Fractal Model of the Heat Conductivity for Carbon Fiber-Reinforced Aromatic Polyamide

G. V. Kozlov,[1] A. I. Burya,[2] I. V. Dolbin,[3] G. E. Zaikov[1]

[1]*Institute of Biochemical Physics, Russian Academy of Science, Moscow 119991, Russia*
[2]*Agrarian State University, Dnepropetrovsk 49027, Ukraine*
[3]*Research Institute of Applied Mathematics and Automatization of Kabardino-Balkarian Scientific Center, Russian Academy of Science, Nal'chik 360000, Russia*

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ABSTRACT: It is shown that the heat conductivity of carbon fiber (CF)-reinforced aromatic polyamide on the basis of phenylone can be described within the framework of a fractal model. Depending on the dimension of filler fibers network (system), such description can be obtained by the application of two limiting cases: random network of resistors (RNR) or random superconducting network (RSN).
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Key words: polyamides; composites; thermal properties; structure–property relations; fractal theory

INTRODUCTION

During the theoretical analysis of the conductivity phenomena in composite solid medium, the general and the inevitable is the assumption of the full geometric order in the distribution of phases. It is assumed that the fibers are distributed in a matrix evenly, at the same distance, and parallel to each other. However, the real composite materials produced—as a result of the performance of complex technological operations—have a structure considerably differing from an ideal model.[1] The microscopic studies of the real composite materials show the noneven distribution of fibers, the deviation from the mutual parallelism, and the existence of porosity. Besides, the insufficient knowledge of the filler and polymeric matrix properties imposes in its turn the additional limitations on the possibility of the application of theoretical equations for the prediction of the thermodynamic properties of composite materials.[1] That is why the following simple way is often used. In the equation for the calculation of the conductivity coefficients, instead of the real physical values characterizing the separate components of the composite material and instead of the variables coordinating the experimental and the calculated data, the volume conductivity coefficient of the fiber system can be introduced, which takes into account not only the physical properties but also the geometrical features of the composite material. Such an approach is not new: fibrous and porous insulants are usually characterized by their volumetric properties.[1]

Within the framework of the fractal analysis for the description of particles system (particles aggregate) of a filler, the fractal dimension of the network of filler particles D_N is used, which characterizes the density of filling of the polymeric matrix space by particles or fibers of a filler.[2,3] Then the fractal model considers a random mixture of components A and B, in which there are well and badly conducting area.[4] Such a model entirely corresponds to the polymer composites whose heat conductivities of carbon fibers (CF) and polymeric matrix can differ by three orders of value.[1] Two limiting cases of this task[4] claim the special attention:

1. The random network of resistors (RNR). In this case, it is assumed that the areas occupied by bad conductor B have zero conductivity.
2. The random superconducting network (RSN). In this case, the conductivity of good conductor A is infinite.

The purpose of the present article was to study the heat conductivity of CF-reinforced aromatic polyamide on the basis of phenylone within the framework of the considered above fractal model.[4]

EXPERIMENTAL

Aromatic polyamide–phenylone[5] is used as the polymer matrix and CF with a diameter of 7–9 μm and a

Correspondence to: G. E. Zaikov (chembio@sky.chph.ras.ru).

length of 3 μm is used as the filler. The mass content of CF makes up 15% that corresponds to the nominal volume content $\varphi_f \approx 0.115$. The composites are produced by "dry" method, including the blending of components in a rotating electromagnetic field. For this, in the reactor powdery polymer, CF and nonequiaxial ferromagnetic particles with length of 40 mm were placed. Then, the reactor was placed in the end window of the generator of the electromagnetic apparatus. Under the action of rotating electromagnetic field, the ferromagnetic particles begin to rotate and collid between themselves, which results in the equipartition (chaotic) distribution of CF in the polymer matrix. As a result of the collisions, the particles are worn down and the products of the wear fall into the composition. For taking away ferromagnetic particles after blending, two methods are used: magnetic separation and mechanical separation.[6]

Specimens for studying thermal properties were prepared by method of not pressing at a temperature of 603 K and a pressure of 55 MPa.

The measurement of the heat conductivity λ was made according to the state standard for plastics on the apparatus UT-λ-400 in the temperature range of 323–523 K with an interval of 25 K. The measurement error was $\pm$ 3%.

The thermal properties were determined on the differential scanning colorimeter (model UT-S-400) at a heating rate of 10 K/min.

RESULTS AND DISCUSSION

As it was shown in an earlier study,[4] the heat conductivity λ for the two above-considered limiting cases is given by the following relationships:

$$\lambda \sim L^{d_u} \tag{1}$$

for RNR and

$$\lambda \sim L^{d_w - D_N} \tag{2}$$

for RSN.

