Archives of Materials Science and Engineering

Volume 37
Issue 1
May 2009
Pages 37-44

International Scientific Journal
published monthly by the
World Academy of Materials
and Manufacturing Engineering

Influence of graphite on electrical properties of polymeric composites

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Received 18.01.2009; published in revised form 01.05.2009

ABSTRACT

Purpose: of this work was to prepare polymeric composite materials with different contents of graphite and to search the influence of graphite on electrical properties of these materials.

Design/methodology/approach: Five specimens were prepared using gravity casting method. Composites with epoxy resin as a matrix and with respectively 3, 6, 9 and 12%vol of graphite PV60/65 as a filler were cast. Surface resistivity was applied as a measure of electrical properties. The idea of the test was to define electrical resistivity in sequential layers with different content of conductive component (graphite). First, specimen's thickness was measured and electrical resistivity was tested. Next, outer layer was removed by grinding and electrical measurements performed. The procedure was repeated for all subsequent layers. In effect surface and volume resistivity dependence on depth of the layer was determined.

Findings: The experimental results demonstrated that addition of conductive filler (graphite) to epoxy resin caused change of surface and volume resistivity of these materials.

Research limitations/implications: Further investigations with higher carbon content and/or with different matrix are needed.

Practical implications: Addition of 3-6%vol. of graphite to epoxy resin caused limited, almost linear, decrease of surface resistivity in depth direction of specimens. Higher content of filler (9-12%vol) in polymeric composite caused rapid, non-linear with layer depth, decrease of surface and volume resistivity.

Originality/value: This paper is original because in the research programme gravitational casting was used to prepare polymeric composite materials with gradient of electrical properties.

Keywords: Electrical properties; Polymeric composite materials; Graphite; Filler

Reference to this paper should be given in the following way:

M. Szczepanik, J. Stabik, M. Łazarczyk, A. Dybowska, Influence of graphite on electrical properties of polymeric composites, Archives of Materials Science and Engineering 37/1 (2009) 37-44.

PROPERTIES

1. Introduction

Composite are engineering materials made from two or more constituents with significantly different physical or chemical properties which remain separate and distinct on a macroscopic level within the finished structure. Most of composites are made up of just two materials. One material (the matrix or binder) surrounds and binds together a cluster of fibres or fragments of a much stronger material (the reinforcement). For the matrix, many modern composites use thermosetting or thermoplastic polymers (also called resins). The plastics hold the reinforcement together and help to determine the physical properties of the end product. Based on the form of reinforcement, common composite materials can be classified as follows [1-4]:

1. Fibre (short and long) reinforced composites;
2. Particle (flakes, beads, spheres, needles, irregular) reinforced composites;
3. Gas reinforced composites (foams).

Although glass fibres are by far the most common reinforcement, many advanced composites now use fine fibres of pure carbon [1,4]. Precious property of composites is possibility of planning structure in purpose to obtain established characteristics of these materials. In effect composite materials are commonly applied in modern technology. Structural composite materials have been also used in other fields such as automotive, naval transportation and civil engineering but the high cost still limits their applications [2-12].

One of the largest areas of application for polymers, polymer blends and composites on their basis are electronic and electrical industries. Pure polymers are generally electrical insulators in their nature, so they are applied as electrically insulating materials. Polymers contain a very low concentration of free charge carriers, and thus they are non-conductive and transparent to electromagnetic radiation. For that reason they are not capable for being used as enclosures for electronic equipment as they cannot shield it from outside radiation or prevent the escape of radiation from the component. They also cannot provide protection against electrostatic discharge in handling sensitive electronic devices. These drawbacks have led to the growth in the research for electrically conductive polymers. Conductive polymers can be either inherently conductive (such as polyaniline) or insulating polymers filled with conductive particles. A critical concentration of filler, beyond which the polymer composite becomes conductive, is referred to as the percolation threshold. At this point a conductive network is formed through the matrix. This permits the movement of charge carriers in the fillers through the polymeric matrix, and so the composite achieves a certain degree of electrical conductivity. Conductive polymers have many advantages over metallic conductors. They can be easily shaped with low cost technologies; they have light weight; they provide corrosion resistance and they can offer a wide range of electrical conductivities. Numerous fillers can be compounded into the insulating matrix in order to achieve different conductivity ranges. Each filler can affect other properties besides conductivity, i.e. certain fillers are more appropriate than others for functioning in special applications. In electrical conductive polymers the formation of the conductive network depends mainly on the filler concentration and geometry (size and shape) [13-15].

