

ELECTRODUCING POLYMER COMPOSITES BASED ON HIGH DENSITY POLYETHYLENE AND TECHNICAL-CARBON

T.A. Borukaev^{1*}, D.S. Gaev¹, R.A. Shetov¹, A.Kh. Shaov¹, A.V. Orlov²

¹Kabardino-Balkar State University, named H. M. Berbekov 360004, Nalchik, Chernyshevskogo street, 173, Russia

²Institute of petrochemical synthesis of RAS, named A.V. Topchiev, Moscow, Leninsky prospect, 29, Russia

*e-mail: boruk-chemical@mail.ru

Abstract. Electrically conductive polymer composites based on high-density polyethylene and carbon black are obtained. It is shown that polymer composites possess a positive temperature coefficient of electrical resistance. The amount of carbon black required to form electrically conductive paths in a polymer matrix is determined. Dependence of physico-mechanical and rheological characteristics of composites on the content of carbon black is revealed. The concentration interval of carbon black is determined, in which the optimal combination of physico-mechanical, rheological and electro physical properties of composites.

Keywords: polyethylene; carbon black; composites; properties; electrical; mechanical; rheological; morphology.

1. Introduction

Electrically conductive polymeric composite materials (PCM) with an increased positive temperature coefficient of electrical resistance and devices based on them began to be developed and patented in the 80s of the last century [1-3]. Electrically conductive PCMs and products based on them are produced in countries such as the USA, Germany, China, France, Korea, etc. Particularly widespread electroconductive PKM was found in the production of self-regulating heating cables and other heating elements [4, 5]. Their use significantly saves energy. In addition to self-regulating heating elements, these materials can be used in other industries, in particular, as electrodes, means for electromagnetic screening, for protection against electrostatic electricity, as thermoresistors, fuses, in medicine, etc. [6-8].

To create electrically conductive polymeric composites, metal powders and carbon-containing fillers, such as technical carbon, graphite, carbon black, carbon nanotubes [9] are most often used as conductive additives.

Powders of metals (copper, aluminum, iron, etc.) were not widely used due to the oxidizability of metals. The formation of an oxide film leads to a rapid decrease in the conductivity of the composition. Sometimes these powders are silver. In addition, dispersed metals are not prone to the formation of chain structures that cause the electrical conductivity of the material (metal particles are disoriented), and a decrease in their content below 50-60% causes a sharp drop in conductivity. The high content of metal powders significantly impairs the mechanical properties of polymers. Due to the high density, metal powders are not evenly distributed in the polymer matrix, and this leads to a non-homogeneity of the material with respect to electrical conductivity and poor reproducibility of the specified properties. In this regard, carbon-containing fillers are more promising materials.

The purpose of this work is to produce composite materials on the basis of high density polyethylene (HDPE) and carbon black with electrical conductivity.

2. Experimental

As a polymer matrix, high-density polyethylene (HDPE) of grade 277-73 was used, and an electrical conducting filler was a technical carbon (TC) (Russia) with the following characteristics: particle size 20-35 nm; specific surface area $114 \times 10^2 \text{ m}^2/\text{kg}$; bulk density of 355 kg/m^3 ; the specific electric resistance is $2 \times 10^{-3} \text{ Om} \times \text{m}$.

Composite materials based on HDPE and TC were obtained by mixing in the polymer melt and additive in a twin-screw extruder with a screw diameter of 20 mm at a temperature of 180-200 ° C. The mixing time did not exceed 10 minutes. The content of TC in composites varied in the range of 10-30 mass.%. The extrudates were then granulated and used to prepare suitable test pieces.

Investigation of the morphology of the surface and structure of composite materials was carried out using the scanning electron microscopy (SEM) method on an electron-ion microscope Helios Nanolab 650. To reduce the effect of charging the samples during electron scanning, samples were deposited on a gold film thick $\sim 20 \text{ nm}$. Measurement of electrical conductivity was carried out on a teraohmmeter E6-13A with the placement of samples in the climatic chamber. The electrical conductivity was measured at least 3 samples for one concentration of the filler.

The melt flow index of the initial HDPE and composites based on HDPE and TC was determined on an automatic capillary viscometer of the IIRT-A type at a temperature of 190 ° C and a load of 2.16 kg in accordance with GOST 11645-73.

