

TABLE 2. Comparison of the Results of the Same Series of Measurements Analyzed According to Two Methods

Measured quantities	Method [5]			Present method	
	$T_2=50^\circ\text{C}$	$T_2=65^\circ\text{C}$	$T_2=80^\circ\text{C}$	at $21^\circ\text{C}$	at $80^\circ\text{C}$
$\tau$	0,463	0,455	0,448	0,528	0,484
$\rho$	0,124	0,123	0,122	0,132	0,126
$\varepsilon$	0,413	0,422	0,430	0,340	0,390

$\tau$ , about -5% for  $\rho$ , and about +15% for  $\varepsilon$ . This proves that the proposed method significantly corrects the errors in the known methods. It is also proved that the correction is larger for higher absolute values of temperature gradients of the measured quantity.

Summarizing the obtained results, we note that taking into account the temperature dependence of the integral radiation, transmission, and reflection coefficients (which is taken to be linear in the temperature range of the three employed blackbodies) of spectrally selective materials contributes to the lowering of methodical measurement errors that are present in the known methods. With an additional analysis of the measurement results it is possible at the same time to determine the temperature gradients of the sought integral coefficients, which cannot be achieved by other measurement methods.

#### NOTATION

$\alpha$ , absorption coefficient;  $\varepsilon$ , emission coefficient;  $\rho$ , reflection coefficient;  $\tau$ , transmission coefficient;  $\sigma$ , Stefan-Boltzmann constant;  $\lambda$ , wavelength;  $L$ , irradiance;  $T$ , temperature;  $e$ ,  $r$ ,  $t$ , temperature gradients of the integral emission ( $e$ ), reflection ( $r$ ), and transmission ( $t$ ) coefficients;  $U$ , electrical signal at the output of the photodetecting system (PDS). Indices: single indices pertain to blackbodies at the temperatures of  $o$ , sample, 1, first (isothermal chamber), 2, second, and 3, third;  $ij$  ( $i, j = 1, 2, 3$ ) refers to the sample under the conditions of a simultaneous irradiation of its visible side by a blackbody at temperature  $T_i$  and of its opposite side by a blackbody at temperature  $T_j$ .

#### LITERATURE CITED

1. V. S. Dozhnikov, V. G. Zhuravlev, Yu. N. Zhuravleva, et al., *Izmer. Tekh.*, No. 11, 60-62 (1985).
2. V. H. Meyers, A. Ono, and D. P. De Witt, *AIAA Papers*, No. 83-150 (1983).
3. M. A. Bramson, *Infrared Radiation of Heated Bodies* [in Russian], Moscow (1964).
4. D. L. Stierwalt, *Applied Optics*, 5, No. 12, 1911-1915 (1966).
5. G. K. Kholopov and V. I. Kopysov, *Inzh.-Fiz. Zh.*, 58, No. 2, 254-260 (1990).

#### THERMAL CONDUCTIVITY OF POLYMER COMPOSITES WITH A DISPERSE FILLER

I. A. Furgel', O. V. Molin,  
V. E. Borshch, E. M. Sigal,  
and M. A. Tyrtsakova

UDC 536.2:621.762

A method is proposed for predicting the thermal conductivity of polyolefin composite materials with a disperse filler. The method is based on the combined application of percolation theory and generalized conduction theory. The results of the calculations are in good agreement with experimental data over a wide range of filler concentrations at various temperatures. It is shown that the thermal conductivity of certain composites can be an order of magnitude higher than the thermal conductivity of their matrices.

The thermophysical properties of polymer composites depend on the properties of the basic components: the polymer matrix and the filler. The fillers have superior thermophysical

Institute of Low-Temperature Engineering and Power, Odessa. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 62, No. 3, pp. 453-458, March, 1992. Original article submitted July 16, 1991.

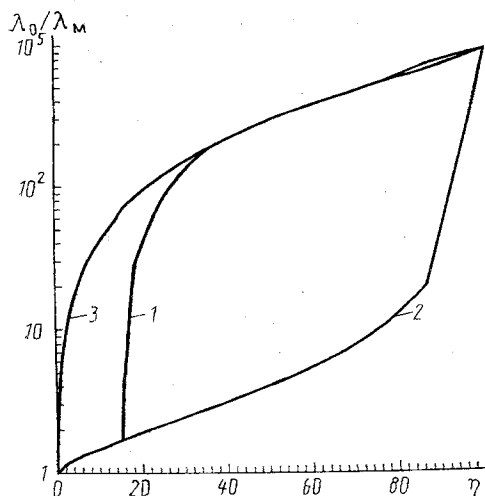


Fig. 1. Typical calculated graph of the relative thermal conductivity of a polymer composite vs the volume concentration  $\eta$  (%) of dispersed filler. 1) According to the proposed procedure; 2) according to Eqs. (1) and (2); 3) according to Eqs. (3)-(5).

