Electrical Conductivity Modeling and Research of Polypropylene Composites Filled with Carbon Black

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Abstract. Composites of polypropylene filled with carbon black (PP/CB composite) at different concentrations were prepared by melt mixing followed by compression molding. The dependence of electrical resistance on the filler mass fraction was experimentally received. It was shown that the received dependence had the threshold character. The composite kept dielectric properties at the filler concentration below the threshold and at the concentration above the threshold the electrical resistance decreased more than on 8-10 orders. The theoretical description of electrical conductivity of the composite was offered. Experimental data of the dependence between electrical resistance and the filler mass fraction agreed with the theoretical. The process of conductivity in the PP/CB composite was simulated by means of the Monte-Carlo method for threshold mass fraction estimation.

1. Introduction

Nowadays the great attention is paid to creation of new materials which have specially set properties included antistatic effect. One of the ways to achieve necessary properties is the preparation of polymeric composite materials [1-3]. Usually thermoplastic materials are used as a matrix because of their good physical and mechanical properties, availability and simply processing. One of the most widespread industrial thermoplastic polymers is polypropylene (PP) [4]. Conductive carbon fillers can considerably reduce the initial polymer resistance. So, carbon black (CB) is very appropriate as the electric conductive filler due to the number of characteristics: the high adsorption by the surface (the existence of foreign components worsens the structure), high void ratio. An average diameter of CB particles is from 10 to 300 nanometers, electrical conductivity fluctuates in the wide range, the most widespread trade names have conductivity from 1 to 100 $\text{m}^{-1}$ [5].

We received polypropylene/carbon black composite material. It was necessary to make a theoretical description of conductivity process in such materials because there are a lot of works devoted to different technologies of preparation, but it is not enough works which can illustrate the unusual dependence of electro conductivity between concentration of the filler [1-2].

2. Sample preparation, measuring technique of electrical resistance

Samples of PP/CB composite material were received in the form of films and blocks by compression molding. For this purpose micro-compounder ‘DSM Xplore’ was used. The polymer used in this study
was isotactic polypropylene (PP) (trade name 01270 Balen), released in the form of granules. Carbon black (trade name P-805E) was used as a filler (table 1).

Table 1. Carbon black and polypropylene characteristics

|                      | Carbon black | Polypropylene |
|----------------------|--------------|---------------|
| Aspect ratio         | ~1           |               |
| Density, g/sm³       | 1.8-2.1      | 0.9           |
| Electrical resistivity, Ohm·m | 1.3·10⁻³     | 10¹⁵          |
| Modulus of elasticity, GPa | ~15         | 1.2           |

For electrical resistance calculation volt-ampere characteristic was found under normal conditions and room temperature. The scheme of the automated device for resistance measurement based on double-probe system is shown on Figure 1. The sample (1) is placed in the screened chamber (2). Contacts on the sample were made with the silver paste. The power supply (3) gives constant voltage on one of electrodes (4). The electric current passes through a sample (1) on the second electrode (4) and further on the picoammeter (5), showing the value of current in the chain.

Figure 1. The scheme of the automated device for electrical resistance calculation volt-ampere characteristic: 1 – sample; 2 - screened chamber; 3 - power supply; 4 - electrode; 5 - picoammeter

3. Experimental Results
The dependence of electrical conductivity on the filler mass ratio was measured. Apparently from figure 2, change of electrical resistance from CB mass ratio has threshold character. At the small filler concentration the composite material was dielectric. If concentration was increased, at CB mass ratio 23-27% for film samples and 33-37% for blocks the threshold of electric resistance was observed. At high filler concentrations the composite behaved as carrying-out material.

4. The theoretical description of PP/CB composite conductivity. Task of spheres.
In the studied PP/CB material there are a few free electrons (charge carriers). So, the electrical conductivity in such structures is described within the theory of hopping conductivity where electron "jumps" from one donor to another [5]. In our case CB particles are donors. So, the electron can carry out transition from one donor to another passing the free condition and without occupying energy from thermal movement of atoms. Such process is called tunnelling. The event of tunnel transition is the improbable event therefore the dependence of electrical resistance from the concentration of conductive particles has to have exponential character [5-7].

Threshold nature of dependence between electrical resistance of composite from the mass fraction of the filler was experimentally observed, therefore the process of conductivity can be considered from the point of view of the percolation theory. According to this theory at the certain volume fraction of
CB, the CB particles are formed into the infinite carrying-out cluster at the expense of what considerable decrease in electrical resistance is observed.

As the studied PP/CB composite material is the polymorphic structure, i.e. there are areas of various degree of orderliness in material structure; the studied material has no ordered crystal lattice, that’s why the process was considered by the task of spheres of the percolation [8].

It was made the averaging by the size of agglomerates of CB particles, also "spheres" was constructed for all agglomerates, all such spheres had identical radius. If the center of one sphere lied in other sphere, such spheres were considered as the connected. It allows to take into account the polymorphic structure and localization of wave functions in a studied composite. At the certain concentration of CB the spheres formed the infinite cluster at the expense of what considerable decrease in specific resistance of the PP/CB composite material was observed.

According to the solution of the task of spheres the dependence of electric resistance on the filler concentration, described by expression [6], was found:

\[
\rho = R_0 \cdot \left( \frac{3}{4\pi N} \cdot \left( \frac{3}{4\pi N} \cdot \frac{1}{g a_b^*} \right)^{1/g} \right)^{2.139} \cdot \frac{3}{4\pi N} a_b^* \cdot \frac{e^2}{1.39 \cdot 3^{3/4} \pi N^{3/4}} \cdot \frac{1}{\nu}
\]

where \( R_0 \) - normalizing constant, \( R_0 = 1 \) Ohm, \( g=2 \), \( N \) — volume concentration of the filler, \( \nu = 0.8 \) — for block samples; \( \nu = 1.3 \) — for film samples, \( a_b^* \) — radius of the connected sphere.

**Figure 2.** The dependence of electrical resistance on a filler mass fraction for films and blocks

The proximity of experimental and theoretical results was observed (fig. 2), however theoretical dependences had smoother character.

The model by means of the Monte-Carlo method was constructed for more accurate definition of the threshold in composite materials. This model allows to visualize filler distributions in the matrix and to define the threshold values of the concentration. The volume with randomly distributed CB particles was considered (see Figure 3: polypropylene – grey, carbon black – black and red, infinite cluster - red). It is necessary to consider the mechanism of hopping conductivity therefore the assumption was made: electrical contact between CB particles can be carried out not only at the direct contact between particles, but also through some dielectric layer, thickness of an equal one cell. Values of percolation thresholds were found. For film samples the threshold was observed at the CB mass fraction \( \sim 25\% \), for block samples \( \sim 36\% \). Experimental and theoretical values of the threshold coincided with rather good accuracy.
5. Conclusion

The PP/CB composite material in the form of films and blocks was received. The dependence of the composite electrical resistance on the filler mass fraction was experimentally found. Such dependence had the threshold character. The proximity of experimental and theoretical results was observed (fig. 2), however theoretical dependences had smoother character. For more exact determination of threshold values in block and film samples the process of conductivity was simulated by means of the Monte-Carlo method. Set of the solution of the task of spheres and modeling by means of the Monte-Carlo method allows describing with high precision the conductivity process in the PP/CB composite materials.

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Figure 3. The dispersion of CB in PP matrix (polypropylene – grey, carbon black – black and red, infinite cluster – red)