Electrical properties of polymeric gradient materials based on epoxy resin filled with hard coal

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Properties

ABSTRACT

Purpose: of this paper was to describe functionally the gradient polymeric materials and technology of the gradient production. The experimental part describes preparation of circular disc samples of polymeric gradient material by gravity casting method. Finally electrical surface resistance and surface resistivity was measured and analysed.

Design/methodology/approach: Eight specimens were prepared using gravity casting method. Composites with epoxy resin as a matrix and with respectively 3, 6, 9 and 12%vol of two types of hard coal 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 and type of conductive component (hard coal). 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, dependence of surface resistivity on depth of the layer was determined.

Findings: The experimental results demonstrated that addition of conductive filler (hard coal) to epoxy resin caused a change of surface resistivity of these materials. Hard coal together with epoxy resin formed gradient composite material with different filler content in subsequent layers.

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

Originality/value: This paper is original because in the research programme electrical properties of new type of polymeric gradient composites were tested and presented in it.

Keywords: Electrical properties; Functionally polymeric gradient materials; Hard coal; Filler

1. Introduction

Functionally Gradient Materials (FGMs) are not a quite new group of materials because these materials were known since many years and for the first time they were described in scientific literature in 1972. Bever and Duwez recognized these materials as separate class of composites with a graded structure in their theoretical papers [1, 2]. However, their work had only limited impact, probably due to a lack of suitable production methods of FGMs at that time. Functionally gradient materials [3] are an innovative and attractive class of composite materials. If the functional gradient is properly designed, FGMs may show unexpected properties, which differ from those of their ingredient materials and also from those of the traditional (not graded) composite materials having the same mean composition [4]. The manufacturing process of a FGM can usually be divided into building 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 homogenizing 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 [5]. In order to use FGMs in structural and functional applications, however, a suitable fabrication technique is needed that makes it possible to produce precisely the micro-structural and compositional gradient required and to assure high reproducibility of the gradient [6-11].

Gradient polymer materials are already known also in Poland, even though developed and used on a smaller scale. Most of the publications on functional materials and among them gradient materials concern composites with metallic or ceramic matrixes. Literature describing functional materials based on polymers or with polymeric matrix is still very limited. In polymers, like in other materials, compositional and microstructural gradients are intended to admit an optimum combination of component properties, for example weight, surface hardness, wear resistance, impact resistance, surface and volume resistance and toughness [12].

Gradient polymer materials enable connection of various properties of composite components and are characterized by a gradual change in the chemical composition and/or structure in volume or at least in one direction, what manifests itself in analogues changes in properties. They are usually composite materials in the general sense of this term. The gradient of structure can also be obtained in traditional polymeric materials, monolithic and homogeneous initially, on the basis of structural changes generated by variety of ways. Main possibilities are different processing technologies and they induce an impact of variety of external factors. Such materials may not contain a regularly formed sharp grain boundaries or interfacial surfaces between various areas, as it is the case of conventional composite materials. Thanks to continues composition or structure changes it is possible to reduce concentration of thermal and mechanical stresses in gradient materials. In this way, a lot of new applications are possible and in some extend it is also possible to design materials with needed spatial properties changes. In practice structure of FGMs materials is usually heterogeneous in one direction, typically in a chosen direction because of the future use. Thermoplastics (polyamides, polyolefins, acrylic and vinyl resins) and thermosetting resins (polyester, phenolic, phenol-formaldehyde, epoxy, melamine, silicone) may be applied as polymer matrixes of composite gradient materials. Whereas solid materials used as fillers of polymer matrixes can be in the form of powders (wood flour, chamotte powder, chalk, talc and coal), fibres (natural, metal, glass, aramid or carbon) or gas cavities (foam). There are many methods of forming polymeric gradient materials which are similar to metallic or ceramic FGMs. Methods of manufacturing the functionally gradient materials include: spraying processes, deposition and surfacing processes, methods of powder metallurgy, method of forming, processing, liquid-phase methods, or other specialty methods, such as sequential thin layers casting. A special place occupies plastics modelling techniques with resultant variability of the spatial, functional properties. Polymer modifications are aimed, among others, at improving mechanical characteristics, changing optical properties such as colours, reducing the combustibility of the polymer, increasing the electrical conductivity etc. In addition, modifiers introduced into the polymers, fillers in particular, have significant impact on technological processing characteristics of received materials [13-27].