In this paper structure, electrical properties and possible applications of graphite filled polymeric gradient materials are discussed.

Graphite is pure carbon in a crystal form much like that of mica–sheets of strongly linked atoms, with very weak bonds between the sheets. This structure makes graphite an excellent dry lubricant wherever temperatures do not get too high. Pencils make use of graphite for the same reason, as graphite rubs off on paper so easily. Graphite is very soft, measuring 1 or 1.5 on the Mohs scale of mineral hardness [16].

Graphite fibres reinforced composites have exceptional mechanical properties which are unequalled by other materials. The material is strong, stiff, and lightweight. Polymeric graphite fibres composite is the material of choice for applications where lightweight & superior performance is paramount, such as components for spacecrafts, fighter aircrafts, and race cars. Composite materials are extremely versatile. The engineer can choose from a wide variety of fibres and resins to obtain the desired material properties. Also the material thickness and fibre orientations can be optimized for each application. The influence of graphite additions on the friction and wear behaviour of moulded epoxy resin has been evaluated using a pin-on-disc wear unit under dry sliding conditions. Graphite addition reduces the friction coefficient. Further, wear loss drops significantly when graphite is present in small amounts in the resin. The tests conducted on the composites containing 3wt% or more of graphite yielded extremely small amounts of wear [17].

Scientists work out new technologies to manufacture materials that has continuous distribution of composition and properties. This kind of materials, named Functionally Gradient Materials (FGMs), offer a solution for many advanced applications by suitable connection of two or more materials that have dissimilar properties without definite boundaries between them in macroscopic scale. Till now correct connection of dissimilar materials in FGMs was possible by applying variety of methods like: pressing, centrifugation and gravity casting, UV irradiation, selective laser sintering (SLS) and compression moulding. Arrangement of composite properties, along one or more directions, can be achieved for instance by controlling size or quantity of filler. The main problem during the production of the composite, that changes properties continuously, is suitably choice of technological parameters. These materials have application in aircraft, automotive industry, space equipment, marine equipment and many others [18-21].

In a functionally graded material (FGM) properties change gradually with position. The property gradient in the material is caused by a position-dependent chemical composition, microstructure or atomic order. In the case of a position-dependent chemical composition the gradient can be defined by the so-called transition function $ci(x, y, z)$ which describes the concentration of the component ci as a function of position. Already in 1972, the usefulness of functionally graded composites with a graded structure was recognized in theoretical papers by Bever and Duwez [22], and Shen and Bever [23]. However, their work had only limited impact, probably due to a lack of suitable production methods for FGMs at that time. It took 15 more years until systematic research on manufacturing processes for functionally graded materials was carried out in the framework of a national research program on FGMs in Japan [24]. Since then, a major part of the research on FGMs was dedicated to processing of these materials and a large variety of production methods has been developed. The manufacturing process of a FGM can usually be divided in building the spatially inhomogeneous structure (“gradation”) and transformation of this structure into a bulk material (“consolidation”). Gradation processes can be classified into constitutive, homogenizing and segregating processes. Constitutive processes are based on a stepwise build-up of the graded structure from precursor materials or powders. Advances in automation technology during the last decades have rendered constitutive gradation processes technologically and economically viable. In segregating processes a sharp interface between two materials is converted into a gradient by material transport. Segregating processes start with a macroscopically homogeneous material which is converted into a graded material by material transport caused by an external field (for example a gravitational or electric field). Homogenizing and segregating processes produce continuous gradients, but have limitations concerning the types of gradients which can be produced [25-26].