characteristics in most cases, so that the properties of the polymer matrix limit transfer processes in the composite if there are no structural modifications in the composite. The introduction of various kinds of fillers in a polymer alters its structural characteristics where the degree of modification depends largely on the concentration of the filler and its activity in relation to the polymer and can significantly influence the conductivity of composites. At the present time we do not have any rigorous theories applicable for describing heat-transfer processes in composites, so that one is compelled to use model representations to describe these properties.

Our investigation is based on a natural model of composite structure. It utilizes concepts discussed in [1, 2] about the basic structures of a heterogeneous system (a structure with closed inclusions and a structure with interpenetrating components), along with the ideas of percolation theory [3, 4].

A composite undergoes major structural changes as the concentration of its filler is varied. The particles of a low-concentration filler are uncoupled (if they are randomly distributed throughout the matrix), and the composite represents a structure with closed inclusions. When the volume concentration of the filler reaches a critical value (approximately 17% for three-dimensional systems [3]), an infinite cluster (IC) of filler particles is formed (percolation phase transition). In this case the structure of the composite changes to a mixed type: closed inclusions + interpenetrating components. A further increase in the filler concentration reduces the fraction of closed inclusions in the composite almost to zero and, accordingly, changes its structure into a structure with interpenetrating components. As the volume concentration of filler is varied from 50% to 100%, the structure of the composite evolves in the reverse order to that described above. Consequently, this model is symmetric about the point of equal volume concentrations of filler and matrix. A similar model has been discussed previously [5], but our approach differs significantly in that it treats the structure of the composite over a broad range of filler concentrations, such that a mixed type of structure is achieved. The specific geometry of closed inclusions and an IC is modeled in [5], whereas in our case the statistical concept of "IC power" is used. The IC power is calculated from the critical index, providing a natural means for determining the volume fraction of the IC in the mixed structure, rather than assuming, as in [5], that it is proportional to the filler concentration.

The conductivity of heterogeneous systems has already been calculated [1, 2] on the basis of generalized conduction theory for small filler concentration [up to  $(17 \pm 1)$  vol.%], when a structure with closed inclusions prevails, and for fairly large filler concentrations, when a structure with interpenetrating components occurs. The introduction of the concept of the unit cell, which is subsequently subdivided by a system of adiabatic and isothermal surfaces, enables us to obtain corresponding functional relations for calculating their relative effective thermal conductivity. For structures with closed inclusions the adiabatic subdivision of the unit cell gives [1]

$$\frac{\lambda_0}{\lambda_M} = \frac{\delta - (\delta - 1)(\eta^{1/3} - \eta)}{\delta - \eta^{1/3}(\delta - 1)}, \quad (1)$$

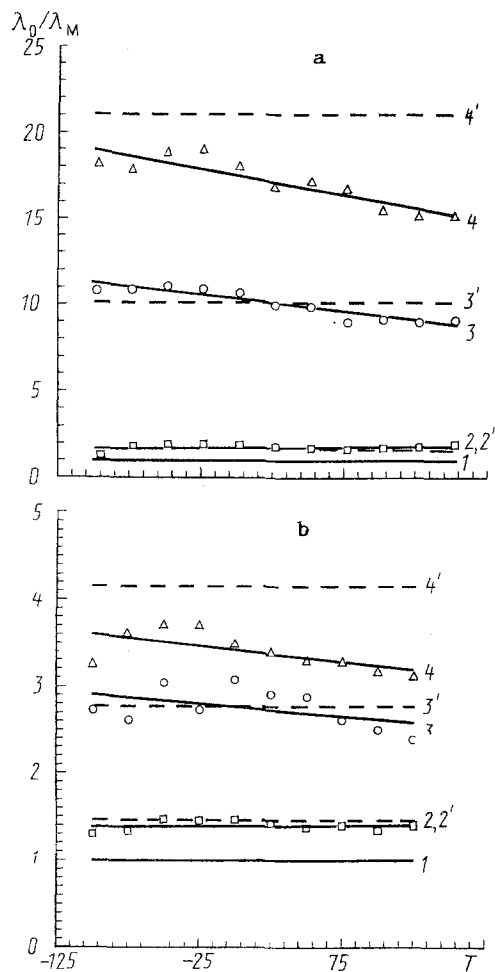


Fig. 2. Relative thermal conductivity  $\lambda_0/\lambda_M$  of polypropylene composites filled with graphite (a) and alundum (b) vs temperature  $T$ , K. a: 1) pure PP; 2, 2') 25% graphite filler (experimental and calculated, respectively); 3, 3') 40%; 4, 4') 50%. b: 1) pure PP; 2, 2') 25% alundum filler (experimental and calculated); 3, 3') 45%; 4, 4') 55%.

