Thermal Conductivity of Filled Polymer Nanocomposites

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ABSTRACT

The effective thermal conduction of filled polymer nanocomposites with chaotic structure has been defined. A Voronoi polyhedron is built to define the thermal conduction of filler aggregated particles. An analysis of influence of the interface layer and filler particle dimension on the effective thermal conduction of a composite is carried out. Fractal sets are used to model the structure of a composite with random distribution of the components (phases). Those fractal sets are obtained on the basis of rectangular lattices. A comparison of the calculation of the thermal conduction of a composite with the experimental data is carried out.

Key words: polymer composites; thermal conductivity; the percolation threshold; critical concentration.

NOMENCLATURE

The following nomenclature is used in the paper:

\[ C \] - effective property of a composite;
\[ C_1, C_2 \] - properties of the first and second component, correspondingly;
\[ P_0(C) \] - distribution function of property \( C \) in the volume of a composite;
\[ \lambda \] - effective thermal conduction of a composite;
\[ \lambda_f \] - filler particle thermal conduction;
\[ \lambda_p \] - polymer thermal conduction;
\[ \lambda_m \] - interface layer thermal conduction;
\[ \lambda_v \] - Voronoi polyhedron thermal conduction;
\[ \lambda_k \] - thermal conduction of a cylindrical body with a spherical insertion;
\[ V \] - volume of the composite;
\[ V_p \] - volume of the polymer in the composite;
\[ V_m \] - volume of the interface layer;
\[ p_f \] - bulk concentration of filler particles;
\[ p_0 \] - limit concentration of filler particles.
\[ \rho_k \] - critical concentration of filler particles;
\[ x \] - bulk concentration of Voronoi polyhedron;
\[ x_c \] - percolation threshold (unstable critical point);
\[ x_k \] - probability of the local area to have the properties of Voronoi polyhedron at the \( k \)-th iteration step;
\[ \lambda^{(k)}_{\text{con}} \] - conductivity of the connecting set at the \( k \)-th iteration step;
\[ \lambda^{(k)}_{\text{non}} \] - conductivity of the non-connecting set at the \( k \)-th iteration step;
\[ d \] - dimension of the system (\( d = 2 \) - two-dimensional system, \( d = 3 \) - three-dimensional one);
\[ k \] - iteration step (iteration number);
\[ l \] - lattice’s dimensions;
\[ l_k \] - lattice’s dimensions at the \( k \)-th iteration step;
\[ R \] - radius of a filler particle (spherical particle);
\[ N \] - average coordination number;
\[ \Delta l \] - thickness of the interface layer at the contact zone;
\[ \Delta l = \Delta l / R \] - ratio of the interface layer thickness to the radius of the particle;
\[ \delta(x) \] - Dirac function;
\[ ds = \rho d \rho d \varphi \] - infinite small area of the base of the prism;
\[ L \] - height of the prism (linear dimension of Voronoi polyhedron);
\[ \Omega_n(l_0, x_0) \] - chaotic fractal set;
\[ Y(l_0, x_0) \] - probability of a connecting set to be formed from Voronoi polyhedron (chaotic fractal);
\[ f(x) = \frac{dY(l, x)}{dx} \] - probability density of the distribution of flowing configurations;
\[ d_f \] - fractal dimension.

1 INTRODUCTION

According to the present conceptions, any effective property, \( C \), of filled polymer composites is defined by partial properties of individual components, \( C_1 \) and \( C_2 \), and the volume concentration of the disperse phase \( p_f \).

The simplest theoretical model of a filled polymer is a structureless medium (polymer - \( \rho \)) containing isolated particles of a disperse phase (filler - \( f \)) with a bulk concentration of \( p_f \). There is an ideal adhesion contact between the phases \( f \)(filler) and \( \rho \)(polymer).

On the basis of such assumptions, equations have been obtained to define the effective thermal conduction of a filled polymer composite. The most common ones are derived from the Maxwell model /1/, the Lewis - Nielsen model /2/, and the model of an effective medium /3/.