Structural gradients in the polymeric system may lead to a desired gradient in a single property, or to a combination of more than one property which may assume optimum values in different regions of the materials. Gradient materials have different functions, which characterize various distribution of properties for instance hardness, Young’s modulus, wear resistance, thermal expansion coefficient, electrical properties etc. It is possible owing to use of different mixtures of engineering materials such as metals, ceramics, and polymers. PGMs (Polymeric Gradient Materials) are inhomogeneous composites containing at least one polymer. In the case when there are more than one component, usually the first one is considered as matrix and the second component is reinforcement. Many different polymeric materials and their mixtures were used in PGMs. Apart others P/PA-6, PVC/PMMA, PP/EVA, alumina/epoxy, SiC/epoxy, UHMWPE/epoxy, PMMA/glass fibre, glass-fibre mat/PP, epoxy/carbon fibre, PP/carbon fibre/glass fibre were applied as PGMs [27]. There are few methods that allow to make effectively PGMs which are similar to FGMs. Some of them (among other gravity casting and centrifugal casting process) are described in this paper.

In polymers, like in other materials, compositional and micro-structural gradients are intended to allow an optimum combination of component properties, for example weight, surface hardness, wear resistance, impact resistance and toughness. Polymers with a porosity gradient, so-called polyurethane integral skin foams provide high impact strength at low weight and have been used since a long time for instrument panels or head rests in cars. Graded polymeric materials that have been processed so far include graded fibre composites, graded interpenetrating polymer networks, graded biodegradable polyesters. Compared to ceramic or metal based systems, the knowledge on processing methods for polymer FGMs is limited. In polymer composites, a gradient of the reinforcement can be introduced by centrifuging prior to polymerization. For example two resins can be used as matrix materials, while SiC particles, aramide particles, glass fibres and carbon fibres can be used as filler materials. Rings and tubes with a gradient in filler content were produced by centrifuging a dispersion of particles in a resin prior to hardening. The average filler content was chosen between 5 and 45%. After centrifugation the filler content in the outer portions of the rings increased up to 27% for glass fibres and to 45% for SiC particles, for an average filler content of 20%. This significant difference between different filler materials was primarily attributed to the aspect ratio of the filler particles, which was about 200 for the glass fibres and 1 for the SiC particles. A smooth gradient in the filler concentration could be produced by adjusting the rotation speed of the centrifuge and the viscosity of the resin. The latter could be increased by curing for a given time before centrifugation. A viscosity 25 Pa s was found suitable for centrifugation of carbon fibres - a lower viscosity of 5 Pa s lead to a complete sedimentation of the carbon fibers during thermosetting. The wear resistance of thermosetting polymers was improved by the addition of the hard filler particles or fibres. It was demonstrated that the gradient in filler content leads to a corresponding gradient in micro-hardness and wear resistance [27-30].

In the framework of the priority program, gradient formation by sedimentation of solid graphite particles in epoxy matrix was investigated. Gravity casting method is one of the methods relying on gravity without applying pressure. It is possible to produce spatially distribution of component materials by casting step-by-step two or more melts. First of all one of melts is poured and when is partially solidified or crosslinked then the second melt is poured [31]. One of the effective methods applied in production of PGMs is the centrifugal technique. The casting method depends upon type of forming material which can be in form of paste or powder. The material is located close to heated mould’s wall. Mould with processed mixture is rotated around one or two perpendicular axis. Mixture during the process is heated inside the mould. As a consequence of applied centrifugal force one of the components sediments gradually on the form’s walls. Next the form is cooled and moulding is took out. In previous works described in literature it was shown that this method could be successfully used for PGMs. The gradation of properties can be controlled for instance by changing rotational velocity and time of centrifugation but also by size, shape and amount of particles. In this way diverse density distribution was obtained in searched materials [32].

During sedimentation in a column differences in the particle velocity caused by different density or size of the powder particles lead to de-mixing of the different particle types If sedimentation occurs in a liquid column free of particles a gradient with a continuous increase or decrease of the concentration of one particle type will be formed. If the sediment is directly formed from the suspension a complicated transition function is retained. The bottom layer will still have the average composition of the suspension followed by an increase of de-mixing and the top of the sediment contains only the powder fraction with the lowest sedimentation velocity. A similar gradient will be obtained for a filtration process accompanied by sedimentation. If sedimentation is carried out in highly loaded suspensions, problems due to inter-particle interactions occur frequently. Another obvious disadvantage of sedimentation processes are limitations of the types of gradients that can be produced [33].

