ELECTRICAL, RHEOLOGICAL AND MECHANICAL PROPERTIES OF POLYVINYL CHLORIDE/COPPER PLATED GRAPHITE COMPOSITES

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***Abstract:** The issue of the creation of electroconductive polyvinylchloride/copper plated graphite (PVC/COGR) composite materials is devoted to the work. There have been presented electrical (specific electrical volume resistivity), mechanical (tensile strength and elongation at break) and rheological (melt flow index) features of PVC/COGR composites in this work. An increase in the volume content of copper plated graphite in the PVC matrix results in monotonically falling curves with a well-defined percolation threshold. The decrease in tensile strength by ~1.4 times and elongation at break by ~6 times has been observed in the PVC/COGR composite films obtained by extrusion and pressing methods. The melt flow index decreases with the increase of copper plated graphite concentration by exponential law over ~3 times. The main factors that affect the electrical, mechanical and rheological properties of compositions have been reviewed.*

***Keywords:** polyvinyl chloride, copper plated graphite, extrusion, pressing, specific electrical volume resistivity.*

1 INTRODUCTION

Due to the complex of its properties, polymer materials are very important in industry and in everyday life. Expansion of plastics scope put the task for the creation of electroconductive polymer materials that combine the properties of polymers and metals.

There are two types of plastics. One is called thermosetting resin which does not soften again and hardened; and the other is called thermoplastic resin which becomes soft or hard when its temperature rises or falls. Thermosetting resin has an older history. Polyvinyl chloride is commonly referred to as PVC or vinyl and is second only to polyethylene in volume use. Normally, PVC has a low degree of crystalline and good transparency. The high chlorine content of the polymer produces advantages in flame resistance, fair heat deflection temperature, good electrical properties and good chemical resistance. However, the chlorine also makes PVC difficult to process. The chlorine atoms have a tendency to split out under the influence of heat during processing and heat and light during end use in finished products, producing discoloration and embrittlement. Therefore, special stabilizer systems are often used with PVC to retard degradation [1].

Due to the high specific electrical resistance, the polymers are mainly used in electrical engineering as insulators. In some cases, it is necessary that the polymers have current conducting properties. Polymeric electroconductive composite materials are widely used for the manufacture of low-power electrically-conductive elements, shielding and antistatic coatings, conductive adhesives, paints, pastes, air filter elements, in medicine to stimulate bone tissue growth, as anthropogenic implants [2].

Increasing the conductivity can be achieved by injection of the electroconductive fillers into composite materials, for example, metal powders or fibers, various types of carbon materials. Phenol-formaldehydes, epoxides, furans and other resins, which as a result of solidification form three-dimensional structures, as well as thermoplastics and rubbers, are often used as the binder [3].

PVC composites filled by carbon black or graphite composites is one of the most extensively studied systems because of its widespread used antistatic, electrostatic dissipative and semi conductive materials. Carbon black with high surface area can lead to electrical current percolation at lower concentrations and to form a conductive carbon network; however, the porous structure of carbon black can decrease mechanical properties of composites, hence, carbon black filler loading within a polymer matrix is limited, Graphite based composite bipolar plates are made on a combination of graphite and a polymer resin with conventional polymer processing methods like compression molding or injection molding.

As one of the commonly used conductive carbon fillers, graphite not only has good conductivity but is also helpful for improving process ability due to its lubricating effect in the melt. Usually, carbon fibers are used for mixing with polymer for reinforcement to improve mechanical properties. However, most of these studies were mainly focused on the mechanical aspects of the composites [1, 4, 5].

Copper filled polymer composites are widely used for electromagnetic interference shielding. They have a lighter weight than metals and are less costly. These composites exhibit several interesting features due to their resistivity variation with thermal, mechanical or chemical treatments. It was found that morphology and structure of conductive pathways within the composite were key parameters determining most of its electrical properties [6].

However, methods for obtaining such materials don't always ensure homogeneity of the filling and the actual results did not correspond to the expected results. The electrical insulation material is considered to be better, the higher its electro-physical properties. The latter is characterized by the values of the specific electrical resistance, electrical resistance to breakdown and dielectric losses. The value of these characteristics depends on the aggressive factors (in particular on moisture absorption), temperature and frequency of the electric field. Prospective materials for the above-mentioned purposes may be PVC/COGR composite systems. They are relatively new composites that combine properties of copper and graphite in the PVC matrix [7-10].

