}, \tag{4.4}$$

where $b_{CS}^{(k)}=2/5\mu_{CS}^{*(k)}(\omega)$, $b_{NCS}^{(k)}=2/5\mu_{NCS}^{*(k)}(\omega)$, $\mu_{CS}^{*(0)}(\omega)=\mu_{v}^{*}(\omega)$ is the Voronoi polyhedron complex shear modulus and $\mu_{NCS}^{*(0)}(\omega)=\mu_{m}^{*}(\omega)$ is the complex shear modulus of the matrix.

Moreover, the concentration of Voronoi polyhedra is changing according to $x^{(k)}=R(l^{(k-1)},x^{(k-1)})$ and $x^{(0)}=x$ is the Voronoi polyhedron bulk concentration.

The probability function $R(l^{(0)},x_f^{(0)})$ is equal to the probability that a set of links forms a connected set (CS) at given $l^{(0)},x_f^{(0)}$. It was determined as the ratio of the number of CS configurations to the number of all configurations on the final lattice [47]:

$$\begin{aligned} R(l^{(0)}=2,x^{(0)}) = {} & (x^{(0)})^2[4 + 8x^{(0)} - 14(x^{(0)})^2 - 40(x^{(0)})^3 \\ & + 16(x^{(0)})^4 + 288(x^{(0)})^5 - 655(x^{(0)})^6 + 672(x^{(0)})^7 \\ & - 376(x^{(0)})^8 + 112(x^{(0)})^9 - 14(x^{(0)})^{10}]. \end{aligned} \tag{4.5}$$

The percolation threshold (the critical point) x_c according to Eq. (4.5) is equal to 0.2085… [this number is determined as the solution of the following equation: $R(l^{(0)}=2,x^{(0)})=x^{(0)}$]. This way a NCS changes to a CS at $x_c \approx 0.20846$.

The iteration procedure finally leads to the effective complex shear modulus of the composite, $\mu^*(\omega)$:

$$\lim_{k\to\infty} \mu_{CS}^{*(k)}(\omega) = \lim_{k\to\infty} \mu_{NCS}^{*(k)}(\omega) = \mu^*(\omega). \tag{4.6}$$

The function R is approaching its final values according to Eq. (4.7):

$$\lim_{k\to\infty} R(l^{(k)},x^{(k)}) = \begin{cases} 1, & x^{(0)} > x_c \\ 0, & x^{(0)} < x_c \end{cases}. \tag{4.7}$$

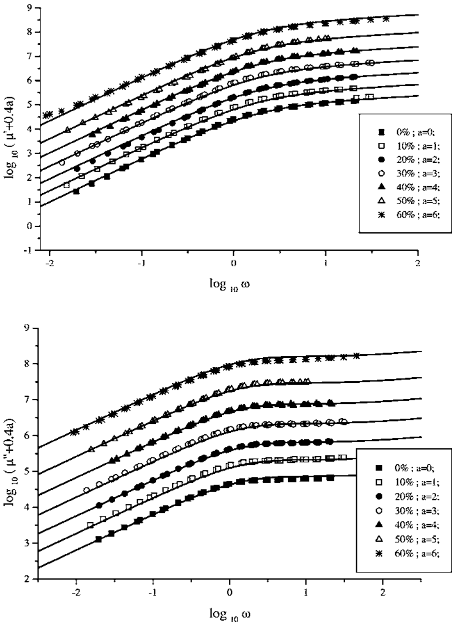

FIG. 5. Comparison of calculations (lines) and experiments (points) for the dependence of (a) storage modulus and (b) loss modulus on frequency for different filler concentrations.

The modulus $\mu^*(i\omega)$ is the modulus of the composite we are interested in and which we compare with experiments and explore its properties in the next paragraph.

V. DISCUSSION

A. Calculations and experiments

To compare calculations with experimental data we make use of a data set on a polystyrene melt filled with glass beads. For details see [48]. The storage and loss moduli of the matrix polymer (polystyrene) are shown in [48]. The viscoelastic properties of the matrix can be approximated very well by the following empirical equations:

$$\mu_p'(\omega) = \left(\frac{39\,957.2\omega^{1.8}}{1 + 0.40\omega^{0.8} + 0.4183\omega^{1.6}}\right)[\text{Pa}], \tag{5.1}$$

$$\mu_p''(\omega) = \frac{65\,053\omega + 0.1804\omega^{1.8}}{1 + 0.40\omega^{0.8} + 0.4183\omega^{1.6}}[\text{Pa}]. \tag{5.2}$$

Furthermore, it is assumed that the filler particle shear modulus can be described by the following relations: $\mu_f'=8\times 10^9$[Pa] and $\mu_f''=0$ [49,50]. The maximal filler concentration is $p_0 \cong 0.6$.