In the present paper, structure, electrical properties and possible applications of hard coal filled with polymeric gradient materials are discussed. Therefore, a short description of solid fillers, especially pulverized hard coal, applied in polymer matrixes is needed.

Powder fillers are products of many different materials disintegration. A very broad particle size interval is applied in polymeric materials. In recent years nanofillers are very popular but particles with diameter up to dozens of millimetres are still widely applied (e.g. polymeric concretes). Most of fillers are inert in relation to matrix material. Fillers are added to polymeric materials mainly to change their properties, but in many cases they are introduced in order to lower the price of the finished product. A distinguished group among mineral powdered fillers are antipyrenes, which play a role of flame retardants and minimize flame influence on the material. The most widely used mineral fillers are oxides of such elements as aluminium, titanium, zinc, magnesium, potassium carbonate, barium, calcium, hydroxides of calcium, magnesium and aluminium. Apart from mineral fillers, a broad range of organic substances is applied. It must be taken into consideration that positive influences of fillers are, in many cases, coupled with negative effects. Usually, when some properties are improved, the others are deteriorated. Mainly processing properties (e.g. viscosity) change negatively in effect of fillers introduction [28-31].

One of the natural resources that can be used as a filler material, and which so far has been used almost exclusively as raw energetic material, is coal. Coal is a natural rock of organic origin, containing 75-97% of carbon, formed mainly in the Carboniferous (Palaeozoic) from plant debris, as a result of coalification without

oxygen access. It has a complex chemical structure. The classification of coal is generally based on the content of volatiles. Coal has a black colour, matte gloss and black scratch. Coal has very good thermal resistance, it burns slowly giving intense heat. The temperature of decomposition of organic matter depends on the degree of metamorphism of coal, and consequently, the carbon content of chemical element C. Mined coal is widely used as fuel but carbon contained in other substances is applied widely as polymer filler. Application of carbon black is generally known as (amorphous carbon), graphite, carbon fibres and carbon nanotubes. Recently, pulverized hard coal has also been applied, mainly to modify thermosetting resins [32-33].

The aim of this work is to prepare materials which will exhibit different electrical properties on cross-section of a sample (saying it in other words, it will exhibit spatial properties variation). It is generally known that epoxy resin is dielectric (insulating) material. On the surface of such materials unbalanced electric charge appears (it is known as electrification of material), it is a menace in coal mining and chemical industry and similar applications. Therefore, it is desirable to decrease static electricity of this material. It can be achieved by lowering electrical resistance on the surface and gradually increasing this resistance in the volume of composite. This means that preparing gradient material with improved electrical conductivity on one side of a sample, it will not change conductivity on the opposite side. Next purpose of this work was to evaluate influence of hard coal on electrical resistivity of as-cast functionally polymeric graded materials. Surface electrical resistivity was determined and analysed.

2. Experimental

Sedimentation process of two types of fine particles of hard coal during gravitational casting produced composites with different filler content throughout the thickness of specimens. On the basis of research results of electrical properties the dependence of surface resistivity on depth of the layer through the specimen thickness was determined. Performed research had a preliminary character because only one polymeric resin and two types of hard coal as filler were applied. It is planned to continue this research for other polymeric systems.

2.1. Materials

The thermosetting matrix used in this study was epoxy resin (EP), Epidian 6, cured at room temperature with Z-1 hardener produced by „Organika – Sarzyna" Chemical Plant S.A. (Poland). The density of the epoxy resin was 1.17 g/cm^3. Two types of hard coal were used as a filler and electric properties modifier. The density of the anthracite coal filler (mined in Kuzbas of the Kuznetsk Basin) was 1.40 g/cm^3 and density of the second type of hard coal acquired from "Zofiówka" coal-mine was 1.39 g/cm^3. Basic characteristics of component materials are shown in Tables 1-4 and SEM micrographs of fillers particles are presented in Fig. 1.