Maxwell Model

Using the theory of potential, the equation was obtained for the effective conductivity \( \lambda \) of a composite consisting of a spherical insertion in a continuous matrix /1/:

\[
\lambda = \lambda_p \left[ \frac{\lambda_f + 2\lambda_p + 2p_f(\lambda_f - \lambda_p)}{\lambda_f + 2\lambda_p - p_f(\lambda_f - \lambda_p)} \right].
\] (1.1)
Lewis - Nielsen Model

The equation for the effective conductivity $\lambda$ was obtained on the basis of the changed Halpin-Tsai theoretical model [2, 4-8]. It takes into consideration the influence of the particle shape and orientation or the packing type for a two-phase system:

$$\lambda = \lambda_p \left( \frac{1 + A \cdot B \cdot p_f}{1 - B \cdot p_f \cdot \psi} \right),$$

(1.2)

where, according to /6/, $A = \lambda_{en} - 1$; $B = \frac{\lambda_f / \lambda_p - 1}{(\lambda_f / \lambda_p) + A}$; $\psi = 1 + \left( \frac{1 - \phi}{\phi^2} \right) p_f$; $A$ - is a geometrical parameter dependent on the aspect ratio of the filler (geometrical shape factor); $\phi$ - the maximum packing fraction of the dispersed particles; $\lambda_{en}$ - the generalized Einstein coefficient /2, 4-8/.

The values of geometrical parameter, $A$, and maximum packing fraction, $\phi$, for many geometric shapes and orientation are given in /2, 4-8/.

Model of an Effective Medium

It is an isolated spherical insertion (component 1) in a continuous medium with the effective (to be found) properties. On its basis, the equation for the effective conductivity was obtained /3/:

$$\lambda = \lambda_f \left( z + \sqrt{z^2 + \frac{a}{2}} \right),$$

(1.3)

where $z = \frac{3}{4} p_f (1 - a) + \frac{1}{2} a - \frac{1}{4}$; $a = \lambda_p / \lambda_f$.

The idea that neither phase has its own structure is certainly a simplification because unfilled flexible chain polymers have natural structural microheterogeneity caused by coexistence of crystal and amorphous areas (in crystallizing polymers) or by frozen fluctuations of density (in non-crystallizing glass-like polymers). The morphologic peculiarities of unfilled polymers must be taken into consideration when analyzing their properties. However, as applied to filled systems, the postulate of the nonstructural nature of the filler and polymer practically comes to the demand of the absence of macro faults in both phases (e.g. cracks at the borders of spherolites in polymers or lacks between filler particles in loosely packed agglomerates). The second postulate about the ideal adhesion contact follows, from the point of view of mechanics, from the condition of preservation of continuity of a filled system (including the interface border between polymer and filler) when there is some influence of outer fields on it.

In practice the optimal adhesion connection between two phases is possible if the energy of the interaction at the interface border is higher (or at least not lower) than the energy of the cohesion of one of the phases. This condition is satisfied by the combination of the low energy continuous phase $p$ (polymer) and high energy disperse phase $f$ (minerals, metals, etc.). Macromolecules of the polymer in layers near filler particles must be dramatically different from macromolecules in the rest of the boundary layer volume, i.e. the border layer of the phase $m$ (interface layer - $m$) formed at the conditions of action of the surplus surface forces of the high energy phase $f$ will be structurally different from the mother phase $p$ only influenced by the forces of adhesion.
Within the limits of traditional approaches, it is impossible to explain the situation when, for the same pair of components, the effective value of $C$ at $p_f = \text{const}$ changes depending on the average dimension of an insertion $2R$, where $R$ - is filler particle radius. This empirical result formally shows that the effective properties of a filled polymer composite depend not only on the properties and relative content of individual components but also on the contribution of the interface areas which evenly grow with the decrease of $2R$. Such an effect can be taken into consideration supposing that in a binary system, along with the initial phases, the third quasi-phase appears as layers with a thickness of $\Delta l$ near the border between the polymer and filler particle (Fig. 1). Such a model has traditionally been used to qualitatively interpret experimental data of the research of different properties of a filled polymer composite /9/.

When the concentration of the filler is increasing, the polymer’s part with changed structure will increase, which is distributed around the filler particle as a layer of a constant thickness of $\Delta l$.

It was proved /10/ that a polymer-filler system retains its thermodynamic stability until the effective thickness of the layer between filler particles, $\Delta l$, becomes less than the inertial radius $R_g$ of an unaffected macromolecular mass, i.e. the stability of a composite is defined by the condition:

$$\Delta l \geq R_g$$

(1.4)

This condition is true for filled composites which are prepared in the conditions ensuring the interaction of individual macromolecular masses with the filler surface, for instance, by putting filler into a diluted solution of a polymer and then removing the filler. It is not exclusive that making a filled polymer in real conditions (blending in a melt) will lead to the situation when the thickness of the by-side layer with an altered conformation state of macromolecules is different from the dimensions of the macromolecule tangle.