Mechanical tests for uniaxial tension were performed on samples in the form of a double-sided blade with dimensions in accordance with GOST 25.601-80. The tests were carried out on a universal test machine Gotech Testing Machine CT-TCS 2000 (made in Taiwan) at a temperature of 20 ° C.

3. Results of the study and their discussion

As a result of extrusion of a mixture of HDPE + TC, extrudates were obtained. Then they made disks with a diameter of 3 cm and a thickness of up to 2 mm, as well as bars measuring $4 \times 6 \times 100 \text{ mm}$ and blades. The values of the specific resistance ρ of the disk samples and the specific electric conductivity of the bars from the concentration of the conductive filler are shown in Table 1 and in Fig. 1, respectively.

Table 1. The values of the specific resistance of HDPE + TC composites.

Indicators	Filler concentration, mass.%						
	0	12	15	18	20	25	30
$\rho, \text{Om} \times \text{m}$	10^{14}	$1,37 \times 10^5$	$1,59 \times 10^5$	$1,33 \times 10^5$	$1,41 \times 10^5$	$0,72 \times 10^5$	$0,65 \times 10^5$
R, Om	10^{14}	$3,8 \times 10^5$	$4,4 \times 10^5$	$3,7 \times 10^5$	$3,9 \times 10^5$	$2,0 \times 10^5$	$1,8 \times 10^5$

From the results presented in Table 1 and in Fig. 1, it can be seen that with an increase in polymer filling up to 18%, the resistivity does not actually change until an electroconductive network is created that provides for the "tunneling" of electrons. Such a state, called the "threshold of penetration" [9], occurs when about 18% of the TC is introduced into the polymer matrix, which is also evident from the value of the specific electrical resistance of this composite. Therefore, to achieve the region of the percolation threshold, it is necessary to introduce at least 18% of the TC into the polymer matrix. Obviously, this amount of TC in the polymer matrix contributes to the formation of a certain supramolecular structure, i.e. To the formation of current-carrying chain-like structures that

make it possible to achieve the required level of electrical properties. A further increase in the TU content leads to a sharp decrease in the resistivity. However, at certain filling levels, the conductive grid is saturated, and a further increase in the amount of TC does not affect the resistance.

It should be noted that the value of the "percolation threshold" will depend on the type of technical carbon, the type of polymer, the production technology (in particular, on the mixing time of the components), as well as on the presence of other additives. In addition, the dispersion of TU has a significant effect on the conductivity of the composite. The better the dispersion, the less the amount of conductive TU is necessary to obtain the required resistivity.

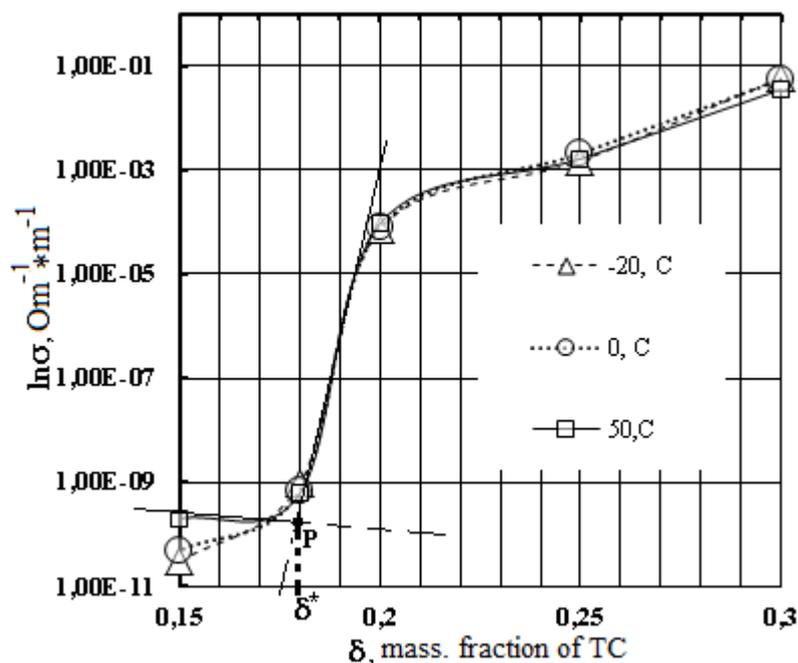


Fig. 1. Dependence of the specific electrical conductivity of composites "HDPE + TC" from the filler content.