2 MATERIALS AND METHODS

Polyvinyl chloride (PVC) brand PVC-C-63M was used as a polymer matrix for the production of electroconductive composite materials. Its characteristics are shown in Table 1.

Table 1 Properties of PVC brand PVC-C-63M

Indicators	The standard for the brand
Appearance	Homogeneous powder of white color
Amount of extraneous substances and dirt [pcs], not more than	6
Amount of transparent dots in 0.1 sm^3 [pcs], not more than	2
Bulk density [kg/m^3]	450-550
Flow rate [s], not more than	16
The weight of absorption plasticizer [grams per 100 grams resin PVC], not less than	18
Temperature stability of the film at 160°C [min], not less than	10
Mass fraction of volatile substances and moisture [%], not more than	0.3
Mass fraction of vinyl chloride [$million^{-1}$], not more than	10

Copper plated graphite, represented as graphite (brand GK-1) covered by copper (brands M-5, M-7 and M-8) were used as conductive filler. It has been established that metallized graphite significantly increases the viscosity of compositions and, due to this, the cooling process of compositions proceeds under conditions of strong adsorption interaction of the binding agent to the filler surface. The use of copper plated graphite makes it possible to create electroconductive polymers with high adhesive strength [7, 8].

The characteristics of copper plated graphite which was used in this paper are given in Table 2.

Table 2 Properties of copper plated graphite

Indicator	The standard for the brand
Copper content [%]	Not more 90
Density [kg/m^3]	Not more 150
Current density [A/sm^2]	3.7-4.5
Limit of flexural [MPa]	1.5
Hardness in Rockwell B	0.05
Average particle size [nm]	104

As a result of the research, the following electroconductive PVC compositions were selected (Table 3). It is difficult to obtain high level of homogeneity with mixture components for electroconductive PVC/COGR compositions. This has been achieved by using overhead mixer. After mixing the composition mixture has been placed in a heated mold. Mold with compositional mixture have been placed in heat chamber for ~10 min at ~160°C [8].

Table 3 Recipes of electroconductive PVC compositions

Components	The content of components in the composition [% vol.]			
PVC-C-63M	55	53	47	42
Dioctyl phtalate	31	29	25	21
Zinc stabilizers	6	5	5	4
Titanium ceruse	1	1	1	1
Calcium stearate	2	2	2	2
Distilled graphite	5	10	20	30

The obtained compositions were studied in laboratory conditions. The value of the specific electrical volume resistivity, tensile strength, elongation at break and melt flow index was determined according to standard methods [2, 3].

3 RESULTS AND DISCUSSION

The results of the research of the dependence of specific electrical volume resistivity to direct current on the volumetric content of copper plated graphite for the PVC composite system are presented in Figure 1.

It is a monotonically falling curve with a well-defined percolation threshold. Sharp reduction of specific volumetric resistance (increase in conductivity) with an increase in the content of the filler up to 10% vol. occurs at the percolation threshold (5% vol.) for compositions made by extrusion (■) and pressing (●). The value of the percolation threshold was found as the point of intersection of straight lines, approximating the low-level branch and the incident site of the characteristic. According to Figure 1, the value of percolation threshold for compositions obtained by extrusion and pressing methods ~5.2% vol., corresponding to the percolation theory of electrical conductivity.

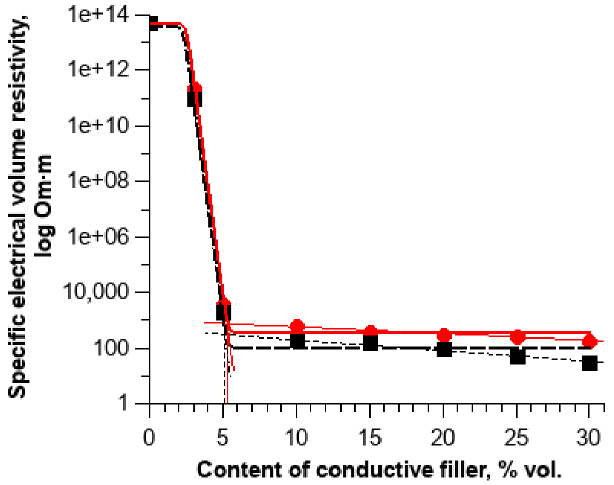

Figure 1 Dependence of specific electrical volume resistivity of conductive PVC compositions on the content of copper plated graphite (obtained by extrusion ■ and pressing ● methods)