Thus, for filled polymer composites (FPC) the existence of three phases is typical (Fig. 1):
- continuous phase (polymer with invariable properties), $p$;
- insertions (filler in the form of different powders), $f$;
- interface border (interface layer), to be exact, an interface area of the finite thickness on the surface of filler particles, $m$.

A sufficiently large number of sources is devoted to the problem of the influence of the interface layer on the effective thermal conduction of filled composites /9, 11-15/. The number of sources devoted to the qualitative description of the influence of the interface layer on the effective thermal conduction is much bigger than those devoted to the models and equations which examine the influence of the interface layer on the effective thermal conduction.

The authors of article /15/ used L.P. Kapitza's work /16/ to examine the thermal conduction of the interface layer (IFL). Here, the interface thermal property is concentrated on the surface of zero thickness, $\Delta l \rightarrow 0$, and characterized...
by the radius \(a_k\) (Kapitza’s radius). It is defined as:

\[
a_k = R \lambda_p, \quad R = \lim_{{\Delta l \to 0}} \left( \frac{\Delta l}{\lambda_m} \right),
\]

where \(\lambda_m\) - is the coefficient of interface layer thermal conduction.

In /15/, the known equations for the effective thermal conduction were transformed (modified) using formulae (1.5). For example, the Maxwell equation for the effective thermal conduction of a composite with spherical insertions was written as:

\[
\lambda = \lambda_p \left[ \frac{\lambda_f (1 + 2\alpha) + 2\lambda_p + 2p_f (\lambda_f (1 - \alpha) - \lambda_p)}{\lambda_f (1 + 2\alpha) + 2\lambda_p - p_f (\lambda_f (1 - \alpha) - \lambda_p)} \right],
\]

where \(\alpha = \frac{a_k}{R}\).

The value of Kapitza’s radius was defined from the coordination of the calculation and experiment /15/.

It is worth mentioning that, according to /15, 16/, formulae (1.5) and (1.6) are solved for the particular case when \(\lambda_m \to 0\); they do not take into consideration the physical and chemical processes in the area of polymer - filler contact. Such modifications of known equations do not permit taking into consideration physical processes in the boundary layer on the surface of filler particles (the interface layer (IFL) properties).

It is nanocomposites that have been widely used recently. Their distinctive feature is ultra small dimensions of filler particles (\(d < 100\,\text{nm}\)). The second important feature of nanocomposites filled with spherical particles is their structure, which is an irregular fractal (Fig. 2).

![Fig. 2: Fragment of fractal structure of filled polymer nanocomposites.](image)

Creating theoretical bases to prognosticate the effective properties of nanocomposites is a topical task nowadays.

In this work, the fractal structural model and iteration averaging method based on the idea of renormal group transformation are proposed to prognosticate the thermal conduction of filled polymer nanocomposites /18/. The averaging on mesolevels is done with the help of Voronoi polyhedron.

2 MODEL OF A DISPERSE MEDIUM AND VORONOI POLYHEDRON

The definition of the effective thermal conduction of a compound material with random structure is a rather complicated task. That is why we will introduce some simplifying assumptions. First of all, we assume that filler
particles are spherical in shape and equal in dimensions, with a radius of $R$.

To illustrate the method of constructing Voronoi polyhedron, we consider a composite at the limit filling (filler concentration $p_f$ equals $p_f = p_0$) (Fig. 3).

![Fig. 3: Conditional depiction of a composite at the limit filling.](image)

First, we draw vectors connecting the particle center with the centers of neighboring particles, then we build planes in the middle of the vectors and perpendicularly to them. We yield a polyhedron whose volume is limited by these planes (a particle plus interparticle volume). It is a Voronoi polyhedron (Fig. 4). Voronoi polyhedron fill the whole volume joining each other without any gaps. We will assume that the polymer in the Voronoi polyhedron has modified structure, i.e. properties of IFL.