Table 1.
Physical and chemical properties of Epidian 6 epoxy resin [33]

Form	Pale, yellow, high-viscosity liquid
Odour	weakly sensible
pH Value	about 7
Combustibility	combustible
Ignition point	>200°C
Autoignition point	>300°C
Boiling point	>200°C
Density in 23^{0}C	1.17 g/cm^3
Viscosity in 25^{0}C	10000 - 15000 mPa·s

Table 2.
Physical and chemical properties of Z-1 curing agent [33]

Form	pale yellow liquid
Odour	typical of triethylenetetramine
pH Value	about 7
Boiling point	277°C
Ignition point	122 ^{o}C
Autoignition point	335 ^{o}C
Density in 23^{0}C	about 0.981 g/cm^3

Table 3.
Basic characteristics of anthracite coal

Carbon content	87.9 %
Ash content	3.37 %
Specific surface	0.146 m^2/g
Range of grain size	$d_{10\%} = 20.12$ μm $d_{50\%} = 132.64$ μm $d_{90\%} = 358.36$ μm
Density	1.37 g/cm^3

Table 4.
Basic characteristics of hard coal from "Zofiówka" coalmine

Carbon content	88.5 %
Ash content	16.78 %
Specific surface	0.939 m^2/g
Range of grain size	$d_{10\%} = 2.92$ μm $d_{50\%} = 17.93$ μm $d_{90\%} = 64.25$ μm
Density	1.40 g/cm^3

a)   b)
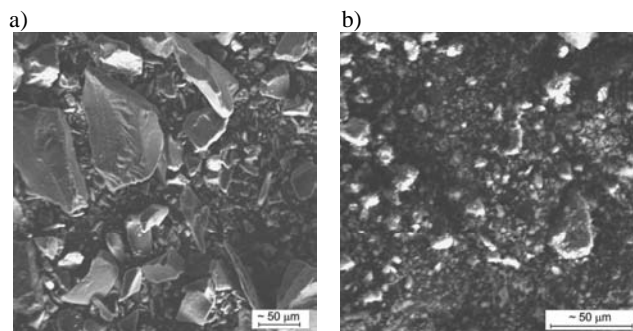
Fig. 1. SEM of coal particles (a) anthracite and (b) type 35 hard coal - "Zofiówka" coal-mine

J. Stabik, M. Szczepanik, A. Dybowska, Ł. Suchoń

2.2. Samples preparation

The specimens were obtained using gravitational casting methods which is one of the technologies about gravity without pressurisation. 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 specimen layer. The procedure of specimen`s preparation is shown schematically in Fig. 2.
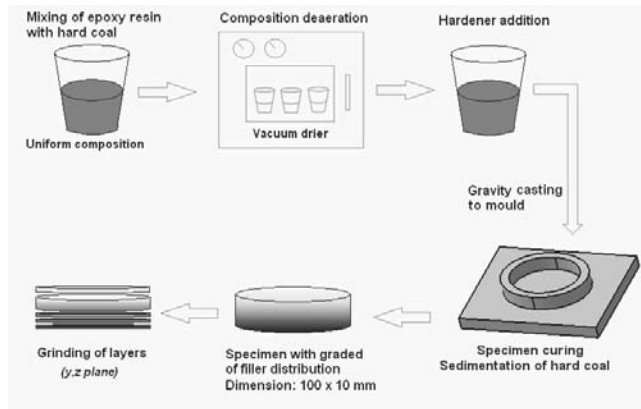

Fig. 2. Scheme of specimen's preparation
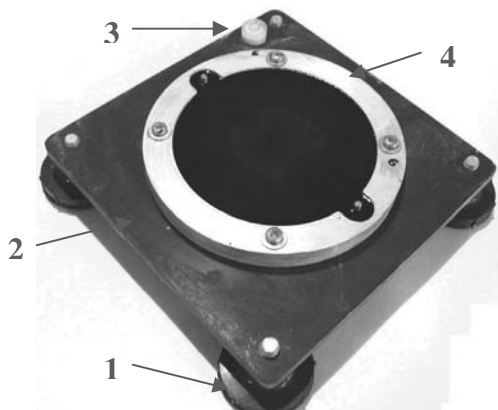
Fig. 3. Casting mould with a cast sample; 1 – mould levelling foot, 2 – bottom plate, 3 – level line, 4 – steel ring
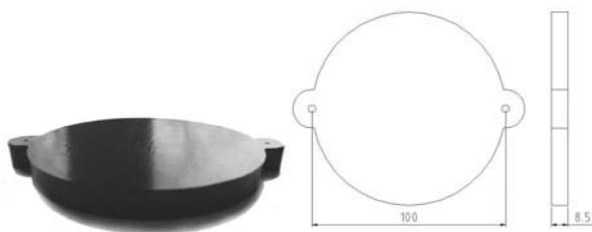
Fig. 4. A picture and shape of the specimen

Specimens were cast into a steel mould of our own design and construction. Casting cavity of the mould has the following dimensions: diameter – 100 mm, depth – 12 mm (Fig. 3). Inner walls of the cavity were made with 3^0 inclinations to facilitate ready specimen's removal. Additionally, for the same reason, all cavity surfaces were covered with Teflon® fabric. In effect, disk shaped specimens with 100 mm x 10 mm dimensions were produced in the mould. Additional side handles were provided to facilitate later grinding of specimen's surface (Fig.4).