The purpose of this work was to evaluate influence of graphite filler on electrical properties of casted composites. Surface and volume electrical resistivity was determined.

2. Experimental

Sedimentation of graphite during gravitational casting produced composites with different filler content throughout the thickness of specimens. On the basis of electrical properties research results the dependence of surface and volume resistivity on specimen thickness was determined. Performed research had a preliminary character because only one polymeric and only one graphite type were applied. It is planned to continue research for other polymeric systems.

2.1. Materials

The thermosetting matrix used in this study was epoxy resin (EP), RE28/A, from GPS CO. GENERAL CHEM (Italy) cured at room temperature with 50% by weight of hardener RE28/B. The density of the epoxy resin was 1.19 g/cm3. Graphite powder PV60/65 (KOH-I-NOOR, Czech Republic) was used as filler and electric properties modifier. The density of the graphite was 2,207 g/cm^3. Basic characteristics of component materials are shown in tables 1-3.

Table 1.
Physical and chemical properties of epoxy resin RE28/A [34]

Form	Black high-viscosity liquid
Odour	weakly sensible
Value pH	about 7
Combustibility	combustible
Explosive properties	uncreated explosive menace
Density in 23^{0}C	1,19 g/cm^3 +/-0,05
Viscosity in 25^{0}C	3000 - 4000 MPa·s

Table 2.
Physical and chemical properties of hardener RE28/B [34]

Form	pale yellow liquid
Odour	weakly sensible
Value pH	about 7
Combustibility	combustible
Explosive properties	uncreated explosive menace
Density in 23^{0}C	0,98 g/cm^3 +/-0,05
Viscosity in 25^{0}C	5000-6000 MPa·s

Table 3.
Basic characteristics of graphite PV 60/65 [35]

Chemical constitution	PV 60/65
Carbon contents	64,8 %
Ash contents	35,2 %
Degree of size reduction	<125 μm 10%
Density	2,207 g/cm^3

2.2. Samples preparation

The specimens were obtained using gravitational casting methods which is one of the technologies relying on gravity without applying pressure. With this method it is possible to produce one dimensional gradient of component materials content in liquid matrix. The gradient is retained after matrix solidification. Due to sedimentation process, the highest filler content is expected in the lowest sample layer. The procedure of samples preparation is shown schematically in Fig. 1.

Specimens were cast into our own design and construction steel mould. Cavity of the mould has the following dimensions: diameter - 100mm, depth - 12mm (Fig. 2). Inner side walls of cavity were made with 3° inclination to facilitate ready specimens removal. In effect disk shaped specimens with 100mmx10mm dimensions were produced in the mould. Additional side handles were provided to facilitate later grinding of specimen surface (Fig. 3).

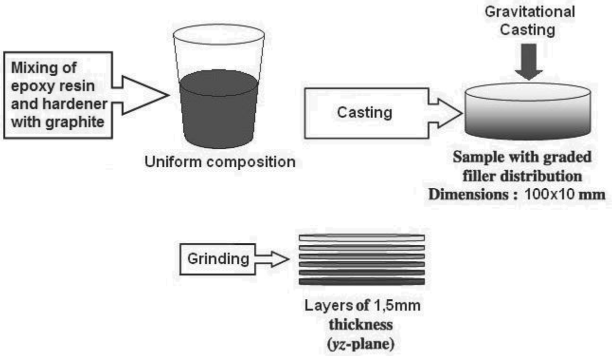

Fig. 1. Scheme of specimens preparation

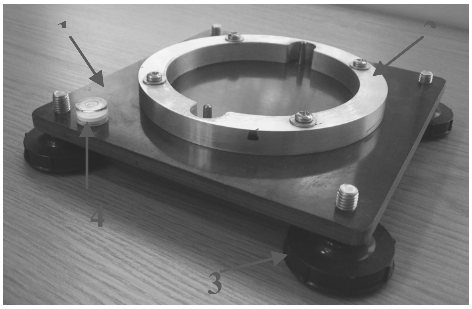

Fig. 2. Mould to specimen casting; 1 –bottom plate, 2 – steel ring, 3 – mould levelling foot, 4 – level line

Fig. 3. Shape of the specimen

2.3. Measurements methodology

Surface and volume resistivity were applied as a measure of electrical properties. Measurements were performed according to Polish standard PN-88/E-04405. The idea of the test was to define electrical resistivity in sequential layers with different content of conductive component (graphite). First, specimen's thickness was measured and electrical resistivity tested. Next outer layer was removed by grinding. Next, following thickness and resistivity measurements and grinding procedures were repeated. Five layers in each specimen were researched. Scheme of measuring surfaces of sequential layers is presented in Fig. 4.