The comparison of our calculations with the experimental data reveals an almost perfect fitting [see Figs. 5(a) and 5(b)]. According to the experimental data [48], the shear modulus $\mu'(\omega)$ of a composite shows a smooth increase when the filler concentration p is changing from small concentrations to the limiting filling p_0. As the comparison of the calculation and the experiment showed [Figs. 5(a) and 5(b)], the iterative method predicts the shear modulus of such a composite in the whole concentration p and frequency ω

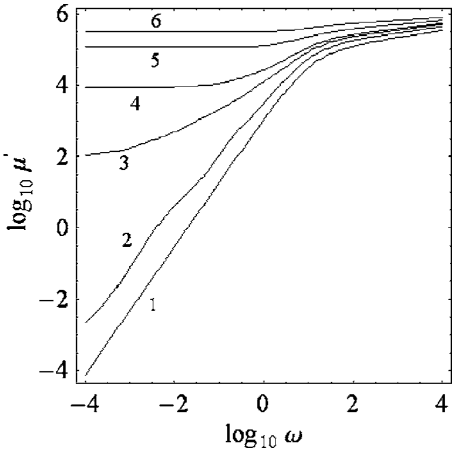

FIG. 6. Calculations of the storage modulus $\mu'(\omega)$ in dependence on frequency for different filler concentrations p: 1—0.01; 2—0.09; 3—0.13; 4—0.15; 5—0.2; and 6—0.25.

range very well. A more detailed comparison of experimental data and calculations of $\mu'(\omega)$ for $p=0.6$ discloses systematic deviations in the range of smallest frequencies. We assume that this deviation is due to the particle's polydispersity which is not encountered in our model. The presence of a fraction of particles with sizes smaller than the average size, which we apply as the only size of particles for the calculations, leads to a slowed down relaxation. Whether this effect is due to the appearance of stronger or more clusters is not known. Nevertheless, our next efforts are dedicated to the modeling of polydispersity effects in filled compounds.

Let us consider another case, namely when there is a percolation leap in the concentration dependence of the shear modulus μ of a composite. We will show that the iterative method describes such systems well enough and that the results of calculations based on the iterative method correspond to the results of the percolation theory. It is to be mentioned that the percolation properties are universal [16–18], that is, they are correct for any inhomogeneous isotropic medium with random structure.

Percolation properties in a filled polymeric composite will show up if the rigidity of particle agglomerates (Voronoi polyhedron shear modulus) is much higher (several powers higher) than the rigidity of the undisturbed polymer [26]. This situation can occur, for example, when a strong adsorption layer of a polymer with properties quite different from a matrix polymer has formed. Such a situation is known for silica reinforced rubbers [26,51,52].

Now, when calculating the effective shear modulus of such a composite, we consider a constant, frequency independent Voronoi polyhedron shear modulus of $\mu'_V=2\times 10^6$[Pa]. The modulus' value was chosen such that the expected percolation phenomena appear in an experimentally accessible frequency and concentration range. Shear moduli of the polymer matrix are defined by formulas (5.1) and (5.2) as before.

Results for the effective shear modulus μ' of a composite are shown in Fig. 6. According to the calculations, the percolation transition appears at $\omega<10^{-4}$ and at a filler concentration of $p\cong 0.12$. According to equations given in Appendix B ($p_c=x_c p_0$) this concentration results from limiting filling properties of the filler (here $p_0=0.6$) and the universal properties of random structure (here $x_c\cong 0.2$) expressed by function $R(l,x)$ [Eq. (4.5)]. At $p>0.12$, a continuous rigid framework of filler particles is formed in the composite.