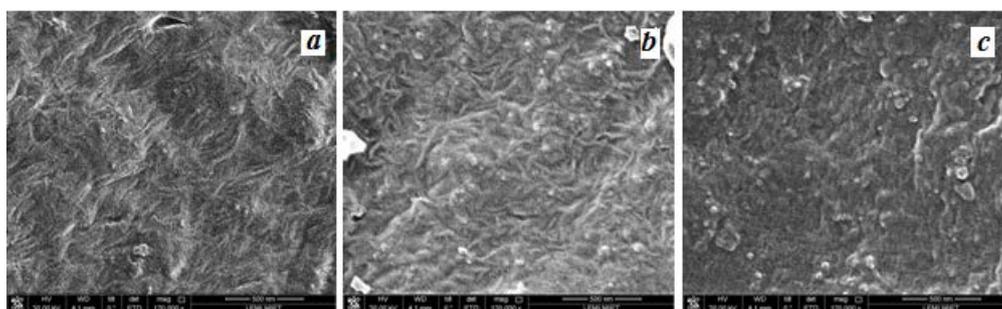


Fig. 2. SEM images of the surface of composite samples; content of TC, mass. %: a – 18, b - 25, c - 30.

Investigation of the surface of composites (brusks) and the surface of their end faces has shown that the morphology of the composite with 18% TU is different from other samples (Figs. 2 and 3). Thus, the results of electron microscopic studies characterize the differences in the structural organization of samples with different mass contents of the filler. Within the framework of known concepts of the structure formation of polymer-carbon composites [10],

these differences can be related to the processes of agglomeration of carbon black particles. The most pronounced carbon agglomerates begin to appear in a sample containing 25 % of TC. Note that the comparative analysis of SEM images (for example, see Fig. 2, a and Fig. 3, a) also indicates differences in the microstructure of the composite on the surface and in its volume.

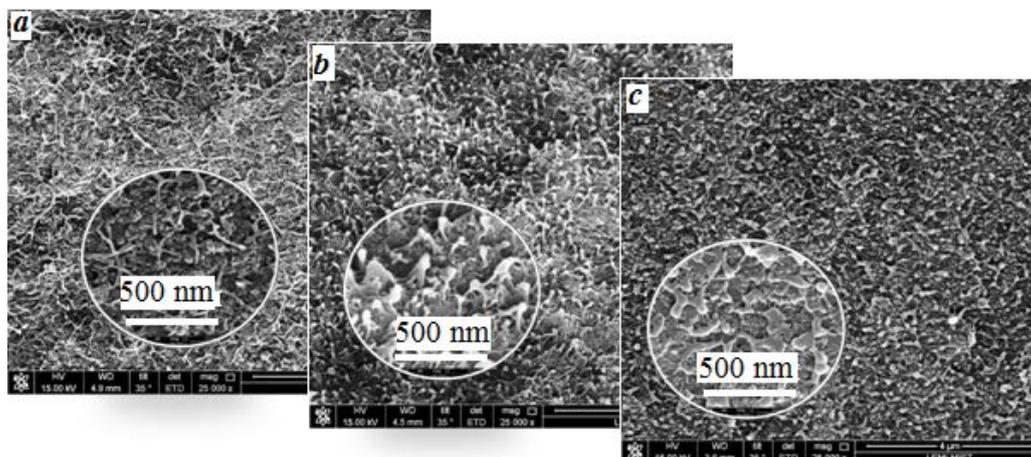


Fig. 3. SEM images of the cleavage surface of composites with different filler content, mass. %: a – 18%, b - 25%, c - 30%.

For fractured surfaces, the fractal dimension was calculated. The calculations used the "perimeter-area" method, recommended in [11]. The results of calculating the fractal dimension are shown in Table 2 below.

Table 2. The results of calculating the fractal dimension of the cleaved.

Parameter	Composition of the sample, mass. % of TC	
	18	30
Fractal dimension of the cleavage surface	2,634±0,034	2,557±0,014

Differences in the fractal dimension of the cleaved surfaces of composites indicate the possibility of using this parameter in problems of assessing the nature of microstructuring of composites. In a particular case, the results obtained indicate a difference in the fractal dimension of the cleavage surface for composites with a subthreshold and post-threshold composition.