Measurements of the electrical conductivity were carried out with a surface and volume resistivity testing device (Insulation Resistance Tester Type P435) presented Fig. 5. The surface resistivity is the ability of a material to leak away localized charges along the surface, and it is related to the ability of a sample to control the electrostatic discharge. It is defined as the electrical resistance of the surface of an insulating material. In this study, it was determined by voltmeter-ammeter method. Parameters of the system for measurement of the surface and volume resistance are presented in Table 4. The electrical conductivity was measured between the two electrodes by applying a voltage across the surface of the sample, measuring the resultant resistance, and then performing the following calculation.

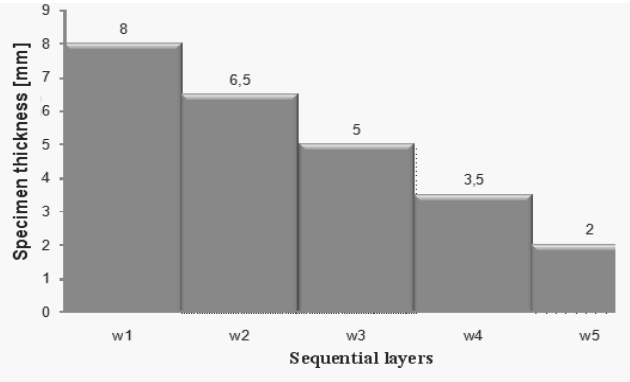

Fig. 4. Scheme of measuring layers

$$R_x = \frac{U \cdot R_B}{U_s} [\Omega] \qquad (1)$$

where, R_x is measured resistance [Ω], R_B is shunt resistance [Ω], U is source voltage [V], U_s is measured voltage [V],

Table 4.
Measurement surface and volume resistance parameters

Electric source voltage U_s [V]	2500
Plate (electrode) outside diameter D [mm]	50
Ring inside diameter [mm]	60
Ring outside diameter [mm]	80
Resistance measurement time [s]	60
Shunt resistance R_B [MΩ]	1
Distance between the electrodes [mm]	5

Fig. 5. Insulation Resistance Tester Type P435

In purpose to determine electric resistivity, specimens were placed in a suitable electrode system and constant voltage with definite value was applied. Total current or his components (surface and volume) were measured. Taking into account measured values surface resistance and volume resistance were calculated and than surface and volume resistivities. The scheme and photograph of the measurement system are presented in Fig. 6 and 7 respectively.

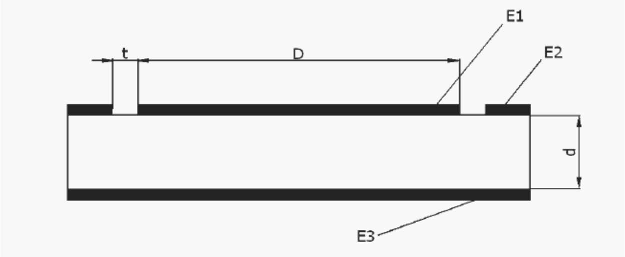

Fig. 6. Scheme of system to surface and volume resistance measurement; E1 – measurement electrode (plate), E2 – voltage electrode (ring), E3 – protective electrode (plate)

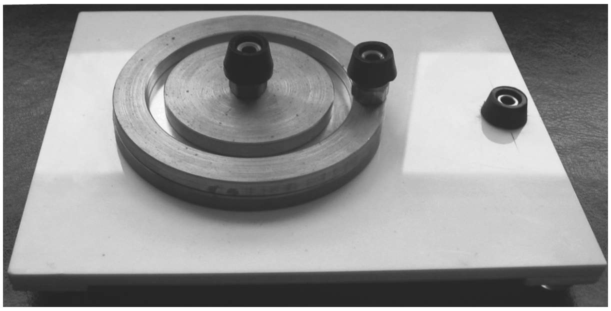

Fig. 7. Measurement system to surface and volume resistance

3. Results and their analysis

On the basis of obtained results graphs showing dependences of surface and volume resistances and resistivities on specimen thicknesses were prepared and analysed. Mean values calculated from six measurements are shown.