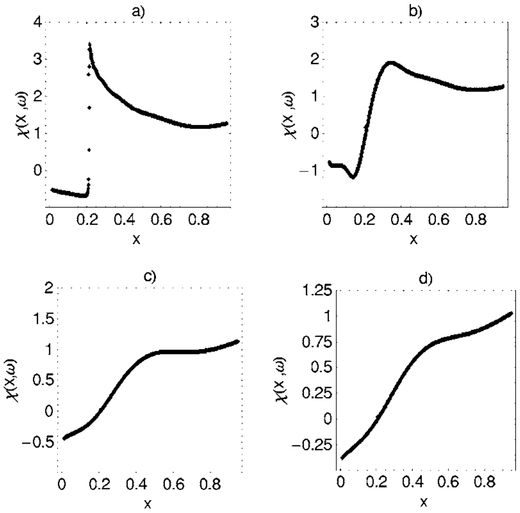

FIG. 7. Dependence of $\chi(x,\omega)$ on concentration x for four frequencies: (a) $\omega\rightarrow 0$; (b) $\omega=10^{-1}$; (c) $\omega=10^{0}$; and (d) $\omega=10^{2}$.

To illustrate more quantitatively the percolation properties inherent to our model we consider the following function $\chi(x,\omega)$:

$$\chi(x,\omega)=\frac{\log_{10}\left(\dfrac{\mu'(x+\Delta x,\omega)}{\mu'(x,\omega)}\right)}{\log_{10}\left(\dfrac{x+\Delta x-x_c}{x-x_c}\right)}, \tag{5.3}$$

where $x=p/p_0$, $x_c=p_c/p_0$. Details for the definition of different concentrations can be found in Appendix A.

The results of corresponding calculations for three different frequencies are shown in Fig. 7. Moreover, knowing the function $\chi(x,\omega)$ the determination of the scaling parameters τ and s included in Eqs. (1.1) and (1.2) is possible:

$$\tau=\lim_{x\rightarrow x_c+0}\chi(x,\omega),$$

$$s=\lim_{x\rightarrow x_c-0}\chi(x,\omega). \tag{5.4}$$

From the calculations, it can be clearly seen [Fig. 7(a)] that for vanishing frequency ($\omega\rightarrow 0$) and at $x\rightarrow x_c\pm 0$ the indices τ and s can be extracted: $0.7\leqslant s\leqslant 0.5$ and $3\leqslant\tau\leqslant 3.5$. These numerical results are in good agreement with the results of the percolation theory [15–18].

Based on the calculations the conclusion can be drawn that dependencies like Eqs. (1.1) and (1.2) are observed at $x\rightarrow x_c\pm 0$:

$$\mu'\cong(x-x_c)^{\tau},\quad x>x_c,\quad \omega\rightarrow 0 \tag{5.5}$$

$$\text{with } 3\leqslant\tau\leqslant 3.5$$

and

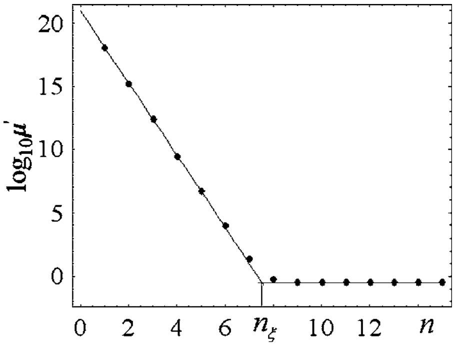

FIG. 8. Dependence of the storage modulus μ' on the number of iterations, $n=\log_{10} l^{(n)}/\log_{10} l^{(0)}$.

$$\mu' \cong |x-x_c|^{-s}, \quad x<x_c, \quad \omega\to 0 \tag{5.6}$$

with $0.5 \leqslant s \leqslant 0.7$.

The obtained results closely correspond to percolation theory [16–18] and are in agreement with experimental results [26,51,52].

B. Fractal properties of the composite for $x\to x_c$, $\omega\to 0$

The calculations of the dependence of $\log_{10}\mu'$ on the iteration number $n=\log_{10} l^{(n)}/\log_{10} l^{(0)}$ are shown in Fig. 8 ($x=x_c-0, \omega\to 0$). On scales $l^{(n)}\leqslant\xi$ (ξ is the correlation length, i.e., the lattice dimension where the shear modulus μ' depends on the scale $l^{(n)}$) a heterogeneous medium behaves like a fractal set:

$$\mu' \cong (l^{(n)})^{\beta}. \tag{5.7}$$

According to our calculations (see Figs. 7 and 8), we obtain $\beta=2.9$, if $n<n_\xi$, where $\beta=\log_{10}\mu'/\log_{10} l^{(n)}$, $n_\xi=\log_{10}\xi/\log_{10} l_0$, ξ is the correlation distance. The points lying on a straight line parallel to the abscissa reveal that on these scales the composite is no longer fractal but a homogeneous medium independent from $l^{(n)}$. Hence filled polymeric materials can show fractal properties on scales $l^{(n)}\leqslant\xi$, if $\omega\to 0$.