![Fig. 4: Illustration to Voronoi polyhedron construction; $f$ is the filler, $m$ is the interface border (interface layer), $\Delta f$ is interface layer thickness.](image)

The number of faces in the polyhedron (Voronoi polyhedron) is equal to the average coordination number $N$. The bulk concentration of Voronoi polyhedron is designated as $x$. The connection between the filler particle bulk concentration, $p_f$, and Voronoi polyhedron bulk concentration, $x$, can be defined as $x = p_f / p_0$, where $p_0$ is the limit concentration of filler particles. When spheres are distributed randomly in the volume, the limit filling equals $p_0 \approx 0.6$ \cite{19, 20}. At the bulk concentration, $x=1$ ($p_f = p_0$), all the volume is occupied by Voronoi polyhedron (cluster of filler particles).

When the bulk concentration of filler particles (Voronoi polyhedron) is decreasing, the alteration in the composite structure can be shown as depicted in Fig. 5.
When $0 < x < 1$, a filled polymer composite can be represented as a random medium of polyhedron of two kinds: ones with particles and ones without particles (Fig. 6).

The results of the percolation theory /21 – 24/ can be applied to such a mixture of polyhedron. According to this theory, at $x < x_c$ ($x_c$ is the percolation threshold) there is an isolated cluster of Voronoi polyhedron, and at $x > x_c$ there is an infinite cluster of Voronoi polyhedron. Knowing that for a three dimensional system ($d = 3$) the percolation threshold $x_c \approx 0.2$ /24/, we can define the critical concentration of filler particles, $p_k$, at which an infinite cluster appears:

$$p_k = P_0 x_c.$$ (2.1)

**Fig. 5:** Illustration of the alteration in the structure at the decrease of Voronoi polyhedron concentration, $x$: a) $x = 1$, b) $x > x_c$, c) $x < x_c$, d) $x \ll 1$.

The limit filling, $P_0$, depends on the interaction of the polymer and filler particles and can generally change in the limits:

$$0 < P_0 \leq 0.74.$$ (2.2)

Thus, if percolation threshold $x_c = 0.2$, then

$$0 < p_k \leq 0.15.$$ (2.3)
Fig. 6: Random mixture of polyhedron of two sorts: a) - mixture of Voronoi polyhedron with filler particles (1), and without filler particles (2); b) - mixture of polyhedron.

The value of $p_k$ shows that percolation transfer in filled polymer composites can occur at the concentration of filler particles $p < 0.15$. Therefore, the critical concentration, $p_k$, is no universal feature of a composite, in contradiction to the percolation threshold, $x_c$.

Let us examine the case when filler particles are covered with a polymer layer, i.e. the thickness of the polymer between the particles in the area of their contact $\Delta l \neq 0$ (Fig. 7).

Fig. 7: To the definition of the thermal condition of Voronoi polyhedron: flat cut of a cylindrical body at the contact zone of particles in the Voronoi polyhedron ($\Delta l \neq 0$).

To simplify the calculations, we will assume that the Voronoi polyhedron is cubic in shape. In this case, the filler particle bulk concentration in the Voronoi polyhedron is equal to:

$$p_0 = \frac{\pi}{6} \left( \frac{1}{1 + \Delta l} \right)^3,$$

(2.4)
where \( p_0 = \frac{v_f}{V_p} \), \( v_f \) is filler particle volume; \( V_p = L^3 \) is Voronoi polyhedron volume \( (L = \left(V_p\right)^{1/3}) \); \( \Delta l = \Delta l / R \), where \( R \) is filler particle radius; \( \Delta l \) is the thickness of the polymer at the zone of particle contact.

It is worth mentioning that the upper limit of filler content (the limit filling \( p_0 \)), the exceeding of which leads to the loss of thermodynamic and mechanic stability of a composite, corresponds to the approaching of the effective thickness of interface layer between the filler particles, \( \Delta l \), to the dimensions of macromolecular chain of polymer in the melt.

Further, the definition of the effective properties of filled polymer composite materials is divided into two stages. At the first stage of the calculations, the properties of Voronoi polyhedron are defined. At the second one, the two-component mixture of polyhedron is examined. In this mix, the first component is a polyhedron with a particle (Voronoi polyhedron), and the second one is a polyhedron filled with polymer, i.e. the mix of Voronoi polyhedron with and without particles.

3 THERMAL CONDUCTION OF VORONOI POLYHEDRON

The thermal flow through Voronoi polyhedron can roughly be divided into two components: the thermal flow through the contact zone between particles (flow through a cylindrical body with a spherical insertion), and the thermal flow through the polymer only (Fig. 8). Thus, to find the thermal conduction of Voronoi polyhedron we will first take a cylindrical body with a particle (Fig. 8b).