where  $\delta \equiv \lambda_f/\lambda_M$ , and its isothermal subdivision gives

$$\frac{\lambda_0}{\lambda_M} = \frac{1 + (\delta - 1)\eta^{2/3}}{1 + (\delta - 1)(\eta^{2/3} - \eta)} \quad (2)$$

Analytical equations have been derived [1] for structures with interpenetrating components:

$$\frac{\lambda_0}{\lambda_M} = \delta k^2 + (1 - k)^2 + \frac{2k(1 - k)}{1 - k + k\delta^{-1}} \quad (3)$$

for adiabatic subdivision of the unit cell, and

$$\frac{\lambda_0}{\lambda_M} = \left[ \frac{1 - k}{1 + (\delta - 1)k^2} + \frac{k}{(\delta - 1)(2 - k)k + 1} \right]^{-1} \quad (4)$$

for isothermal subdivision, where

$$k = \frac{1}{2} + \text{sgn}(1 - 2\eta) \cos(\varphi/3), \quad \varphi = \arccos(|1 - 2\eta|), \quad \frac{3\pi}{2} \leq \varphi \leq 2\pi. \quad (5)$$

The arithmetic mean of the results of adiabatic and isothermal subdivision yields the complete solution of the problem of the approximate calculation of the thermal conductivity of a heterogeneous system with the corresponding structure (closed inclusions or interpenetrating components) [1].

Thus, our problem is, first, to determine the filler volume concentration at which the transition is made from a mixed-type structure to a structure with interpenetrating components and, second, to calculate the thermal conductivity of the composites in the intermediate range of filler concentrations, where the composite has a mixed-type structure.

Percolation theory predicts the onset of anomalies in the behavior of the parameters of composites near the percolation threshold. The formation of an IC is a structural phase

transition. It is customarily assumed [3, 4] that the anomalies in the behavior of the characteristics of the system near the critical point have a power-law character. In particular, the probability of a particle belonging to an IC (the IC power) is

$$P(\tau) = \tau, \quad 0 \leq \tau < 1, \quad (6)$$

where  $\tau = (\eta - \eta_c)\eta_c$ .

The critical concentration  $\eta_c$  depends on the dimensionality of the space in which percolation takes place [4]. As the number of dimensions of the space increases, the probability of the formation of bypass routes increases, and the critical concentration becomes lower. If the length of the sample in directions perpendicular to the conduction direction is much greater than the characteristic diameter of the filler particles, percolation takes place in three-dimensional space. Within the framework of a continuum model for three-dimensional space percolation theory gives the critical concentration  $\eta_c = 0.17 \pm 0.01$  [3, 4].

Since the critical indices are determined mainly by the large-scale structure of the cluster, the nature of the interaction at small distances has scarcely any influence on them. For this reason the critical indices are invariant for all types of problems (lattice or continuum) and depend only on the dimensionality of the space. In three-dimensional space we have  $\beta = 0.40$  [3, 4].

Equation (6) can be used to estimate the upper bound of filler volume concentrations at which the mixed-type structure can exist. Inasmuch as  $P(\eta)$  is the probability that a particle belongs to an IC, the number of particles belonging to the IC is  $N_{IC} = P(\eta)N$  ( $N$  is the total number of filler particles), so that

$$\eta_{IC} = \eta P(\eta). \quad (7)$$

It is obvious that for unit IC power [ $P(\eta) = 1$ ] all the filler particles belong to the IC, and the composite acquires a structure with interpenetrating components. The condition  $P(\eta) = 1$  corresponds to  $\eta = 2\eta_c$ , i.e.,  $\eta \approx 0.34$ .

