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Features of Thermal Conductivity of Composites Based on Thermoplastic Polymers and Aluminum Particles

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The results of the experimental studies and theoretical analysis of thermal conductivity of composites based on thermoplastic polymers and aluminum particles are presented. It is revealed that the studied systems exhibit percolation behavior. It is established that for composites filled with aluminum particles the double percolation effect is observed. A combined percolation model which very accurately describes the concentration behavior of thermal conductivity and takes into account two percolation transitions is offered.

Keywords: Polymer composites, Percolation behavior, Thermal conductivity, Aluminum particles, Thermoplastic polymers.

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1. INTRODUCTION

Polymer materials were long used as heat insulators because of their low thermal conductivity. It is possible to obtain materials with radically different properties by modifying a polymer matrix with various fillers (in nature, geometry, sizes) [1-3]. An increased interest to such materials is associated with the possibility to form new composite polymer materials with improved corrosion properties and relatively high thermal conductivity. Today, the majority of products of heat-and-power complex are produced based on metals or their alloys. And high thermal conductivity is a key requirement to the products. The use of polymer composite materials (PCM), which contain metal particles with a high coefficient of thermal conductivity (aluminum, copper, metal oxides, etc.), is an alternative to the use of metals. This allows (at certain concentrations of the filler) to obtain materials with the coefficients of thermal conductivity commensurable with those for the metals.

Metals and metal oxides are of great interest for the production of heat-conducting elements, since they sharply increase the electrical, mechanical and thermophysical properties of polymer matrices with a small filling [4-8]. It was shown in [9] that thermal conductivity of composite materials at the same content of copper was larger for the composite material with smaller sizes of copper particles. Moreover, analysis of the performed studies in the field of manufacture of inorganic nanoparticles, such as silicon dioxide and aluminum oxide, has shown that they can be used as the fillers for the improvement of ductility and impact strength of the polymers [10]. Since metal fillers, for example, silver, copper, possess simultaneously high electrical and thermal conductivity, then dielectric and heat insulating polymer matrices significantly change the properties due to the introduction of a small amount of these particles [11-13]. As shown in numerous works [14-16], both the electrical and thermal conductivities at the same mass content of metal particles depend on the method of introduction of particles into a polymer matrix, sizes and geometry of particles, uniformity of the particle distribution. We should note that either effects of increase in the thermal conductivity with a small filling (to 1 %) of composites (particles smaller than 100 nm) or effects of increase in the thermal conductivity with substantial filling (20-60 %) of composites (particles are larger than 100 nm) are considered in the mentioned works.

Most experimental data on thermal conductivity of composite materials are analyzed within different theoretical models; however, these models cannot describe the thermal conductivity of the systems in the whole concentration range of fillings [17, 18].

The aim of this work is to study the influence of the filler on the thermal conductivity of PCM based on thermoplastic polymers and aluminum particles in a wide concentration range and development of the generalized theoretical model for the analysis of these results.

2. EXPERIMENTAL

2.1 Description of the study materials

The systems based on thermoplastic polymer matrices, which are most often used in industry, and dispersed aluminum particles were used in order to establish the impact of the filler on the features of thermal conductivity of polymer composite materials.

Industrial polyethylene (PE) by SABIC®HDPE Eurotrubplast Holding Co., Ltd. (Saudi Arabia) and industrial polycarbonate (PC) by Weifang Union Biochemistry Co., Ltd. (China) were taken as the studied polymer matrix. These polymers are used as a raw material in the manufacture of the products of heat-and-power complex.

Dispersed particles of aluminum (DPAl) (aluminum powder) by Ferrotreid Co., Ltd. (Ukraine) were used as the fillers. Dispersed aluminum particles have a platelet shape and are covered by a thin oxide film. The powder is a silver-grey product, which does not contain foreign impurities visible by unaided eye. The average linear size of the particles is equal to 1 μm. The filler density is 3.9-4.0 g/cm^3, specific area – 150 m^2/g, coefficient of thermal conductivity – 39-50 W/m·K.

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PCM based on thermoplastic polymers and aluminum powder were prepared by the hot pressing method for the direct study. The initial components in the powdered state were preliminarily mixed during an hour by the magnetic mixer.

2.2 Methods of study

Thermal conductivity of the investigated samples was measured by the method of dynamic calorimetry using the device IT-λ-400 (thermal conductivity meter) with an improved cell [18]. The meter was calibrated by means of measurements of the thermal conductivity of reference quartz and copper samples. Measurements were carried out in the monotonic heating mode. Thermal conductivity of the studied samples was calculated by the formula

$$\lambda = \frac{h}{R_S}, \qquad (1)$$

where λ is the thermal conductivity; h is the sample thickness; R_S is the thermal resistance.