The thermal conduction of a cylindrical body (averaged contact between particles) can be found using the method of integral cuts [25, 26].

\[ \lambda_k = 2\left(1 + \overline{\Delta l}\right) \int_0^{\chi(\rho)} \rho \, d\rho, \]  

where

Fig. 8: Simplified representation of Voronoi polyhedron: a) sphere in a cube; b) sphere in a cylinder.

The method of integral cuts is based on conditional division of a heterogeneous body in the given direction (in thermal flow direction) into prisms with infinitely small base area \( ds = \rho d\rho d\varphi \) and a height of \( L \) (Fig. 8b), where \( L \) is a linear dimension of the Voronoi polyhedron. In this case, the thermal conduction of a cylindrical body with a spherical insertion (Fig. 8b) can be defined as /25, 26/:

\[ \lambda_k = 2\left(1 + \overline{\Delta l}\right) \int_0^{\chi(\rho)} \rho \, d\rho. \]  

(3.1)
After integrating (3.1), the thermal conduction of the Voronoi polyhedron, $\lambda_v$, is defined as:

$$\lambda_v = \pi_2 \lambda_k + (1 - \pi_2) \lambda_p,$$

where $\lambda_p$ is the thermal conduction of the polymer; and $\lambda_k$ can be defined as:

$$\lambda_k = \frac{\lambda_m}{\pi_1} \left[ \gamma - 1 + (1 + \Delta l) \left( \log \frac{1 + \Delta l}{\gamma + \Delta l} \right) \right],$$

where $\gamma = \lambda_m / \lambda_f$; $\pi_1$, $\pi_2$ can be defined as:

$$\pi_1 = \frac{(1 - \gamma)^2}{2(1 + \Delta l)},$$

$$\pi_2 = \frac{\pi R^2}{4(R + \Delta l)^2} = \frac{\pi}{4} \frac{1}{(1 + \Delta l)^2}.$$ 

Fractal sets are used to model the chaotic structure of a heterogeneous medium (blend of polyhedra).

### 4 FRACTAL SETS BUILT ON SQUARE LATTICES

Figure 9(a) shows a heterogeneous medium with chaotic structure, Figure 9(b) illustrates the division of a heterogeneous medium into hierarchic levels.

First we have a random blend of polyhedra of two sorts: polyhedra with particles (Voronoi polyhedra) with concentration $x$, and polyhedra without particles with concentration $1 - x$ (Fig. 6). Further we proceed from this structure to a lattice with chaotic distribution of two sorts of bonds.

Connecting the particle centers at $p_k = 1$ ($p_1 = p_0$), we obtain the lattice consisting of two sorts of bonds, 1 and 2 (Fig. 10): 1 has properties of Voronoi polyhedron (composite particle); 2 has properties of polymer.

Generally, these bonds are randomly distributed on the lattice. We will assume that the bond distribution on the lattice is non-correlated, i.e. one bond does not influence the other bonds nearby (in the future, correlated bonds on a lattice might be examined as well).

Thus, the thermal conduction of a filled polymer composite can be modeled by a lattice with randomly distributed bonds of two sorts on it: sort 1 and 2 (Fig. 10).

Two configurations essentially affect the effective thermal conduction of filled polymer materials: connecting sets (CS) of the bonds having properties of Voronoi polyhedron (composite particle), and non-connecting sets (NCS). A CS is a set of bonds where it is possible to pass from one side of the sample to its opposite side only over the sort 1 bonds.

Thus, filler particles are modeled by the knots of the lattice, and the contacts between the particles by the bonds between the adjacent knots of the lattice.
Fig. 9: a) random cluster of particles; b) dividing a heterogeneous medium into hierarchic levels.

Fig. 10: Illustration of transfer from polyhedron structure to the lattice of two sorts of bonds.
As the contacts between filler particles have prevailing influence on the macroscopic properties of a heterogeneous medium, the task of bonds must be considered. The main set of bonds $\Omega_n(l_0, x_0)$ is obtained by the iteration process. At the initial step, $k = 0$, the limit lattice is taken with the probability $x_0$ of the bond between adjacent knots to be conducting and the probability $(1 - x_0)$ of the bond between adjacent knots to be badly conducting. Thus, the bonds of the lattice are randomly colored black and white (bonds of one color have the same properties).