The obtained electroconductive composites based on HDPE and technical carbon are characterized by significant changes in electrical conductivity with increasing temperature. These changes are most typical for composites with a content of more than 18%. In Fig. 4 shows the dependence of the specific resistance of the composite HDPE + 18 % TC on temperature.

This nature of the polytherm of conductivity is explained by the thermal expansion of the polymer matrix, which leads to an increase in the distance between the TU aggregates and the rupture of conducting clusters on their basis. Such properties of composites suggest that these materials will have the ability to self-regulate the released power. The principle of self-regulation is as follows: when the environment is cold, the electrically conductive material is compressed, thereby creating a plurality of conductive tracks of carbon black particles, thereby reducing the electrical resistance. When electric current passes through such material, the heat energy is released. In more heated areas of the electrically conductive composite, the

material expands, thereby reducing the number of conductive paths. The electrical resistance of the material rises, resulting in a decrease in heat production. In hot areas, the expansion of the material of the conductive composite almost completely breaks the conductive paths. In this case, the electrical resistance of the material becomes very high maximum in this temperature range, which leads to a significant decrease in the release of thermal energy. This property of the electrically conductive polymer composite will allow it to be used as heating elements for self-regulating heating cables, where the main element is the fuel matrix.

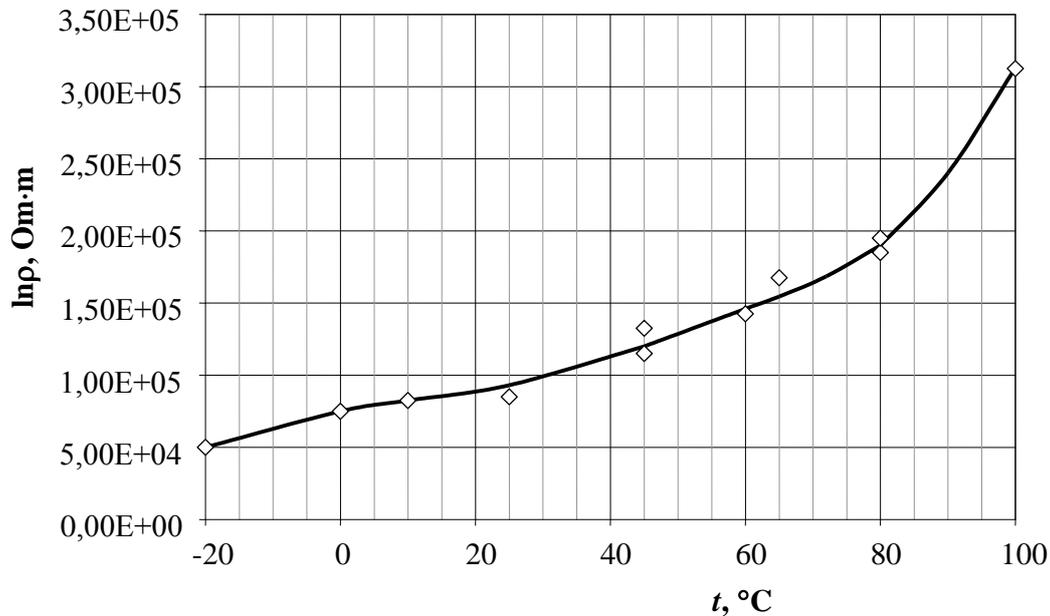


Fig. 4. Dependence of the resistivity of the composite (18 mass. % of TC) on temperature.