VI. SUMMARY AND CONCLUSIONS

The model of a filled polymeric material including a structural model has been elaborated, which allows one to examine viscoelastic properties in a wide range of parameters. The concept of the Voronoi polyhedron (VP) was applied to filled polymeric materials, which allows one to define effective properties on the scale commensurable to the dimensions of filler particles. Effective viscoelastic properties of the composite are appearing as a consequence of the developed iteration procedure on connected and nonconnected sets of two sorts of VPa.

The influence of frequency and properties of phases (filler and matrix) on the effective viscoelastic properties of composite has been studied. The comparison of the calculations and experiments showed good agreement. Moreover, the calculation results coincide with the results of percolation theory for different ratios of filler and matrix properties, z_k, if $z_k\to\mathbf{0}$ and correspond to experimental data at finite values of z_k.

Due to the good qualitative and quantitative agreement of the model with experimental facts we conclude that the averaging procedure on the lowest level of modeling (VP) together with the averaging of properties on the macro level is an effective way to account for relevant effects appearing in filled polymeric materials. Our future efforts are directed to the consideration of polydispersity and interfacial effects in these compounds using the presented procedure.

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APPENDIX A

The change from the isolated clusters of Voronoi polyhedra to the infinite one occurs at the Voronoi polyhedron bulk concentration x_c, i.e., x equals the percolation threshold $x_c\cong 0,2$ [15–17]. Taking into account that $x=g\ p$, from $x|_{p=p_0}=1$ we obtain $g=1/p_0$, that is, $x=p_f/p_0$, where p_0 is the limiting filling bulk concentration.

Knowing that the percolation threshold x_c is a universal constant we can define the particle bulk concentration p_c at which the percolation change from the isolated clusters of Voronoi polyhedra to the infinite cluster of Voronoi polyhedra occurs $p_c=x_c p_0$

The limiting filling concentration p_0 depends on the interaction between the polymer and the filler particles and may generally vary within the following limits: $0.1\leqslant p_0\leqslant 0.6$. Thus if $x_c=0.2$ then $0.02\leqslant p_c\leqslant 0.12$, that is, at the particle bulk concentration $p=p_c$ the change from isolated clusters to the infinite cluster of Voronoi polyhedra occurs. The maximum value $p_0\cong 0.6$ corresponds to the maximal filling with randomly distributed spheres (the polymer thickness between the particles at their contact points is zero $\Delta l\sim 0$ [41].

The polymer bulk concentration $q_V=1-p_V$ in a Voronoi polyhedron is $p_V=V_f/V_V$, where V_f is the volume of a filler particle, and V_V is the volume of a Voronoi polyhedron. The filler bulk concentration equals $p=V_f/(V_f+V_m)$ where V_m is the polymer volume in a composite. By the increase of the particle bulk concentration p the density of the cluster of densely packed particles is increased, and consequently, the average coordination number increases as well. Thus the average coordination number equals approximately 2 at the filler particle concentration p close to the critical concentration p_c, and approximately 7 at p close to $p_0=0.6$. When the particle bulk concentration p increases, the polymer bulk concentration in a Voronoi polyhedron $q_V=1-p_V$ will decrease, and so will the thickness of a polymer layer at particle contact points.

APPENDIX B

Let us consider PV as "a sphere in a cubic cell" [Fig. 9(a)] and estimate its shear modulus in a given direction. At the

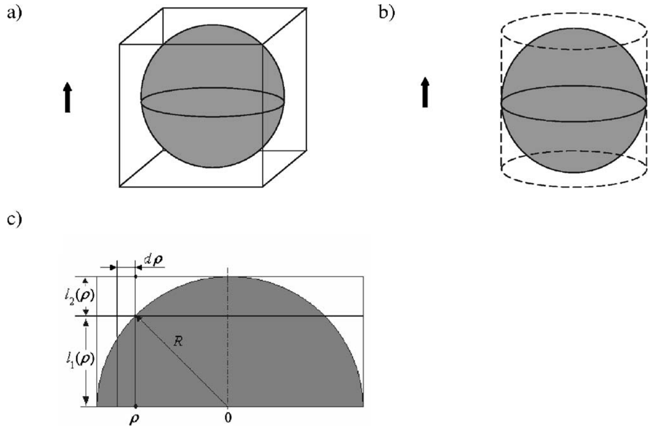

FIG. 9. Simplified presentation of a Voronoi polyhedron as (a) sphere in a cube and (b) sphere in a cylinder. (c) presents a section through a sphere in a cylinder.

beginning, we define the shear modulus μ_k of a cylindrical body [Fig. 9(b)]. The essence of the method of integral cuts is that an inhomogeneous body [Fig. 9(b)] is cut into prisms with infinitely small bases $ds=\rho d\rho d\varphi$ and altitudes of $L=l_1(\rho)+l_2(\rho)$.

