Electrical conductivity modelling of polypropylene composites with carbon fillers

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Electrical conductivity modelling of polypropylene composites with carbon fillers

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Abstract. Samples of a composite material based on polypropylene matrix and carbon fillers (carbon black and carbon nanofibers) were obtained. It was experimentally shown that the dependences of the electrical conductivity on the filler mass fraction have a threshold nature/ When the mass fraction of the filler is higher than the threshold the values of the electrical conductivity increases by more than 8-10 orders. Determination of the electrical conductivity value near the percolation threshold is difficult. In the article the simulation method was proposed which considers the presence of a dielectric layer between the filler particles, presented a method for its evaluation: the percolation curve near the percolation threshold was described. A fairly good agreement between the experimental and theoretical values of conductivity for various geometries and types of fillers is shown in this work.

1. Introduction

The creation of composite materials with a number of useful properties for quite a long time has been one of the main aims of the materials science. Much attention is paid to the development of materials with antistatic properties. To achieve the goal electrically conductive fillers are added into the polymer matrix [1-5]. The most common industrial polymers are thermoplastics and among them is polypropylene [6]. Carbon fillers are often used as electrically conductive fillers

Carbon black is effective as an electrically conductive filler due to a number of characteristics: high specific surface adsorption, high porosity, high structural degree, besides this material is affordable and inexpensive. Carbon nanofibers have unique heat-conducting properties (up to 1200 W / m · K), which makes it possible to obtain not only antistatic, but also heat-removing materials [7-9]. In addition, at low mass fractions of carbon nanofibers promote the strength increase of the polymer composite in compression with the original matrix material [10-11]

The purpose of this work was an experimental study and theoretical description of electrical conductive properties of a composite material based on a polypropylene matrix and carbon nanofillers.

2. Experimental study of the conductive properties of polymer composites

Polypropylene/carbon black PP/CB and polypropylene/carbon fibers PP/CF composite material samples were obtained as films and blocks. Samples were manufactured by melt technology by dispersing a specified amount of filler into the polypropylene melt. The content of the filler was calculated by the

mass fraction of carbon filler. Next, the extrusion and cooling of the melt through a die for the films or pressmold for blocks.

To calculate the electrical conductivity, the current-voltage characteristic was obtained at normal pressure and room temperature by a four-contact method. According to measurement results the dependences between the electrical conductivity and the filler mass fraction were obtained (shown in figure 1). Such dependences have a threshold character: at low mass fractions of the filler, the composite material is a dielectric; with mass fraction increasing the resistance decrease sharply (percolation threshold); at high filler mass fractions the composite behaves as a conductive material. In table 1 the values of the threshold mass fractions for all types of samples are presented.

Table 1. The threshold value of the mass fraction in composite materials polypropylene/carbon fillers.

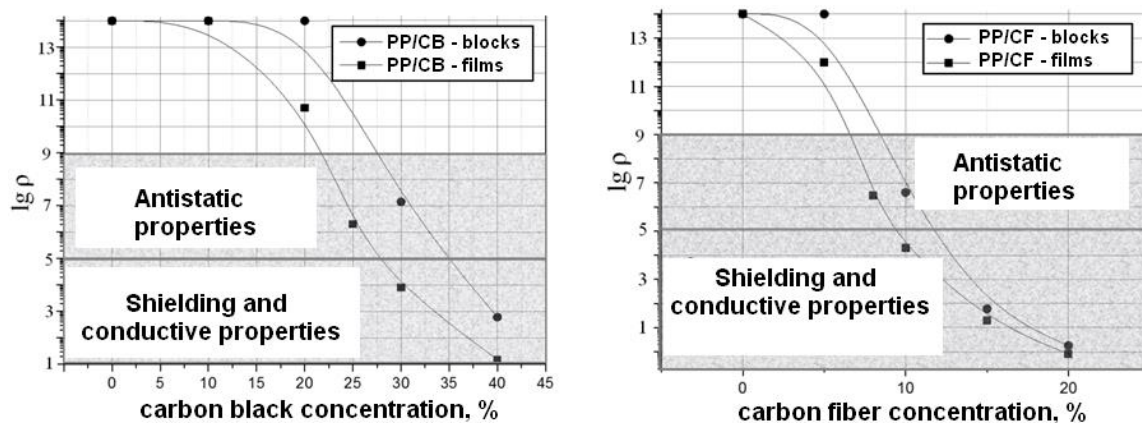|	Carbon black		Polypropylene	
	Films	Blocks	films	Blocks
Mass fraction (experiment), %	10-20%	20-30%	3-5%	5-10%
Mass fraction (modeling), %	10%	21%	4%	6%
Dielectric layer width, nm	8-14	8-14	500	500
Filler size	Diameter ~100 nm		Length ~ 80 μm	

Figure 1. Experimental dependences of the electrical resistance on the mass fraction of composites: polypropylene / carbon black (left), polypropylene/carbon fibers (right).

Dependencies having a threshold character are quite successfully described by the percolation theory in its various models above and below the percolation threshold [12-14]. However, there are difficulties in the theoretical determination of the threshold mass fraction, as well as the description of the percolation process directly near the threshold especially since that in our case there is a percolation region which is quite wide.