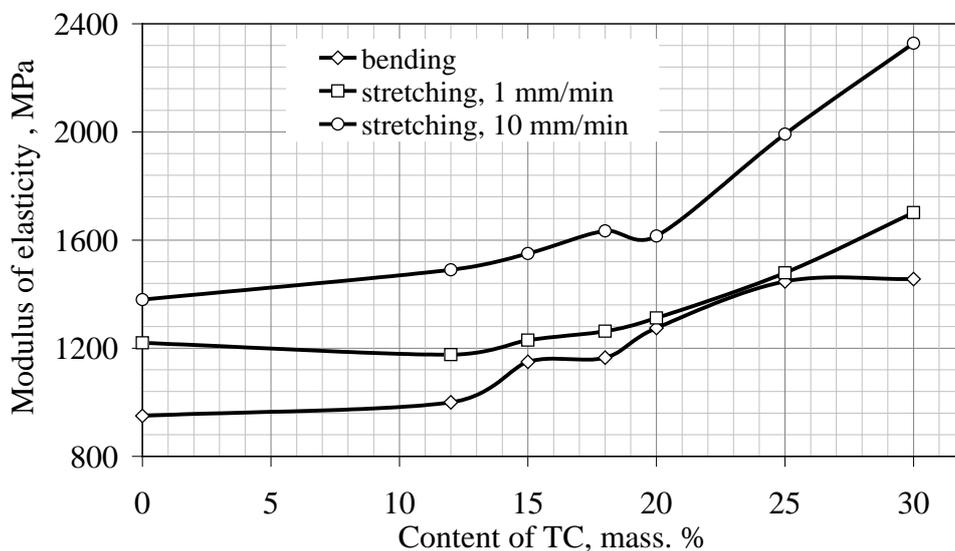


Fig. 5. Concentration dependences of the modulus of elasticity in bending and stretching for samples of the composition "HDPE + TC".

It should be noted that the introduction of nano-sized additives in polymeric materials generally leads to a change in its basic physico-mechanical and technological properties [12]. In this connection, it was of interest to study the effect of technical carbon on the thermal and mechanical properties of the polymer matrix - HDPE. In particular, the modulus of elasticity when stretching filled compositions with increasing content of TU regularly grows up to

30 mass.% of TC (Fig. 5).

As can be seen from the figure, on the site with a TC content of 15-25 mass. % there is a local peak at 18 mass. % of TC for the elastic modulus measured at a higher degree of stretching. With bending and at a stretching speed of 1 mm/min, the increase in the elastic-guest module with a maximum filler content was ~ 25%, with stretching at a speed of 10 mm / min - almost 100%, i.e. twice. Such an increase in the stiffness of the filled polymer material is quite understandable and the concentration dependences of the strength characteristics and plasticity are of interest.

If we evaluate and compare the samples of the filled polymer by such a characteristic as the deformation before destruction of ε_p , then its sharp decrease, i.e. the maximum embrittlement is observed, as can be seen from Fig. 6, in samples with a maximum filler content of 25-30 mass. % of carbon black. However, this characteristic is stable up to a TC content of 12 mass. %, And, only after its excess, a sharp drop begins with a further increase in the content of the filler. Thus, the composite material remains quite ductile at a constant increase in rigidity, down to a carbon black concentration of 18 mass. %. Such correlations allow us to assume that the introduction of sufficiently large amounts of TC into the polymer matrix (up to 18-20 mass. %) does not lead, at least, to an increase in the defectiveness of its structure.

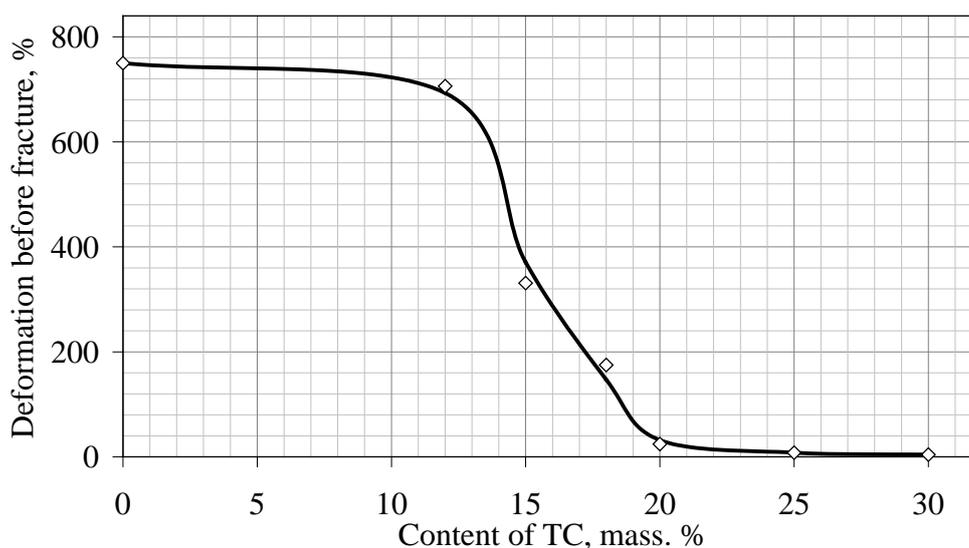


Fig. 6. Dependence of deformation before fracture (tearing) ε_p upon stretching from the content of TC for samples of the composition "HDPE + TC".