In this case, the shear modulus of a cylindrical body equals [46]

$$\mu_k = 2\int_0^1 \gamma(\rho)\rho d\rho, \tag{B1}$$

where

$$\gamma(\rho) = \left(\frac{\pi_1\sqrt{1-\rho^2}}{\mu_f} + \frac{1-\pi_1\sqrt{1-\rho^2}}{\mu_p} \right)^{-1}, \quad \pi_1 = c\left(\frac{3(p_V)}{4\pi}\right)^{1/3} \tag{B2}$$

$c=L/R$, $L=(V_V)^{1/3}$, V_V is the Voronoi polyhedron volume; R is the filler particle radius; $p_V=V_f/V_V$, $1-V_V$ is the volume of the polymer in the Voronoi polyhedron and $l_1(\rho)/R = \pi_1\sqrt{1-\rho^2}$; $l_2(\rho)/R=1-\pi_1\sqrt{1-\rho^2}$.

After integrating Eq. (B1) we obtain

$$\mu_k = \frac{\mu_m\mu_f}{(\mu_f-\mu_m)^2\pi_1^2} \times \left[(\mu_f-\mu_m)\pi_1 + \mu_f \log\left(\frac{\mu_f}{\mu_f-(\mu_f-\mu_m)\pi_1} \right) \right]. \tag{B3}$$

Taking into consideration Eq. (B3), the Voronoi polyhedron shear modulus in a given direction (see Fig. 9) can be defined as

$$\mu_V = \frac{\mu_m\mu_f}{(\mu_f-\mu_m)^2\pi_1} \times \left[(\mu_f-\mu_m)\pi_1 + \mu_f \log\left(\frac{\mu_f}{\mu_f-(\mu_f-\mu_m)\pi_1} \right) \right] + (1-\pi_1)\mu_m. \tag{B4}$$

On the basis of the correspondence principle, the Voronoi polyhedron complex shear modulus $\mu_V^*(i\omega)$ was obtained as

$$\mu_V^*(i\omega) = 2\frac{\mu_m^*(i\omega)\mu_f^*(i\omega)}{[\mu_f^*(i\omega)-\mu_m^*(i\omega)]^2\pi_1} \times \left[[\mu_f^*(i\omega)-\mu_m^*(i\omega)]\pi_1 + \mu_f^*(i\omega)\log_{10}\left(\frac{\mu_f^*(i\omega)}{\mu_f^*(i\omega)-[\mu_f^*(i\omega)-\mu_m^*(i\omega)]\pi_1} \right) \right] + (1-\pi_1)\mu_m^*. \tag{B5}$$

In Eqs. (B4) and (B5) $c=L/R$ is a linear dimension of VP measured in radii of filler particles R. If the coordination number of a filler particle in VP is $N=6$, then $c=2$; if $N>6$, $c<2$, if $N<6$, $c>2$. At the limiting filling $p_0=0.6$ the constant c amounts to $c=1.912$.

The number of faces in the Voronoi polyhedron depends on the average coordination number N of filler particles in the cluster. According to the experimental data on the chaotic packing of spheres of equal dimensions [42] we can define $N=17.4(p_V)^{3/2}$. In the cluster of filler particles which connects opposite sides of the sample for the first time the average coordination number is approximately equal to 3 [14–18]. In this case ($N=3$), according to the equation $N=17.4(p_V)^{3/2}$, we obtain $q_V|_{N=3}=0.7$ ($q_V=1-p_V$). The polymer bulk concentration in the Voronoi polyhedron at the limiting filling is $p_V=p_0$. Assuming that $p_0=0.6$ and that the density of the cluster is changing linearly with p, we obtain

$$q_V = 0.73 - 0.54p \quad (p_c < p \leqslant p_0,). \tag{B6}$$

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