In order to increase the measurement accuracy, thermal conductivity of each sample was measured 3 times with subsequent averaging of the results. The measurement error was equal to 4-5 %.

3. RESULTS AND DISCUSSION

Addition of fine metal fillers with high thermal conductivity to the composition of the polymer material significantly changes its thermophysical properties. When introducing a small amount of these particles, thermal conductivity of the material sharply increases that leads to the transition of the composite polymer material from the state of heat insulator to the state of conductor [19].

Such a sharp change in the thermophysical properties of the material is explained by the mechanism of percolation thermal conductivity, according to which if a certain threshold concentration is exceeded, filler particles contact with each other forming heat-conducting channels in the material [20]. Percolation model describes the disordered systems of filled polymer composites with random geometric structure [21]. The following assumptions were the basis of the percolation model for filled polymers: fillers in the polymer composite are distributed in such a way that this leads to the change in the geometric structure of the polymer; nonlinear change in the thermal conductivity of polymer composites (sharp jump) occurs at a certain critical concentration of the filler, which is called the percolation threshold; percolation threshold and thermal conductivity of composites are associated with the size and shape of the particles; a fully continuous phase of the filler particles (percolation cluster) can be formed in the composite.

According to the percolation theory, which considers a random distribution of a heat-conducting component in a non-conducting medium, dependence of the coefficient of thermal conductivity of the composite (λ_{ef}) on the filler content can be described by the scaling equations [18]

$$\lambda_{\text{ef}} \propto (p - p_c)^k, \text{ at } p > p_c, \qquad (2)$$

$$\lambda_{\text{ef}} \propto (p_c - p)^{-q}, \text{ at } p_c > p, \qquad (3)$$

where p is the content of the heat-conducting filler; p_c is the critical concentration of the filler particles (percolation threshold); k and q are the critical indices of the thermal conductivity.

In Fig. 1 we present the dependence of the thermal conductivity on the filler content for the studied systems based on thermoplastic polymers and aluminum particles.

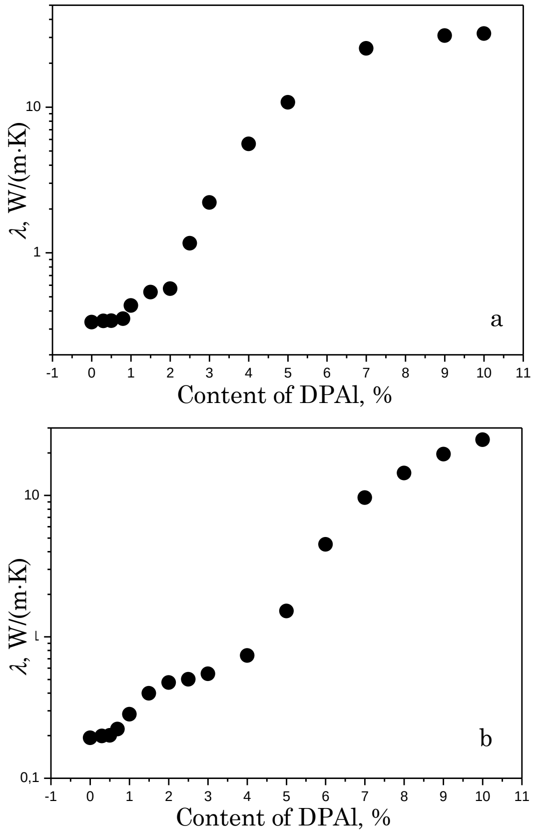

Fig. 1 – Dependence of the coefficient of thermal conductivity on the filler content for PCM: a) PE-DPAl; b) PC-DPAl

A step-like change in the thermal conductivity associated with the percolation phenomenon is observed in the concentration range of 1-4 %. At the content of 4 % of DPAl, thermal conductivity of the systems is 2 orders of magnitude higher than the thermal conductivity before the percolation threshold. As seen from Fig. 1, behavior of the concentration dependences of the thermal conductivities for the systems based on different thermoplastic polymers substantially differs that is connected with the peculiarities of polymer matrices.

Applying the least-squares method and equations (2) and (3) for the description of the experimental data (see Fig. 1), one can determine the values of the percolation htreshold p_c and critical indies k and q.