2.3. Measurements methodology

Surface resistivity was applied as a measure of electrical properties. Measurements were performed according to the Polish standard PN-88/E-04405. The idea of the test was to define electrical resistivity in sequential layers of different content of conductive component (hard coal). The bottom of the sample was treated as the outer surface (Fig.5). First, specimen's thickness was measured and electrical resistivity tested. Then, the outer layer was removed by grinding. Next, following thickness and resistivity measurements, grinding procedures were repeated. Four layers (marked as w1-w4 in the Fig. 5) in each specimen were researched. Scheme of measuring surfaces of sequential layers is presented in Figs. 5 and 6.
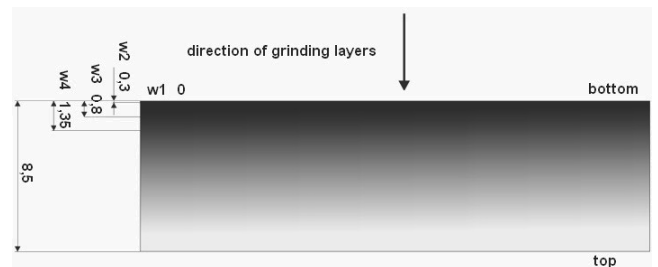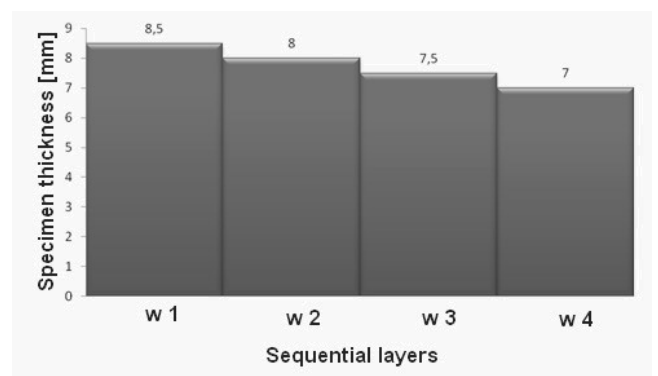

Fig. 5. Direction of layers grinding

Fig. 6. Scheme of layers measuring

Measurements of the electrical conductivity were carried out with a testing device for surface resistivity (Resistance Tester - Milli TO3 type) presented in Fig. 7. The surface resistivity is the ability of a material to distribute localized charges evenly 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 the voltmeter-ammeter method. Parameters of the system for measurement of the surface resistance are presented in Table 5. The electrical conductivity was measured between the two electrodes by feeding voltage across the surface of the sample, measuring the resultant resistance R_s, and then performing the following calculation of the resistivity ρ_s (1):

$$\rho_s = \frac{R_s \cdot B}{g} \, [\Omega] \tag{1}$$

where, R_s - measured resistance [Ω], B - effective length (circumference) of measurements electrode [m] (2), g - gap width [m].

$$B = \pi \cdot (D + g) \, [m] \tag{2}$$

where, D – centre electrode diameter.

Table 5.
Parameters of surface resistance measurement

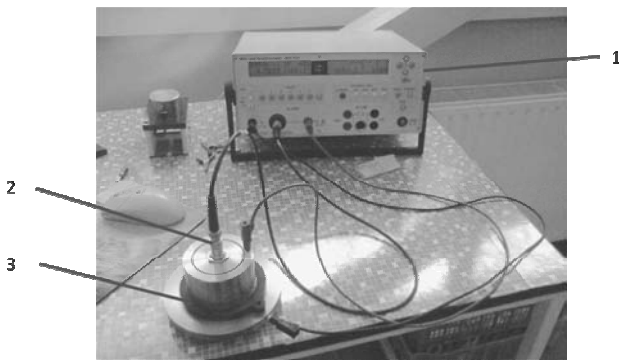|	
Electric source voltage - U_s	500 [V]
Centre electrode diameter - D	50 [mm]
Inner ring diameter	60 [mm]
Outer ring diameter	80 [mm]
Resistance measurement time	60 [s]
Distance between the electrodes – g	5 [mm]

Fig. 7. System for surface resistance measurement: 1 - Resistance Tester - Milli-TO3 type, 2 – measurement electrodes, 3 – specimen.