At the next step, $k = 1, 2, \ldots, n$, each bond in the lattice is replaced by the one obtained at the previous step (Fig. 11). The iteration process finishes when the properties of the lattice do not depend on the iteration number, $k$. Thus, the set of bonds obtained by the iteration procedure $\Omega_n(l_0, x_0)$ depends on the dimensions of the initial lattice, $l$, and the probability, $x$. Such stage-by-stage modification of scales is known as the renormalization group method.

![Fig. 11: Illustration for obtaining fractal set $\Omega_n(l_0, x_0)$ when $l_0 = 2$ at the second iteration step ($k = 2$).](image)

The probability $Y(l_0, x_0)$ that the given configuration belongs to a connecting set (CS) is an important characteristic of a chaotic fractal set $\Omega_n(l_0, x_0)$.

This probability depends on the concentration of black bonds, $x_0$, and on the initial lattice dimensions, $l_0$, and can be found as a ratio of the number of connecting configurations to the whole number of possible configurations.

The concentration of Voronoi polyhedron is changing according to $x_k = Y(l_{k-1}, x_{k-1})$, where $x_0 = x$ is the Voronoi polyhedron bulk concentration. The probability function $Y(l_0, x_0)$ is equal to the probability that a set of links forms a connected set (CS) at given $l_0$ and $x_0$. The probability function $Y(x)$ was determined as the ratio of the number of CS configurations to the number of all configurations on the final lattice and used in our calculations /27/.
\[ Y(x) = 5x^2 (1-x)^{12} + 68x^3 (1-x)^{11} + 398x^4 (1-x)^{10} + \\
   + 1298x^5 (1-x)^9 + 2575x^6 (1-x)^8 + 3288x^7 (1-x)^7 + \\
   + 2977x^8 (1-x)^6 + 2000x^9 (1-x)^5 + 1001x^{10} (1-x)^4 + \\
   + 364x^{11} (1-x)^3 + 91x^{12} (1-x)^2 + 14x^{13} (1-x) + x^{14}. \]  

(4.1)

According to (4.1), the percolation threshold \( x_c \) for \( Y(x) \) is equal to 0.178... (root of equation \( x = Y(x) \)), i.e. an NCS becomes a CS when \( x \) is \( x_c \):

\[ x_c = 0.178. \]  

(4.2)

The value of the derivative \( Y(x) \) at point \( x = x_c \) is equal to:

\[ \frac{dY(x)}{dx} \bigg|_{x = x_c} = \mu. \]  

(4.3)

For function (4.1), the value of \( \mu \) is equal to:

\[ \mu \equiv 1.9578. \]  

(4.4)

The dependencies of function \( Y(x) \) and its derivative \( f(x) = \frac{dY(x)}{dx} \) on concentration \( x \) are shown in Fig. 12.

### 5 THE ITERATION AVERAGING METHOD. CONDUCTIVITY

There is a two-phase system with the distribution function:

\[ P_0(C) = (1-x_0)\delta(C-C_2^{(0)}) + x_0\delta(C-C_1^{(0)}), \]  

(5.1)

where \( \delta(x) \) is Dirac function; \( x_0 \) is the probability of the given local area to possess property \( C_1^{(0)} \) (black color), and \( (1-x_0) \) is its probability to possess property \( C_2^{(0)} \) (white color).

After \( k \) steps of the renormalization group method transformation, the distribution function becomes:

\[ P_k(C) = (1-x_k)\delta(C-C_2^{(k)}) + x_k\delta(C-C_1^{(k)}), \]  

(5.2)

here

\[ x_k = Y(x_{k-1}), \]  

(5.3)

the density of the connecting set (CS) of bonds equals the ratio of the number of CS to the number of all the scatters (colors) on a square lattice.

In general, the definition of effective properties can be carried out according to the following scheme: firstly, properties of different configurations are found at the initial stage, then they are averaged, and after that they are handed over to the next step.
Fig. 12: a) dependence of probability function $Y(x)$ on concentration $x$; b) dependence of derivative $f(x) = \frac{dY(x)}{dx}$ on concentration $x$.

The definition of properties of all possible configurations leads to rather cumbersome calculations. That is why we will use an approximate method.

We will single out two kinds of sets of bond configurations: connecting sets of conducting bonds (CS), and non-connecting sets (NCS).