The Figure 1 consists of three sections: a high-altitude section (section I: 0-3% vol.) where the resistance is determined by the resistivity of the polymer matrix. The area of maximum change (section II: 3-5% vol.), where the resistance of the composite is no longer determined by the resistivity of the matrix, but also not determined by the resistivity of the conductor and the section (section III: 5-30% vol.) of the minimum resistance, where the dependence is weak, since the specific electrical volume resistivity is determined by the resistance of the conductor.

The effect of the dispersed filler on the strength of the filled compositions depends on the nature of the distribution of the particles of the filler, their size and interaction at the boundary of the phase separation [6, 7]. When the film is stretched, the polymer matrix is deformed by the destruction of adhesive bonds with the filler, which reduces the strength and elongation at the tensile strength for highly filled by dispersed particles compositions.

With the increase of the dispersed filler content in the PVC composition, the material becomes more fragile and the strength and elongation at break decrease. It should be noted that the destruction of the sample compositions was without formation of a neck. This is due to a decrease in deformation in the midgesferolite areas in which the filler is mainly concentrated, as a result of a decrease in the mobility of macromolecules under the influence of a solid surface. The deformation of the spherulites themselves is complicated because they are surrounded by fragile non-deformable, high-content filler substrates and therefore a fragile break occurs along the midgesferolite boundaries before the stress for the stepwise destruction of the structured sites is achieved. The dependence of the strength and elongation at break of composite material on the content of copper plated graphite is shown in Figures 2 and 3.

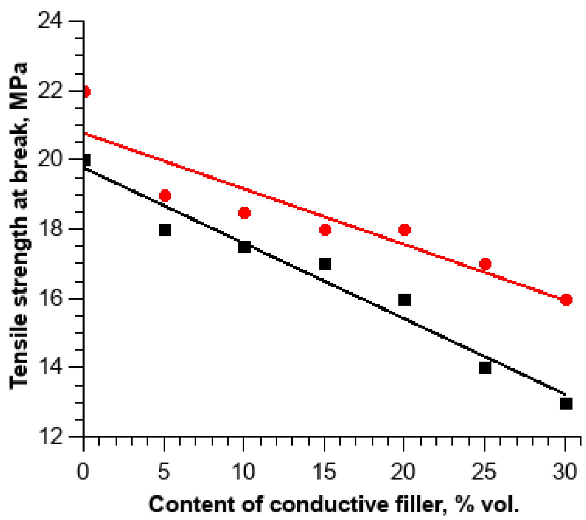

Figure 2 Dependence of tensile strength for conductive PVC compositions on the content of copper plated graphite (obtained by extrusion ■ and pressing ● methods)

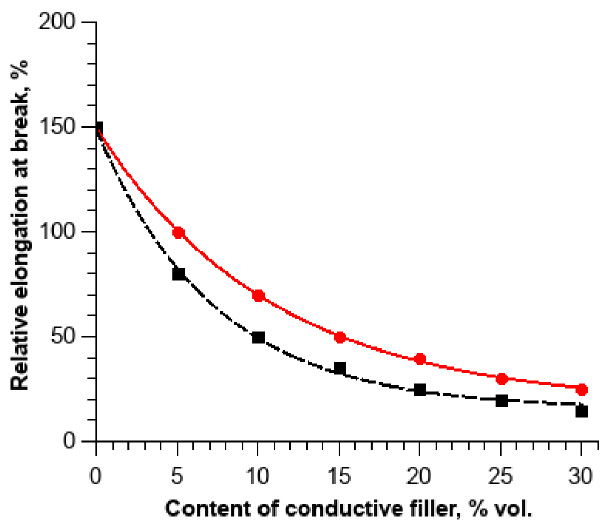

Figure 3 Dependence of relative elongation at break for conductive PVC compositions on the content of copper plated graphite (obtained by extrusion ■ and pressing ● methods)