3. Simulation of the electrical conductivity in composite materials polypropylene /carbon fillers

To describe the electrical conductivity process near the percolation threshold we used a solution to the percolation theory problem, in which the resistance between two conductive inclusions is calculated based on the possibility of interaction between particles through a potential barrier, taking into account the tunneling current. Thus the solution of such a problem is reduced to the solution of a quantum mechanical problem [15-16]:

$$R_{\max} = R_0 e^{-\frac{2r_c}{a^*}},$$

(1)

where $R_0 \sim 1$ Ohm is the normalization factor, a^* - particle size (diameter in the case of carbon black, length in the case of carbon nanofibers), r_C is the sum of the particle size and width of the dielectric interlayer. In order to find the resistivity in the whole volume under study, we use the expression

$$\rho = R\frac{S}{l},$$ (2)

According to the solution of the problem, the dependence of the electrical resistance on the filler mass fraction was found. It can be described by the expression [15]:

$$\rho = R_0 \cdot \sqrt[3]{\frac{3}{4\pi N}} \cdot (\sqrt[3]{\frac{3}{4\pi N}}\frac{1}{ga^*})^\gamma \cdot e^{\frac{2\cdot 1,39\cdot \sqrt[3]{\frac{3}{4\pi N}}}{a^*}},$$ (3)

where g = 2 is the empirical coefficient, N is the volume mass fraction of the filler, ν is the parameter responsible for the filler geometry (for block samples γ = 0.8, for film samples γ = 1.3). To use this model it is necessary to estimate the value of the dielectric layer between the conductive particles.

For this purpose a model based on the Monte Carlo method has been proposed. It allows visualization of the filler distribution in the matrix and mass fraction threshold value determination for both block and film samples of the composite material polypropylene / carbon fillers. For each type of samples (PP/CB and PP/CF), two types of tasks were considered: 2D (for films) and 3D (for blocks) tasks. The main assumption made in modelling is the shape of particles: the particles of carbon black were approximated by spheres, the particles of carbon fibers were long threads, since the fiber diameter is fewer orders of magnitude less than the length.

Let us consider an algorithm using the example of a 3D task for the PP/CB material. Some cubic volume is randomly filled with spheres. There are two assumptions. First, the spheres cannot interpenetrate each other. Second, there is a possibility of the contact between spheres through the dielectric layer. The magnitude of the dielectric layer was chosen empirically, while the program gave the mass fraction value falling into the percolation threshold (21%). The thickness of the dielectric layer can be considered equal to 1/10 of the ball diameter, i.e. about 8-14 nm. It should be noted that for PP/CB film samples, the same value of the dielectric layer of 8-14 nm was obtained at a threshold value of mass fraction of 10%.

The orientation of carbon fibers in the polymer matrix was considered in the model. It was considered that the filler distribution in block samples was random, in the film samples - at an angle from 0 ° to 60 ° relative to the film drawing axis [17]. The width of the dielectric layer was 0.5 μm at a mass fraction of 4% for film materials and 6% for block materials.

Figure 2 shows good agreement between the experimental and theoretical results in accordance with formula 3 for all types of samples.
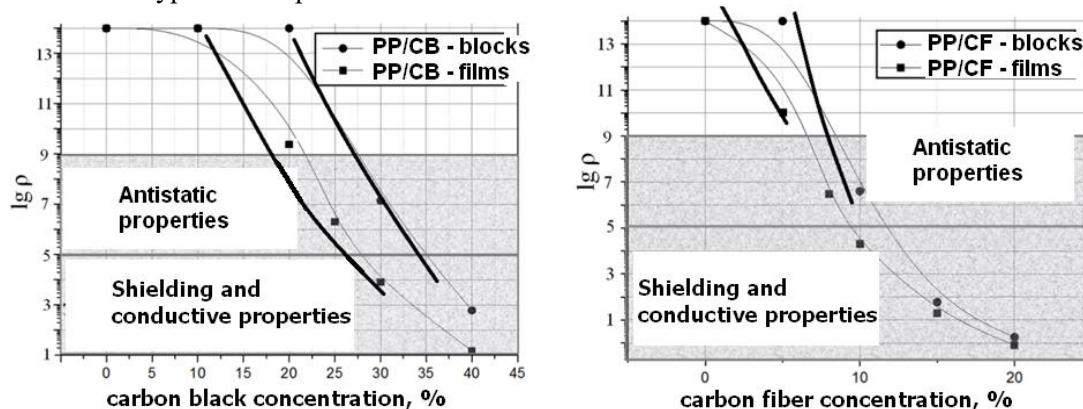

Figure 2. Experimental dependences (■, ●) of the electrical resistance on the mass fraction of composites: polypropylene / carbon black (left), polypropylene/carbon fibers (right) and blocks and the simulation results (▬▬▬▬).

4. Conclusion

Composite materials in the form of films and blocks based on polypropylene and carbon fillers have been obtained. The dependences of the electrical resistivity on the filler mass fraction were experimentally found. Such dependencies have a threshold character. For the theoretical description the solution of the percolation problem was used taking into account the presence of a potential barrier. To estimate the width of the dielectric layer (potential barrier) the Monte Carlo method was used for all types of samples near the percolation threshold. This model allows accurately describe the process of electrical conductivity in a composite material based on a polymer matrix and carbon fillers.

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