In purpose to determine electric resistivity, specimens were placed in a suitable electrode system and constant voltage of definite value was fed. Total current or its components (surface) were measured. Taking the measured values into account, surface resistance and then surface resistivities was calculated. The scheme and photograph of the measurement electrodes system are presented in Figs. 8 and 9, respectively.
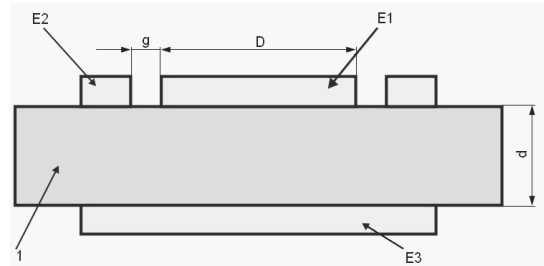

Fig. 8. Scheme of electrodes system for the surface resistance measurement: 1 – specimen, E1 – measuring electrode (plate), E2 – voltage electrode (ring), E3 – protective electrode (plate), D - electrode diameter, g - gap width, d – specimen thickness
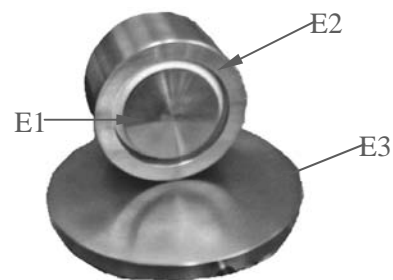

Fig. 9. Surface resistance measuring electrodes

3. Results and their analysis

On the basis of obtained results, the graphs showing dependences of surface resistances and resistivity's on depth of the layer were prepared and analysed. Mean values calculated from six measurements are shown.

3.1. Surface resistivity

Surface resistivity gradually increased along with depth of tested layer up to the surface resistvity of clear epoxy resin. It is an obvious result of hard coal filler content decrease in sequential, deeper placed layers (Figs. 10-13).

Addition of 3%vol. of hard coal to epoxy resin gave gradient composite a rapid, non-linear increase of surface resistance and resistivity along with the depth position of the layer (Fig. 10). But addition of 6-9%vol of hard coal to polymeric composite allowed achieving gradient material with limited, almost linear, increase of surface resistance and resistivity in depth direction of specimens (Figs. 11, 12). It is in accordance with earlier mentioned possibility to form spatial network by conductive filler particles. For 12%vol fracture, hard coal from "Zofiówka coalmine exhibited slower increase of surface resistivity than anthracite (Fig. 13). It was probably caused by smaller particle size of this coal and consequently by slower sedimentation resulting in broader filler distribution in thickness direction of sample.
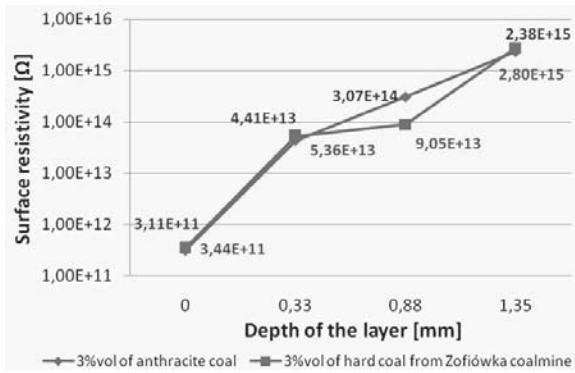
Fig. 10. Relationship between surface resistivity and depth of the layer for specimens containing 3%vol of two hard coal types
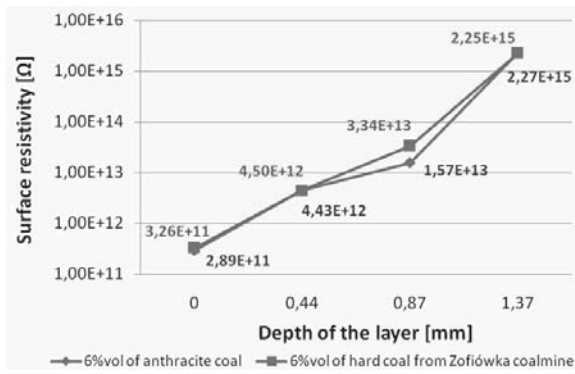