3.1. Surface resistance and resistivity

Surface resistance and resistivity decreased together with decreasement of specimen thickness. It is obvious result of increasing content of graphite filler in sequential, deeper placed layers (Fig. 8-13). Addition of 3-6%vol. of graphite to epoxy resin caused limited, almost linear, decrease of surface resistance and resistivity in depth direction of specimens (Fig. 8,10,11). But addition of 9-12%vol of graphite in polymeric composite caused rapid, non-linear with layer depth, decrease of surface resistance and resistivity (Fig. 9,12,13). It is in accordance with earlier mentioned possibility of forming spatial network by conductive filler particles. Results scatter for composite with 12%vol of graphite (Fig. 9,13) was probably caused by non-homogenous filler distribution in composite volume. High viscosity of this composite made mixing very difficult. Long lasting mixing was impossible because of limited pot life of this formulation.

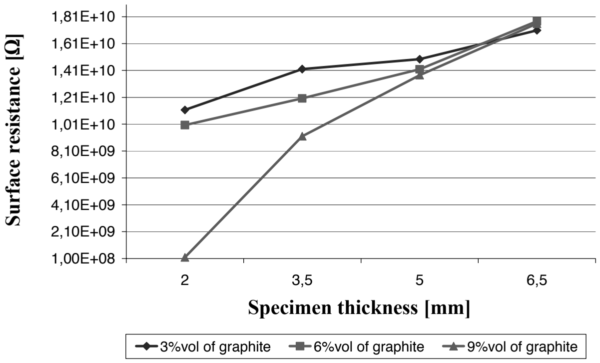

Fig. 8. Relationship between surface resistance and specimen thickness for specimen containing 3-9%vol of graphite PV60/65

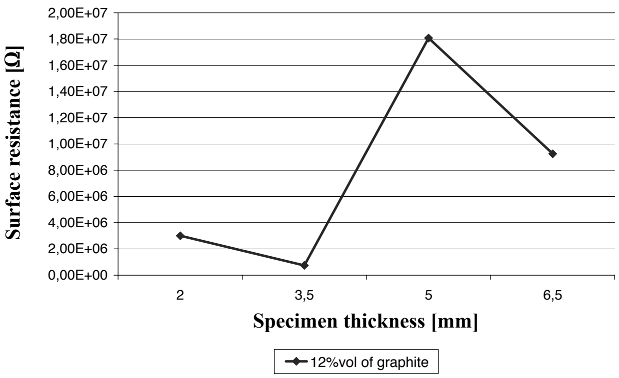

Fig. 9. Relationship between surface resistance and specimen thickness for specimen containing 12%vol of graphite PV60/65

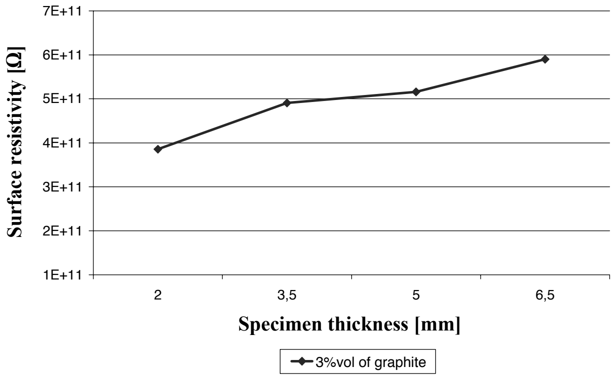

Fig. 10. Relationship between surface resistivity and specimen thickness for specimen containing 3%vol of graphite PV60/65