To calculate the thermal conductivity of the composite in the interval of filler concentrations for a mixed structure [i.e., when  $0 < P(\eta) < 1$ ], we regard the composite as a three-component system: matrix + closed filler inclusions + IC filler particles. We first calculate the thermal conductivity of the two-component system matrix + closed inclusions according to Eqs. (1)-(5), but with renormalized values of the concentrations:

$$\eta'_M = \frac{\eta_M}{\eta_M + \eta_{ci}}, \quad \eta'_{ci} = \frac{\eta_{ci}}{\eta_M + \eta_{ci}}, \quad (8)$$

where  $\eta'_M$  and  $\eta'_{ci}$  are the renormalized concentrations of the matrix and the closed inclusions, respectively,  $\eta_M = 1 - \eta$ , and  $\eta_{ci} = \eta - \eta_{IC}$ . We then treat the composite once again as a binary system, which contains a binder component having the thermal conductivity  $\lambda'$  and concentration  $\eta' = 1 - \eta_{IC}$  and IC filler particles with the thermal conductivity  $\lambda_f$  and concentration  $\eta_{IC}$ , and again we calculate the thermal conductivity of this system according to Eqs. (1)-(5). The corresponding expressions are too cumbersome to give here, but the calculated dependence of the thermal conductivity of the composite on the volume concentration of filler has been determined by the above-described procedure and is shown in Fig. 1. It is evident from the figure that the thermal conductivity of the composite jumps concurrently with the formation of the IC (at  $\eta \approx 17\%$ , provided that  $\delta \gg 1$ ), and then it increases rapidly with increasing IC power. The rate of growth of the thermal conductivity of the composite decreases somewhat when the IC power becomes equal to unity (at  $\eta \approx 34\%$ ).

A decrease in the filler-to-matrix density ratio ( $\rho_f/\rho_M$ ) is accompanied by a lowering of the critical mass concentration of filler at which the IC is formed, thus affording the opportunity of synthesizing a material with good mechanical properties and improved thermal characteristics.

Having indirect notions about the phase state of the components of the composite, we can find the qualitative temperature dependence of its thermal conductivity. According to Eqs. (1)-(4), the temperature dependence of the relative thermal conductivity of composites is contained in the temperature dependence of the parameter  $\delta(T)$ .

The filler and matrix can exist in three different phase states: crystalline, amorphous glassy, and amorphous rubber-elastic (or hyperelastic) states (the case of gas inclusions is not considered here) [6]. In the normal temperature range the temperature dependence of the thermal conductivities of crystals, glasses, and elastomers has the respective forms [6, 7]

$$\begin{aligned}\lambda_{cr}(T) &\sim T^{-1}, \quad 150 \text{ K} \lesssim T < T_m; \\ \lambda_g(T) &\sim T, \quad 30 \text{ K} \lesssim T < T_g; \\ \lambda_r(T) &\sim \sqrt{T_b - T}, \quad T_g < T < T_m,\end{aligned}\tag{9}$$

where  $T_b \approx 1.36T_m$  [7].

Equation (9) can be used to determine the function  $\delta(T) = \lambda_f(T)/\lambda_M(T)$  along with the function  $\lambda_0(T)$ . In particular, if the composite filler is crystalline and if its matrix is in the glassy state, we have  $\delta(T) = \lambda_f(T)/\lambda_M(T) \sim T^{-1}/T \sim T^{-2}$ , or

$$\delta(T) = \frac{\lambda_f(T_0)}{\lambda_M(T_0)} \left(\frac{T}{T_0}\right)^{-2} = \delta(T_0) \left(\frac{T}{T_0}\right)^{-2},\tag{10}$$

where  $T_0$  is a certain base temperature, for which the value of  $\delta(T_0)$  is known, and  $\lambda_f(T_0)$  and  $\lambda_M(T_0)$  are the thermal conductivities of the filler and the matrix (respectively) at  $T = T_0$ . The function  $\delta(T)$  is determined analogously for any other combination of filler and matrix phase states.

The thermal conductivity of polymer composites has been calculated by software implementation of the above-described approach, making it possible to predict, essentially in real time, the properties of newly synthesized polymer composites with disperse fillers. On the other hand, it must be borne in mind that the sample preparation technology can influence the density, degree of crystallinity, and grain size of the matrix. Moreover, the proposed model disregards the role of the phase interface, but this approximation is justified by the good adhesive properties of the polyolefins relative to a very broad class of materials. These factors can introduce corrections in the synthesis of the properties of polymer composites.

The thermophysical properties of polymer composites have been investigated experimentally by the monotonic regime procedure [8]. The measurement error was of the order of 10%. The experiments were carried out with mark 21060 polypropylene (PP) composites filled with dispersed materials. The fillers were dispersed materials with particle diameters up to 50  $\mu\text{m}$ . The thermal conductivities of the fillers were determined on the basis of independent laboratory experiments. The procedure used to mix the components and form the samples is described in [9].