In the relationships (1) and (2), L is the cluster size, d_u is the fractal dimension of its unscreened perimeter, and d_w is the walk dimension of fractal.

The necessary for further calculation dimensions can be calculated according to the following method. The value of d_u is determined according to the equation[4]:

$$d_u = (D_N - 1) + (d - D_N)/d_w, \tag{3}$$

where d is the dimension of Euclidean space, in which the fractal is considered (in our case, it is obvious that $d = 3$) and the dimension d_w can be estimated according to Alexander–Orbach rule[7]:

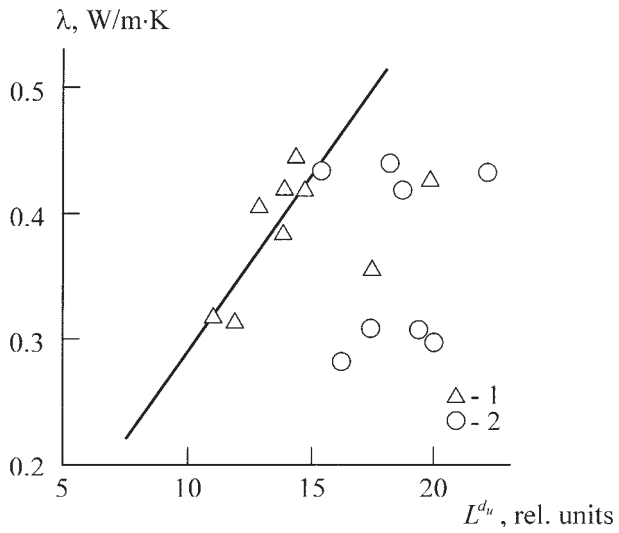

Figure 1 The dependence of heat conductivity λ on parameter L^{d_u} for CF-reinforced aromatic polyamide on the basis of phenylone produced using magnetic (1) and mechanical (2) separations.

$$d_w = \frac{3}{2} D_N. \tag{4}$$

And finally, the dimension D_N for the studied CF-reinforced aromatic polyamide can be calculated according to the equation[3]:

$$D_N = 2 + \frac{\varphi_{\text{int}} d_{\text{surf}}}{1.20}, \tag{5}$$

where φ_{int} is a relative fraction of the interfacial regions, d_{surf} is a fractal of the surface of filler fiber. As for the considered CF-reinforced aromatic polyamide, in virtue of the production technology, the aggregation process of fibers is expressed weakly,[8] and thus it was accepted $d_{\text{surf}} = \text{const} = 2.13$.[9] In its turn, the value φ_{int} is determined according to the equation[10]:

$$\varphi_{\text{int}} = 1 - \frac{\Delta C_p^c}{\Delta C_p^p} \tag{6}$$

where ΔC_p^c and ΔC_p^p are the values of jump of the heat capacity at the constant pressure at the glass-transition temperature for composite and matrix polymer, accordingly.

In Figure 1, the dependence λ on parameter L^{d_u} where value L is accepted arbitrary equal to 5 relative units is shown. As it can be seen, in case of the composite modeling by RNR, half of the data points lie down on the straight line passing through the origin (not shown in the figure), i.e., they agree with the mentioned model but half of the points have the large scatter, i.e., they do not agree with the model of RNR.

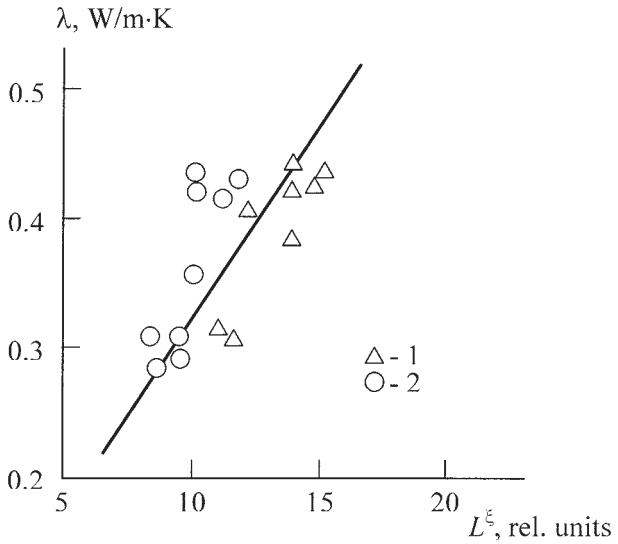

Figure 2 The dependence of heat conductivity λ on parameter $L\xi$ at $\xi = d_u$ (1) and $\xi = (d_w - D_N)$ (2) for CF-reinforced aromatic polyamide on the basis of phenylone.