In Fig. 2 we illustrate the dependence of the thermal conductivity on the content of DPAl in the coordinates of equations (2) and (3). As seen from Fig. 2, equations (2), (3) only partially describe the experimental data. This indicates that using the standard percolation model, it is impossible to describe with a high degree of accuracy the concentration dependence of the thermal conductivity of the thermoplastic polymer-DPAl systems. This is caused by the presence of two percolation transitions observed for the mentioned systems. Existence of two percolation transitions (at relatively low and relatively high filler concentrations in the system) was observed by the authors of [19] in the study of the thermal conductivity of the PE-Al_2O_3 system. However, because of the insufficient number of points at low filler concentrations, the authors did not ascribe this change in the thermal conductivity to the percolation transition.

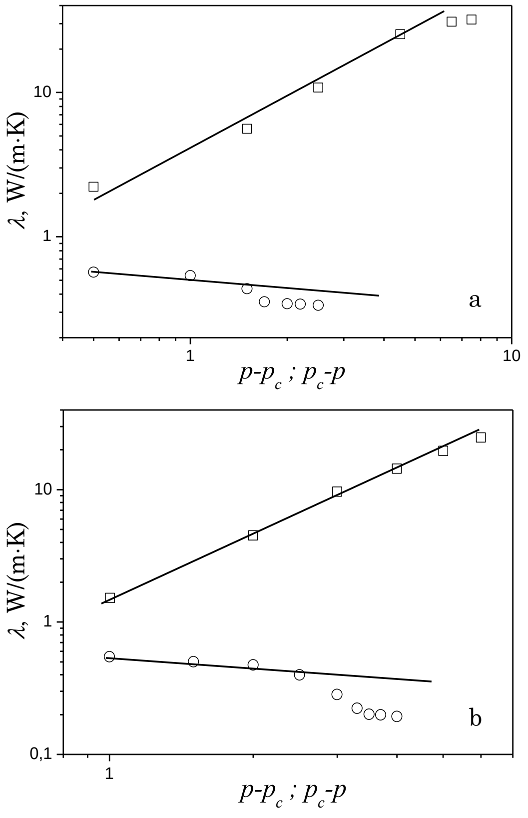

Fig. 2 – Dependence of the thermal conductivity on the filler content for PCM: a) PE-DPAl; b) PC-DPAl. Experimental data, solid line – approximation of equations (2) and (3)

For a more precise description of the experimental data, a combined percolation model was offered, which provides that filler particles form a percolation net twice (firstly, on the level of aluminum particles and then on the level of their aggregates). Since two percolation transitions are observed in the thermoplastic polymer-DPAl systems, then the dependence can be divided into three regions (Fig. 3). Concentration dependence of the thermal conductivity in the region I (before the first percolation threshold) can be described by the equation (2). Regions II and III, in which the formation of heat-conducting clusters and a non-monotonic increase in the thermal conductivity are observed, can be described by the equation (3) (for each region).

According to the combined percolation model, the total thermal conductivity of the heterogeneous system is expressed by the following formula:

$$\lambda_{\text{ef}} = \lambda_1 \left(p_{c1} - p\right)^{-q} + \lambda_2 \left(p - p_{c1}\right)^{k_1} + \lambda_3 \left(p - p_{c2}\right)^{k_2}, \quad (4)$$

where λ_1, λ_2, λ_3 are the constants, p is the mass fraction of the filler, p_{c1} and p_{c2} are the percolation thresholds, k_1 and k_2 are the critical indices of thermal conductivity, q is the critical index.

In Fig. 3 we present the concentration dependences of the thermal conductivity of the thermoplastic polymer-DPAl systems modeled using the combined percolation model (equation (4)). It is seen from the figure that this model describes with a high degree of accuracy the experimental data. Thus, assumption about the formation of a double percolation net is true. Parameters of the equation (4) are given in Table 1.