From the above-mentioned dependencies it is clearly visible that the strength and elongation at break decreases by the increase of the filler concentration for the compositions obtained by extrusion and pressing methods. This can be explained by an increase of the filler content which is localized during crystallization in the disordered parts of the polymer. If these particles are large in comparison with the unordered regions, then they affect these parts with their entire surface, touching several such regions and also the crystalline regions which they affect less. Depending on the strength of this interaction between polymer matrix and filler, there is a different reduction of the flexibility of the macromolecules that interact with the surface of the particles of the filler, which can reach values less than critical. The phenomenon is accompanied by a deterioration of strength and elongation at break. In this filling interval, the tendency to aggregate filler particles may increase, which can cause negative effects on the properties of the compositions.

At even higher concentrations of the filler, the growth of defective spherulites and other supramolecular formations increases, the size of their distribution diminishes, the degree of crystallinity decreases, the crystallite's size and degree of perfection diminishes, overstrain and defects occur. They are present at low concentrations, but their negative effects are often overlapped by the positive effects of the fillers on the supramolecular structure and the flexibility of the structural units (relaxation behavior) of the polymer.

Qualitatively, the effect of the filler on the viscosity of composite materials can be estimated depending on the melt flow index (MFI) from the filler content. As can be seen on Figure 4, with the increase in the content of the MFI filler decreases by exponential law for extruded (■) and pressed (●) specimens. The decrease in MFI indicates an increase of the composition viscosity.

The melt flow index of the filled polymers depends on the nature of the filler, on its concentration and the nature of the interaction with the polymer. The study of these dependencies allows us to select the filler, establish its optimal concentration and also determine the energy load on the equipment and conditions of processing, in which qualitative products can be obtained.

Changing the melt flow index of the filled system is explained by hydrodynamic effects and mechanical forces on the polymer matrix. Hydrodynamic effects are due to the fact that the conditions of flow for one particle affect the nature of the flow for the dispersion medium near other particles, more precisely with no rigidity or sphericity of the particles formed by macromolecules and their associates. The change in the properties of the polymer medium in the composition is due to the adsorption interaction of the particles with the polymer and the limitation of the molecular mobility of the chains in the adsorption layer.

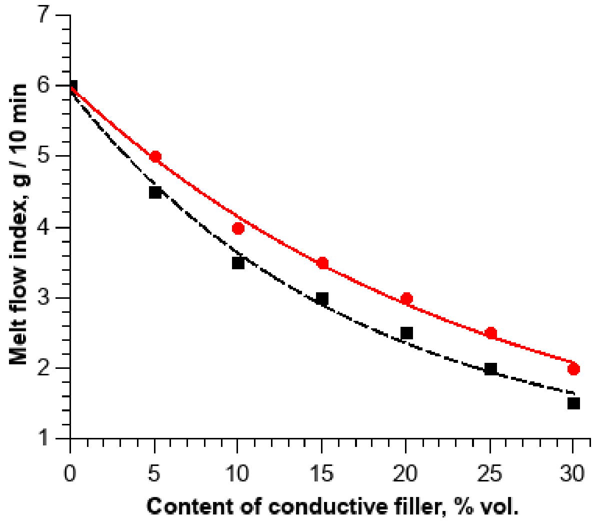

Figure 4 Dependence of the melt flow index for conductive PVC compositions on the content of impregnated graphite (obtained by extrusion ■ and pressing ● methods)

4 CONCLUSIONS

The dependencies of electro-physical, mechanical and rheological properties of compositions based on PVC on the content of copper plated graphite were determined.

It was established that a sharp decrease of the specific electrical volume resistivity with an increase of the filler content up to 10% vol. occurs at the percolation threshold (5% vol.) and the value of the percolation threshold for the compositions obtained by extrusion and pressing methods is ~5.2% vol., corresponding to the percolation theory of electrical conductivity.

It has been established that an increase of the filler content up to 30% vol. leads to a monotonous decrease in the tensile strength, elongation at break and index of melt flow for the extruded and pressed compositions.

The obtained results of experimental research can be applied at a choice for rational structure of conductive PVC with the given electro-physical, mechanical and rheological properties.

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