Fig. 11. Relationship between surface resistivity and depth of the layer for specimens containing 6%vol of two hard coal types
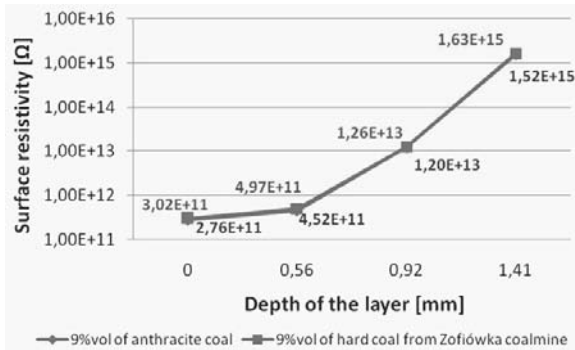

Fig. 12. Relationship between surface resistivity and depth of the layer for specimens containing 9%vol of two hard coal types

Relations for all volume fractures are presented in Fig. 14 and Fig. 15. Surface resistivity of outer surface is almost the same for all composites. It proves that due to sedimentation process maximum packing of filler particles was achieved independently on initial volume fracture of the filler. Very pronounced surface resistivity decrease was achieved for this surface what is a very positive result of performed research. Substantial differences appear in deeper layers. Here, the higher initial filler content is, the lower is the measured surface resistivity. It shows that maximum packing was not achieved in these composite regions. For layers located 1.3 mm

deep and deeper surface resistivity is once more the same for all composites and is equal to surface resistivity of unfilled epoxy resin. It indicates that all filler particles in ready composites are comprised from bottom to 1.3 mm depth. The only exception is composite with 12%vol content of hard coal from "Zofiówka" coalmine which was discussed earlier.
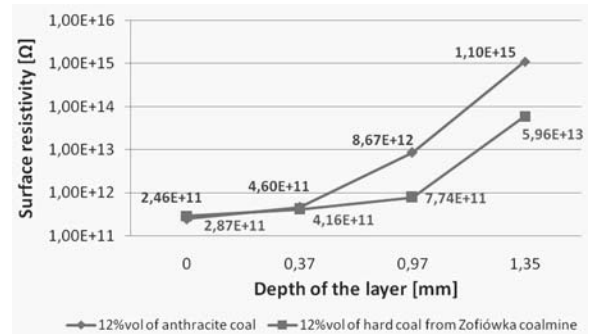

Fig. 13. Relationship between surface resistivity and depth of the layer for specimens containing 12%vol of two hard coal types

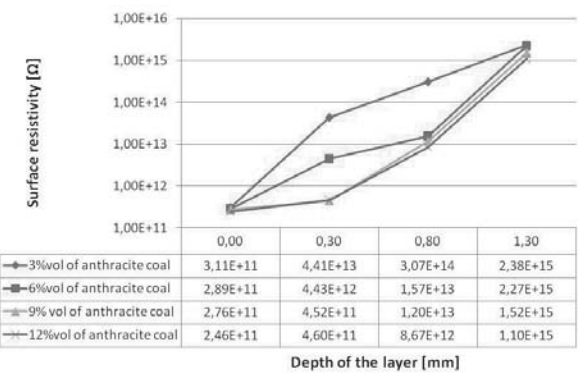Fig. 14. Relationship between surface resistivity and depth of the layer for specimens containing 3-12%vol of anthracite coal
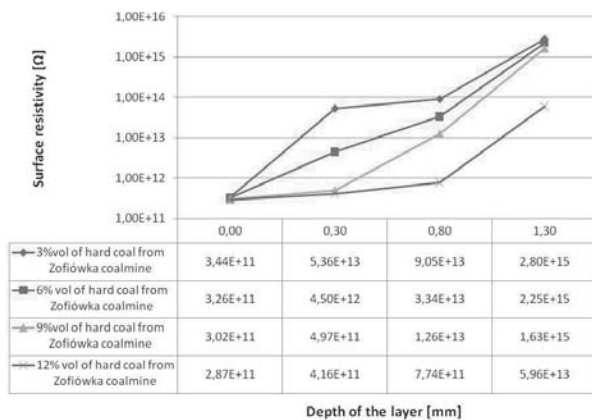