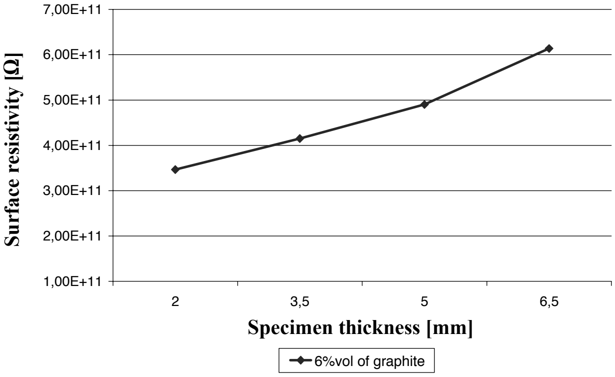

Fig. 11. Relationship between surface resistivity and specimen thickness for specimen containing 6%vol of graphite PV60/65

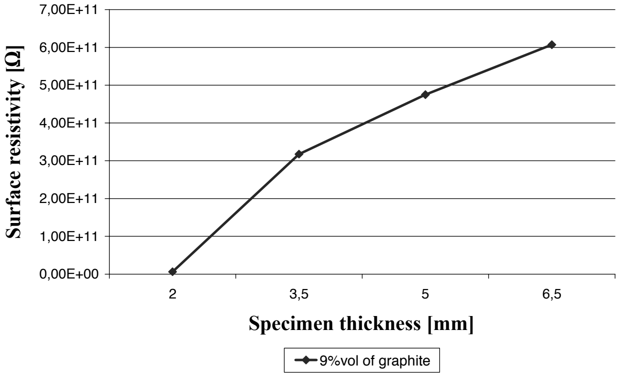

Fig. 12. Relationship between surface resistivity and specimen thickness for specimen containing 9%vol of graphite PV60/65

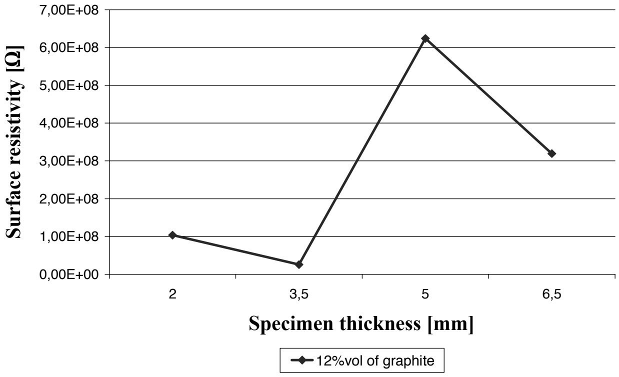

Fig. 13. Relationship between surface resistivity and specimen thickness for specimen containing 12%vol of graphite PV60/65

Achieved results show that applied casting method is suitable for producing PGM with very low surface resistivity on one side of a plate and very high surface resistivity on the other side. Inside of this composites continuous gradient of surface resistivity was achieved. Such composites may be very attractive in many applications where surface static electricity have to be avoided and simultaneously high volume resistivity retained. Possible applications include electronic elements and appliances, parts of mining machines and equipment, parts working in explosive atmospheres and many others.

3.2. Volume resistance and resistivity

Graphs of relationships between volume resistance and resistivity and specimen thickness for composites containing 9 and 12%vol of graphite are shown in figures 14-17. Lesser addition of graphite filler (3-6%vol) did not have substantial influence on volume resistance and resistivity. Only for deepest layer, with highest graphite content, minute resistance decrease was observed. On the other hand 9-12%vol. content of filler in polymeric composite caused rapid, non-linear decrease of volume resistivity with layer depth.