This assumption is confirmed when considering the concentration dependence of σ_f and σ_y - stress of fracture (rupture) and yield strength (Fig. 7). These two strength parameters change simbarically as the content of carbon black increases with the general tendency to increase. An obvious feature - yield is not observed in the most fragile samples with a filling of 30 mass. % of TC. There is also a local maximum region of σ_f and σ_y at 18-25 mass. % of TC.

Thus, the deformation behavior of a composite material reduces to the following. The toughest composition corresponds to the maximum strength with its minimum value of ε_f . Composition compositions in the range of 12-20 mass. % of the filler combine an increased stiffness with a higher strength (σ_f) than the original polymer and an important plasticity index – the yield strength σ_y . Note that the latter value is also the most important limiting characteristic of the ability of a sample to withstand mechanical loads, and the presence of

plasticity assumes optimal integration of the expected chain structures of technical carbon into the polymer matrix, which is extremely important for the creation of a composite material that is supposed to regulate electro physical characteristics In a rather wide range of values.

The melt flow index of the composite material with increasing filler content naturally decreases, and is opposite to the growth of strength and plasticity (Fig. 8). We note that the rate of the observed increase in the viscosity of the melt of the composition with an increase in the filler content is higher than for strength and plasticity. So, if σ_f and σ_y increase by 33 %, the increase in melt viscosity (decrease in MFR) even with a filler content of 20 mass.% - 3 times.

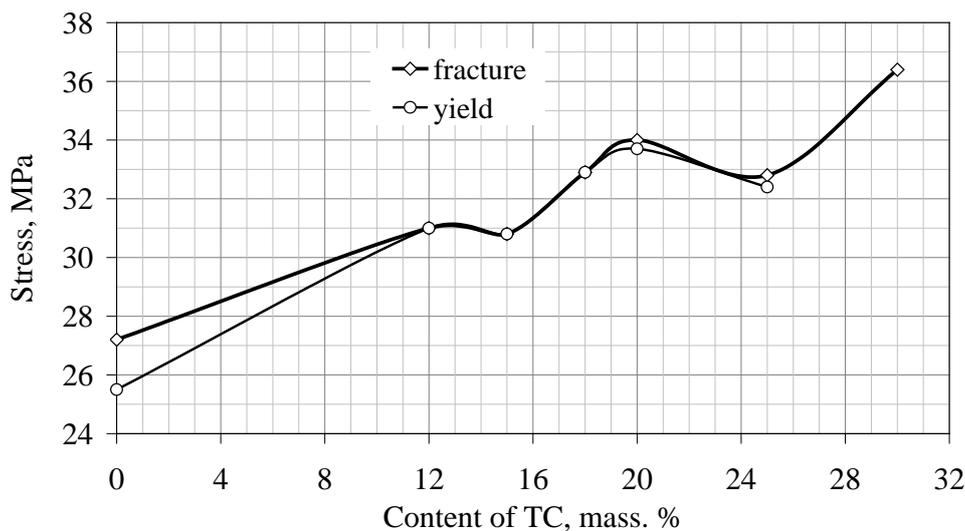


Fig. 7. Concentration dependencies of the fracture stress and yield strength upon stretching for the samples of the composition "HDPE + TC".