The sphere-in-sphere cell is used as a model for the CS and NCS (Fig. 13).

That is why the calculations of properties of the CS and NCS structure are modeled by a sphere-in-sphere cell at each step of the iteration process. The CS is a continuous mass of the well conducting phase (outer sphere) with an insertion of a sphere from the badly conducting phase (inner sphere); the NCS is a continuous mass of the badly conducting phase (outer sphere) with an insertion of a sphere from the well conducting phase (inner sphere).

The formulae obtained on the basis of variation evaluations are used to calculate the conductivity of the connecting and non-connecting sets /28, 29/. Also we used iteration averaging method which was proposed in /24/ to calculate the elastic properties of inhomogeneous isotropic medium with random structure. Applying this method and the correspondence principle, the calculation of the effective thermal conductivity of filled polymer nanocomposites can be made.
The conductivity of the connecting set at the $k$-th iteration step is defined as:

$$
\lambda_{con}^{(k)} = x_{k-1} \lambda_{con}^{(k-1)} + (1-x_{k-1}) \lambda_{non}^{(k-1)} - \frac{x_{k-1} \left(1-x_{k-1}\right) \left(\lambda_{con}^{(k-1)} - \lambda_{non}^{(k-1)}\right)^2}{x_{k-1} \lambda_{non}^{(k-1)} + (1-x_{k-1}) \lambda_{con}^{(k-1)} + 2 \lambda_{non}^{(k-1)}}.
$$

To define the conductivity of the non-connecting set at the $k$-th iteration step it is necessary to replace indices in (5.4) as follows:

$$
\lambda_{non}^{(k)} = x_{k-1} \lambda_{con}^{(k-1)} + (1-x_{k-1}) \lambda_{non}^{(k-1)} - \frac{x_{k-1} \left(1-x_{k-1}\right) \left(\lambda_{con}^{(k-1)} - \lambda_{non}^{(k-1)}\right)^2}{x_{k-1} \lambda_{non}^{(k-1)} + (1-x_{k-1}) \lambda_{con}^{(k-1)} + 2 \lambda_{non}^{(k-1)}},
$$

where $\lambda_{con}^{(0)} = \lambda_1$; $\lambda_{non}^{(0)} = \lambda_2$; $x_k = Y(x_{k-1})$, at this $x_0 = x$ - is the concentration of the component with a conductivity of $\lambda_1$.

The lower indices in (5.4) and (5.5) mean that this value refers to: non - the non-connecting set; con - to the connecting one; the upper index $k$ shows the iteration step number.

The iteration procedure finishes when the conductivity of the connecting set, $\lambda_{con}^{(k)}$, and the conductivity of the non-connecting set, $\lambda_{non}^{(k)}$, do not depend on the iteration number $k$ and are equal to:

$$
\lim_{k \to \infty} \lambda_{con}^{(k)} = \lim_{k \to \infty} \lambda_{non}^{(k)} = \lambda,
$$

where $\lambda$ - is the effective thermal conduction of the composite at given $\lambda_{con}^{(0)} = \lambda_1$; $\lambda_{non}^{(0)} = \lambda_2$ and $x_0 = x$. 

**Fig. 13:** Model of: a) a connecting set (CS); b) a non-connecting set (NCS)
6 CALCULATION RESULTS

The calculations have been carried out for a two-component composite. For the determination of the thermal conduction of the composite, the values of $\Delta l$ and $\lambda_m$ are determined from the comparison of the calculations and experimental dates.

Figure 14 shows the calculation results of the effective thermal conduction of the composite, $\lambda$, depending on the filler concentration, $p$, at two values of the relative thickness of the IFL ($\Delta l = 0.05R$ for the continuous curve; $\Delta l = 0.3R$ for the dotted curve). In the calculation, for both cases, the value of the interface layer thermal conduction $\lambda_m$ is equal to: $\lambda_m = 5\lambda_p$.

![Graph showing calculation results](image)

Fig. 14: Results of the calculation of thermal conduction of the composite, $\lambda$, depending on filler concentration, $p$: 1) $\Delta l = 0.05R$ - continuous curve; 2) $\Delta l = 0.3R$ - dotted curve.

Assuming that the IFL thickness is constant and approximately equal to $10nm$, it follows from the calculation that the effective thermal conduction of the composite, $\lambda$, becomes $1.5 \sim 2$ times higher when the particle radius, $R$, decreases from $200nm$ to $30nm$ (Fig. 14).