This circumstance allows to assume that second group of points can be described by RSN model. Actually, on Figure 2 dependence $\lambda(L\xi)$ is adduced, where ξ is a conductivity exponent, which is equal to d_u in RNR case and $(d_w - D_N)$ in RSN case, confirms this assumption. The obtained data are approximated by one straight line for both mentioned models, which passes through the origin. The definite scatter of the data for the dependence $\lambda(L\xi)$ can be due, as minimum, to two factors: the arbitrary choice of L and the condition L = const and also approximate estimation d_w according to the Alexander–Orbach rule. Another cause of the mentioned scatter can be the variations of the heat conductivity of a polymer matrix.

The transition from one model of the heat conductivity of composites to another occurs at $D_N \approx 2.62$; at $D_N < 2.62$ the RNR model is correct, and at $D_N > 2.62$ the RSN model is correct. It is necessary to mark that the value D_N is connected to the operating parameter of the synergetic structure of CF-reinforced aromatic polyamide—the factor of fibers orientation η by the following simple relationship[11]:

$$\eta = 0.506(D_N - 2). \tag{7}$$

Then, from eq. (7) it follows that the RNR model is correct for $\eta < 0.313$ and the RSN model is correct for $\eta > 0.313$.

Let us consider the physical premises of the observed transition from the RNR model to the RSN. In the RNR limit, the heat transport does not have the geometric limitations and can be realized both in a polymer matrix and in a network (system) of fibers. Therefore, the value λ is defined by the dimension d_u or a number of the fibers network sites, which are accessible for heat transfer.[4] In the RSN case, the heat transport in the areas with zero conductivity, i.e., in a polymer matrix, is impossible and the value λ is controlled by the dimension D_N, i.e., the fiber network dimension. In Figure 3 the dependence $\lambda(D_N)$ is adduced, which is broken up on two linear sectors and whose boundary is the dimension $D_N \approx 2.62$ (the vertical shaded line in Fig. 3). For $D_N < 2.62$ (RNR limit) the dependence $\lambda(D_N)$ is approximated as follows:

$$\lambda = 0.90(D_N - 2)\ \mathrm{W/m \cdot K}, \tag{8}$$

and for $D_N > 2.62$ (RSN limit) approximation of the dependence $\lambda(D_N)$ has the following form:

$$\lambda = 0.51(D_N - 2)\ \mathrm{W/m \cdot K}. \tag{9}$$

Hence, in the RNR limit, one can observe more fast growth of λ at D_N increase than in the RSN limit. Such conclusion follows directly from the comparison of the relationships (1) and (2) as for the considered CF-reinforced aromatic polyamide $d_u > (d_w - D_N)$.

CONCLUSIONS

Therefore, the results of the present article showed that the heat conductivity of CF-reinforced aromatic

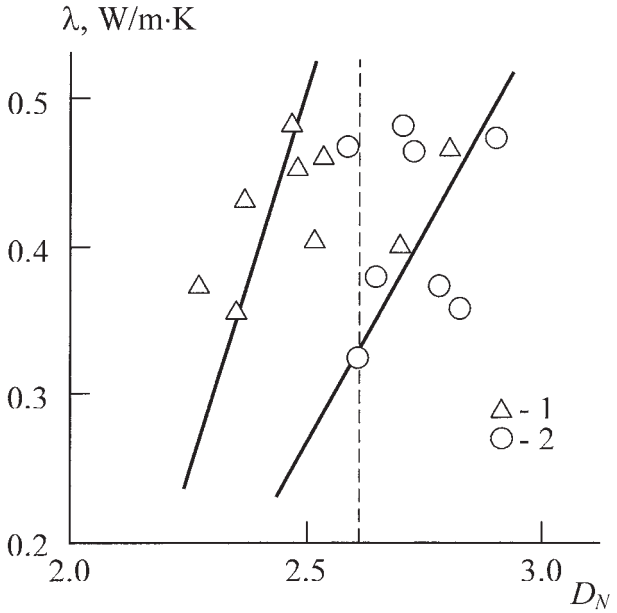

Figure 3 The dependence of heat conductivity λ on fractal dimension of filler fibers network (system) D_N for CF-reinforced aromatic polyamide on the basis of phenylone produced using magnetic (1) and mechanical (2) separations. The vertical shaded line points the value D_N, which is boundary for limiting cases RNR and RSN.

polyamide on the basis of phenylone can be described within the framework of a fractal model. Depending on the dimension of filler fibers network (system), such description can be obtained by the application of two limiting cases: RNR or RSN.

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