Fig. 15. Relationship between surface resistivity and depth of the layer for specimens containing 3-12%vol of hard coal from "Zofiówka" coalmine

The following graphs (Figs. 16-19) show a comparison of results achived for two different types of coal. No considerable differences in measurements results were observed for antracite and a type of 35 hard coal. For each pair of specimens with the same filler content and the same depth of measured layer, surface resistivity was very similar.
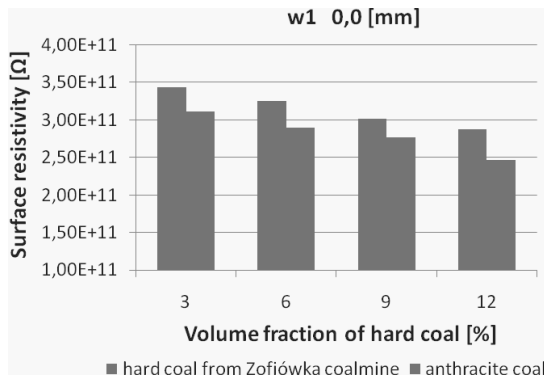

Fig. 16. Relationship between surface resistivity and content by volume of hard coal for the first layer (w1) of specimens
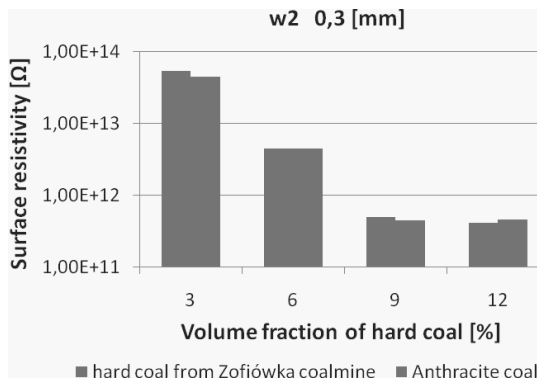

Fig. 17. Relationship between surface resistivity and content by volume of hard coal for the second layer (w2) of specimens
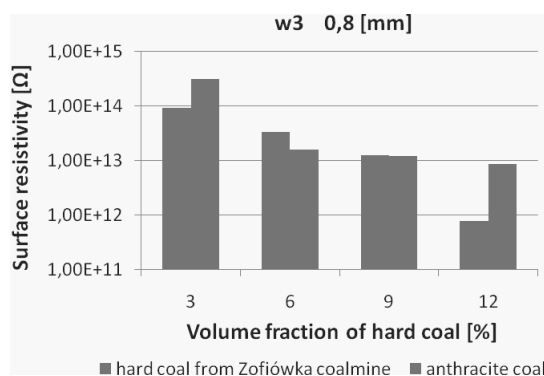

Fig. 18. Relationship between surface resistivity and content by volume of hard coal for the third layer (w3) of specimens
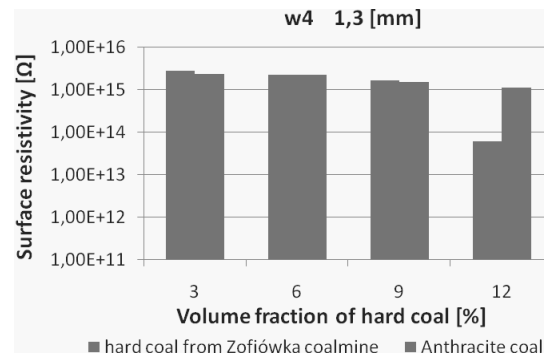

Fig. 19. Relationship between surface resistivity and content by volume of hard coal for the last layer (w4) of specimens

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

4. Conclusions

1. It is possible to produce polymeric graded materials by gravity casting methods.
2. Gradient composites with planned electrical resistivity distribution across sample's thickness were manufactured.
3. Very similar results were achieved for two different types of hard coal. Only specimen containing 12%vol of hard coal from "Zofiówka" coalmine have lower surface resistivity in comparison with anthracite filled specimen.
4. The research showed that all fillers' particles comprise after sedimentation in a layer less than 2 mm thick.
5. Therefore, in the following research it is planned to modify viscosity of a matrix in order to control particles sedimentation. Although, research is planned to determine volume content of particles in specified layers of gradient composite.

Acknowledgements

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