Figure 2 shows the experimental results and calculated graphs of the temperature dependence of the thermal conductivity of the PP composites for various filler concentrations. It is obvious that the thermal conductivity of the PP + graphite composite ( $\lambda = 20 \text{ W/m}\cdot\text{K}$ ) is significantly (an order of magnitude) higher than that of the pure PP over the entire range of measurable temperatures ( $-100^\circ\text{C}$  to  $+150^\circ\text{C}$ ) at graphite concentrations above the percolation threshold ( $\approx 34 \text{ mass } \%$ ). The thermal conductivity of the PP + alundum composite also increases abruptly when the percolation threshold ( $\approx 38 \text{ mass } \%$ ) is exceeded, but only two- or threefold, since the filler itself does not have a very high thermal conductivity ( $\lambda_f = 3 \text{ W/m}\cdot\text{K}$ ). It is evident from Fig. 2 that the temperature dependence of the thermal conductivity for the given composites is very weak [ $|d(\lambda_0/\lambda_m)/dT| \sim 10^{-2}-10^{-3}$ ]. This implies that the matrix and fillers of the investigated composites are in the same phase state (since  $\delta$  no longer depends on the temperature in this case). Good agreement is observed between the results of the calculations and the experimental results for a broad range of filler concentrations. Exceptions are found at large filler concentrations (50 mass % for graphite and 55 mass % for alundum), for which the calculated data are somewhat higher than the experimental thermal conductivities of the composites. This disparity can be attributed to the fact that the diminution of the strength and hyperelasticity of the composites is conducive to their fissuring under mechanical and thermal loading and, as a result, a reduction in their thermal conductivity.

In summary, the above-proposed method for calculating the thermal conductivity of polymer composites with disperse fillers can be used to develop algorithms and analytical expressions for predicting the thermal conductivity of such materials. The good agreement between the experimental and calculated results for different fillers over a broad range of concentrations and temperatures leads to the conclusion that the theoretical approach developed here is consistent with real heat-conduction processes in composites. The above-described method (and its software implementation) can be used to predict the thermal conductivity of newly synthesized composite materials for specific (heat-conducting or heat-insulating) applications.

## NOTATION

$\lambda_0$ , thermal conductivity of composite;  $\lambda_M$ , thermal conductivity of matrix;  $\lambda_f$ , thermal conductivity of filler;  $\eta$ , volume concentration of filler;  $\delta$ , relative thermal conductivity of filler;  $k$ , filler concentration factor;  $P$ , probability that a particle (or unit cell) belongs to an infinite cluster;  $\tau$ , relative deviation of filler concentration from its critical value;  $\eta_C$ , percolation threshold (concentration);  $\beta$ , critical index;  $\eta_{IC}$ , relative content of infinite cluster in composite;  $\eta_{ci}$ , relative content of closed inclusions in composite;  $\eta_M$ , volume concentration of matrix;  $\eta_{cr}$ , thermal conductivity of crystalline substances;  $\lambda_g$ , thermal conductivity of amorphous substances in glassy state;  $\lambda_r$ , thermal conductivity of amorphous substances in rubber-elastic state;  $T$ , absolute temperature;  $t$ , temperature, °C;  $T_m$ , melting point of matrix;  $T_g$ , glass-transition temperature;  $T_b$ , boiling point of rubber-elastic materials.

## LITERATURE CITED

1. G. N. Dul'nev and Yu. P. Zarichnyak, Thermal Conductivity of Mixtures and Composites [in Russian], Leningrad (1974).
2. G. N. Dul'nev and V. V. Novikov, Inzh.-Fiz. Zh., 45, No. 3, 443-451 (1983).
3. B. I. Shklovskii and A. L. Éfros, Usp. Fiz. Nauk, 117, No. 3, 401-435 (1975).
4. I. M. Sokolov, Usp. Fiz. Nauk, 150, No. 2, 221-255 (1986).
5. D. P. Volkov, G. N. Dul'nev, Yu. P. Zarichnyak, and B. L. Muratova, Inzh.-Fiz. Zh., 46, No. 2, 247-252 (1984).
6. Yu. K. Godovskii, Heat Physics of polymers [in Russian], Moscow (1982).
7. A. Michar, Thermal Conductivity of Solids, Liquids, and Gases and Their Composites [Russian translation], Moscow (1968).
8. E. S. Platunov, Thermophysical Measurements in the Monotonic Regime [in Russian], Leningrad (1973).
9. I. V. Popik et al., Plast. Massy, No. 9, 14-15 (1988).