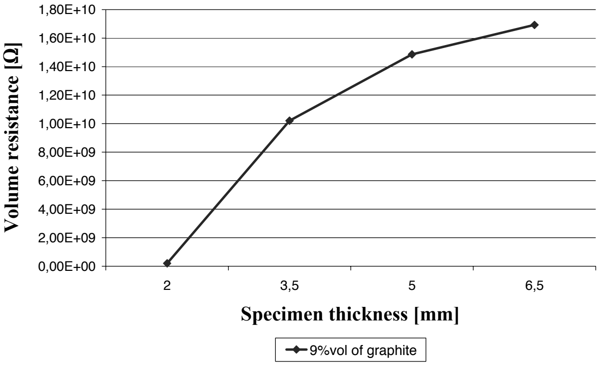

Fig. 14. Relationship between volume resistance and specimen thickness for specimen containing 9%vol of graphite PV60/65

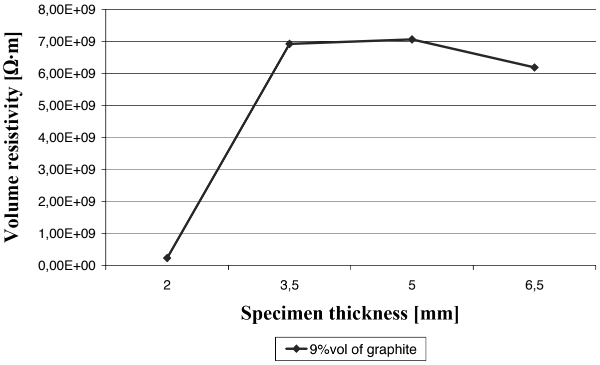

Fig. 15. Relationship between volume resistivity and specimen thickness for specimen containing 9%vol of graphite PV60/65

Presented graphs (Fig. 14-17) show that the most pronounced volume resistivity decrease was achieved for layers with the highest graphite powder content. Once again it proves the possibility of forming spatial network by conductive filler particles in this layer. High level of volume resistivity of samples with full thickness was retained, so earlier mentioned possible applications are confirmed here.

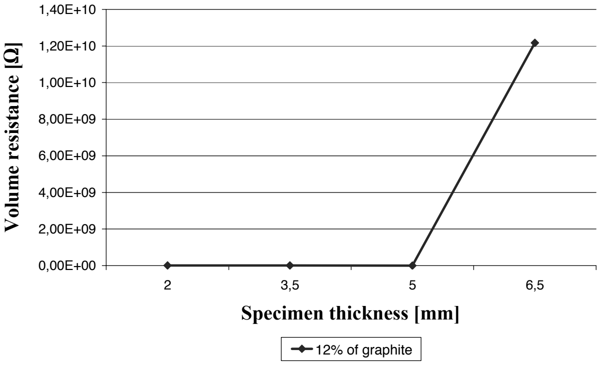

Fig. 16. Relationship between volume resistance and specimen thickness for specimen containing 12%vol of graphite PV60/65

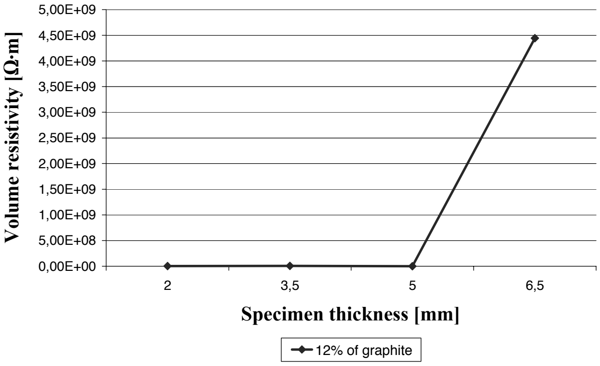

Fig. 17. Relationship between volume resistivity and specimen thickness for specimen containing 12%vol of graphite PV60/65

4. Conclusions

This study was carried out in order to evaluate the electrical properties of the gradient composites. On the basis of obtained results the following conclusions were drawn:

1. Addition of 3-6%vol. of graphite to epoxy resin caused limited, almost linear, decrease of surface resistivity in depth direction of specimens.
2. Higher content of filler (9-12%vol) in polymeric composite caused rapid, non-linear with layer depth, decrease of surface and volume resistivity.
3. Addition of lesser amount of graphite filler (3-6%vol) do not have large influence on volume resistance and resistivity.
4. Applied gravitational casting method is suitable for producing PGMs with very low surface resistivity on one plate side of and very high surface resistivity on the other side. Inside of this composites continuous gradient of electric resistivity may be achieved.
5. Composites with gradient of electrical resistivity may be very attractive in many applications where surface static electricity have to be avoided and simultaneously high volume resistivity retained.

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