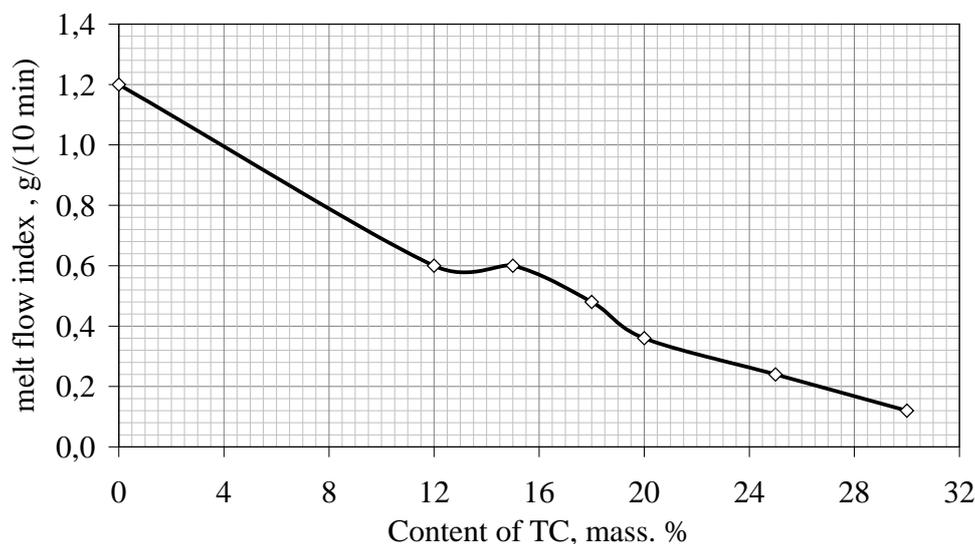


Fig. 8. Dependence of melt flow index on the content of TC for samples of the composition "HDPE + TC".

It is known that the nature of the distribution of the filler in the polymer matrix is largely determined by the interaction at the interface between the individual part of the filler and the polymer medium. The viscosity of the polymer melt and the diameter of the filler

particles are parameters that affect the formation of chain structures. Reducing the size of the filler particles increases the probability of formation of chain structures, and the increase in viscosity increases the time during which these structures are formed. In our case, a filled thermoplastic with a sufficiently small initial particle size of the filler (20-35 nm) it is confirmed by the course of the concentration dependence of the MFR: with increasing viscosity of the polymer melt, the value of the percolation threshold increases.

In our opinion, heat shrinkage is also more stable in the samples of the composition in the indicated concentration range (Fig. 9). According to the thermal shrinkage, the minimum parameter is for compositions with 12-18 mass. % of TC.

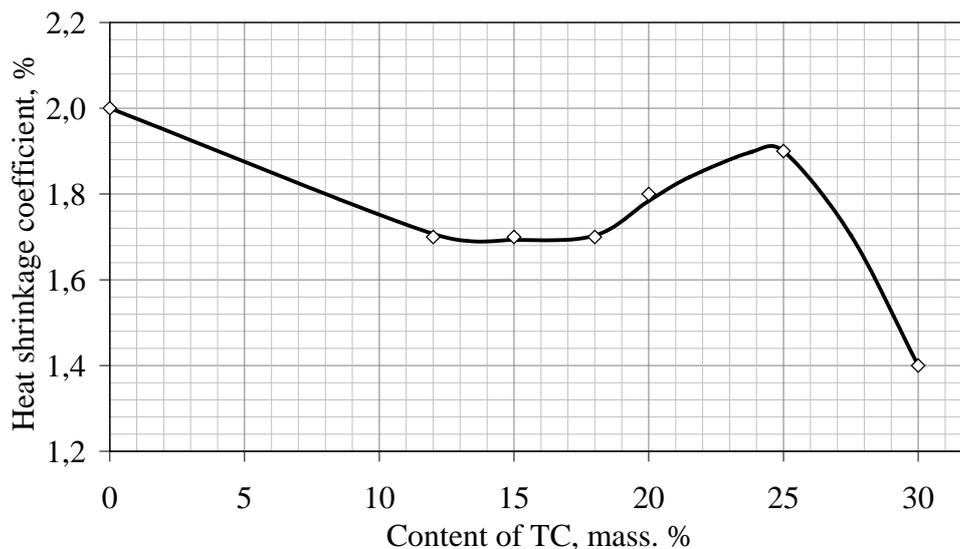


Fig. 9. Dependence of the heat shrinkage coefficient on the content of TC for samples of the composition "HDPE + TU".

4. Conclusions

In the framework of the present work, electrically conductive polymer composites based on HDPE and technical carbon were obtained. It is established that the percolation threshold of conductivity corresponds to the composition of the composite containing 18% of TC. The polytherms of electrical conductivity of composites are characterized by a high value of the positive temperature coefficient of resistivity; the latter indicates the possibility of their use as heating elements in the production of self-regulating heating cables.

Consideration of the concentration dependences of certain physico-mechanical and rheo-logical characteristics of composites allows us to determine the concentration interval 12-18 mass. % of carbon black, in which one should expect an optimal combination of them with the required interval of electro physical properties, the most important of which is electrical conductivity.

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