Figure 15 shows the comparison of the experimental data with the calculations of the effective thermal conduction, $\lambda$, using the formulae obtained on the basis of the Maxwell model, the Lewis - Nielsen model, the model of an effective medium, and the iteration averaging method for a polymer filled with aluminum.

The comparison shows good concordance between the calculations of the effective thermal conduction, $\lambda$, obtained on the basis of the proposed method and the experimental data.

Table 1 gives the values of thermal conduction of a polymer (epoxy resin) $\lambda_p$, thermal conduction of the filler (copper) $\lambda_f$, and the calculated values of Voronoi polyhedron thermal conduction $\lambda_v$. 
Fig. 15: Concentration dependencies of the effective thermal conduction, $\lambda$, of a polymer filled with aluminum obtained on the basis of different models: 1 - Maxwell model; 2 - Lewis - Nielsen model; 3 - iteration averaging method; 4 - model of an effective medium; • - experimental data (dots) /31/.

Table 1

<table>
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<tr>
<th>$T$</th>
<th>300K</th>
<th>194K</th>
</tr>
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<tbody>
<tr>
<td>$\lambda_p$ (W/mK)</td>
<td>0.25</td>
<td>0.2</td>
</tr>
<tr>
<td>$\lambda_f$</td>
<td>Cu</td>
<td>Ag</td>
</tr>
<tr>
<td>390</td>
<td>419</td>
<td>390</td>
</tr>
<tr>
<td>$\lambda_v$</td>
<td>0.97517</td>
<td>0.97539</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>$T$</th>
<th>78K</th>
<th>20K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_p$ (W/mK)</td>
<td>0.15</td>
<td>0.1</td>
</tr>
<tr>
<td>$\lambda_f$</td>
<td>Cu</td>
<td>Ag</td>
</tr>
<tr>
<td>390</td>
<td>419</td>
<td>390</td>
</tr>
<tr>
<td>$\lambda_v$</td>
<td>0.7806</td>
<td>0.7808</td>
</tr>
</tbody>
</table>

Figure 16 shows the comparison of the calculations of thermal conduction of a composite, $\lambda$, depending on filler concentration, $p$, with the experimental data for the epoxy resin-copper powder system at the temperatures 300K, 194K, 78K and 20K /30/.
The calculations and the experimental data agree well at the values of $\Delta l = 0.05$, $\lambda_m \equiv 1.5 \lambda_p$ (Fig. 16). As it is known that the filler particle dimensions are $40 - 100 \mu m$, it follows from the calculations that the thickness of the IFL, $2\Delta l$, is defined by the inequality: $4 \mu m < 2\Delta l < 10 \mu m$.

![Graphs](https://example.com/graphs.png)

**Fig. 16:** Concentration dependence of thermal conduction of the epoxy resin–copper powder system at the values of $\Delta l / R = 0.05$ and different temperatures: a) - 300K; b) - 194K; c) - 78K; d) - 20K. The experimental data are shown as dots.

The comparison of the calculations of the effective thermal conduction using the iteration averaging method with the experimental data shows their rather good concordance (Figs. 15, 16). Thus, the obtained results can be further used to analyze the dependence of the conductivity of a composite not only on the properties of the components, $\lambda_1, \lambda_2$, and their concentrations, $p$, but also on such characteristics of composite structure as the fractal dimension, $d_f$, the percolation threshold, $x_c$, the radius of particles, $R$, the ratio of the IFL thickness to the particle’s radius, $\Delta l$, and the thermal conduction of the IFL.

### 7 CONCLUSION

To prognosticate the thermal conduction of filled polymer nanocomposites, a fractal model of structure and an iteration averaging method have been proposed. This method is based on the idea of renormal group transformation. The averaging on mesolevels was carried out with the help of Voronoi polyhedron construction.
An analysis of the influence of the interface layer and filler particle dimensions on the effective thermal conduction of a composite was carried out.

The dependence of the effective thermal conduction on the radius of filler particles, the thickness and properties of the IFL, and the limit filling was defined.

The difference between the percolation threshold and critical concentration of the filler was shown.

Fractal sets were used to model the structure of a composite with random phase distribution. Those were obtained on rectangular lattices.

A comparison of the calculation and experimental data was made. It shows their good agreement.

REFERENCES