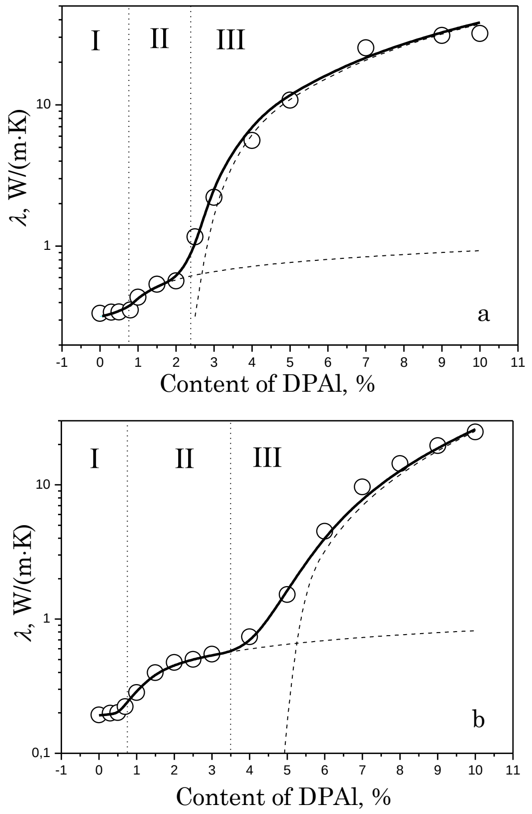

Fig. 3 – Dependence of the coefficient of thermal conductivity on the filler content for PCM: a) PE-DPAl; b) PC-DPAl. Points are the experiment. Solid line is the combined percolation model and dashed lines are the contributions of the standard percolation model

Table 1 – The values of the percolation thresholds and critical indices calculated according to the equation (4)

	p_{c1}, %	p_{c2}, %	k_1	k_2	q
PE-DPAl	0.55	2.4	0.25	1.1	0.04
PC-DPAl	0.70	4.0	0.30	1.8	0.03

According to the work [22], the authors of which have studied the structural organization of DPAl in a matrix of polypropylene, aluminum particles aggregate fractally to a three-layer hierarchical structure: individual particles → small-size aggregates → large-size aggregates (agglomerates). Therefore, formation of a double percolation net in the thermoplastic polymer-DPAl systems can be described as follows. At the filler content below 1 %, aluminum particles are uniformly distributed in a polymer matrix and do not contact with each other (region I in Fig. 3 and Fig. 4a). Therefore, thermal conductivity of the system is not almost changed. At the first percolation concentration (0.6-0.7 %) aluminum particles begin to contact with each other forming a "continuous" percolation cluster (region II in Fig. 3 and Fig. 4b); at that

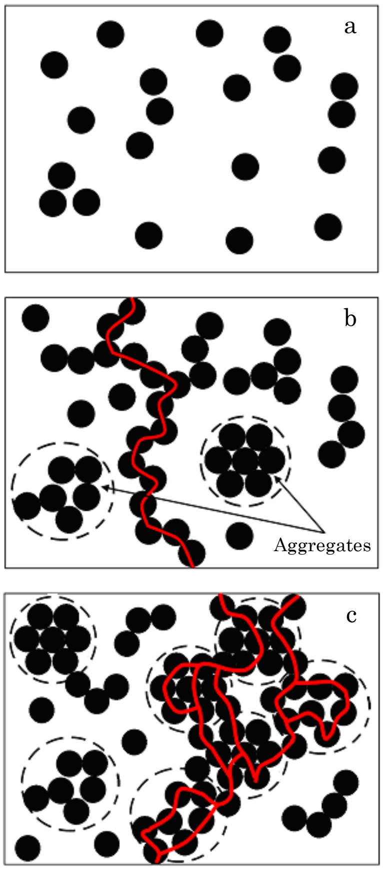

Fig. 4 – Shematic representation of the formation of a double percolation net in the thermoplastic polymer-DPAl systems

thermal conductivity of the system starts to increase. At concentrations higher than pc1, aggregates begin to grow forming more heat-conducting channels (percolation net) (region III in Fig. 3 and Fig. 4c), and therefore thermal conductivity of the system sharply increases again.

4. CONCLUSIONS

The features of the thermal conductivity of polymer composite materials based on thermoplastic polymers and dispersed aluminum particles were studied as a result of the work. It is established that the behavior of the concentration dependences of the thermal conductivities is similar for the investigated thermoplastic polymer matrices. A sharp increase in the thermal conductivity associated with the presence of the percolation transition is observed in the dependences. It is shown that thermal conductivity of the studied composite systems cannot be described with a high degree of accuracy within the framework of the standard percolation model because of the presence of two percolation transitions.

It is established that the percolation process occurring at lower filler concentrations is associated with the formation of an infinite cluster by individual aluminum particles; then during the transition occurring at higher concentrations an infinite cluster is formed by the aggregates of these particles. The formation scheme of two types of the percolation nets is proposed. A combined percolation model which takes into account the existence of two percolation transitions is offered as well.

The model has shown a good correspondence with the experimental data, therefore, it can be used for the theoretical description of the thermal conductivity of polymer composite systems based on thermoplastic matrices.

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