

Chosen manufacture methods of Polymeric Graded Materials with electrical and magnetic properties gradation

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Properties

ABSTRACT

Purpose: The purpose of the paper is to present main results of Polymeric Graded Materials (PGMs) investigations realized in Silesian University of Technology, Division of Metallic and Polymeric Materials Processing. Methods of PGMs manufacture with electrical and magnetic properties gradation are mainly discussed.

Design/methodology/approach: In short introduction general remarks on functionally graded materials (FGMs) and PGMs are presented. Next, methods used to prepare PGMs are presented together with physical basics determining composition, structure and properties gradation. Research methodology and chosen results showing PGMs structure and properties are also presented.

Findings: Achieved results show that it is possible do design graded material structure and composition and to manufacture PGM that not precisely but in high extend meets designed requirements. The basic condition to accomplish this task is that physical basics of structure and composition gradient formation are known and relations between technological process parameters and ready material characteristics are properly applied.

Research limitations/implications: Only chosen methods of PGMs manufacture are presented and only chosen PGMs characteristics are discussed.

Practical implications: Presented technologies are widely used in industry to processing polymeric materials. Defined changes in parameters and properly designed composition will allow to utilize these technologies to PGMs manufacture. Ready parts with properties gradation may be applied in almost all industry branches. Few possible applications are presented in the text.

Originality/value: New types of PGMs are described in the paper. Attention is paid mainly to materials with gradation of electrical and magnetic properties. The paper may be interesting for scientists involved in PGMs and for industry engineers looking for materials with electrical and magnetic properties gradation.

Keywords: Multifunctional materials; Polymeric Graded Materials; Electrical properties; Magnetic properties

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1. Introduction

Many definitions of ‘gradient materials’ or “graded materials” are given in the literature and some diversity of meaning exists [1-4]. Majority of definitions underlines two main characteristics of gradient materials. First of all, graded materials exhibit continuous and smooth variation of their properties in cross-section. Secondly, properties changes are achieved by spatial changes of structure or composition. Graded materials were recognized as a new class of materials when properties gradation was accepted as specially designed and manufactured to achieve planned functionality of given material and parts produced of it. This class of materials was called Functionally Gradient/Graded Materials (FGMs) [2]. Nowadays many scientific and industrial projects are realized to manufacture and apply this class of materials.

The term ‘gradient’ is precisely defined in mathematics in the theory of scalar fields [5]. Exact sense of gradient is applied mainly in physics. The meaning of gradient in materials science is quite different. As gradient materials are recognised all materials that exhibit macroscopic continuous and smooth spatial change of one or more properties. This is generally accepted as the most important characteristic. To determine a gradient at any point in mathematical sense the function describing properties or composition spatial changes has to be differentiable at this point, what means that it has to be continuous and ‘smooth’. But materials scientists and engineers are not interesting in the exact value of gradient vector in ready constructional parts made of gradient material. They are only interested in the direction of gradient and in achieved materials characteristics. The direction of gradient is usually assigned to the whole element and not to every point of this element. Because of this three different types of gradient (graded) materials are specified as unidirectional, two-directional and three-directional. These three types are very simple and special cases of all possible scalar fields for which it is possible to determine the gradient. Also parts of graded materials produced in laboratories and in the industry very often exhibit more complicated structure.

Essential advantage of gradient (graded) materials is the ‘smoothness’ of properties changes and lack of interfaces between phases constituting material. Smooth change of structure or composition is noted only in macroscopic observations. In microscopic scale these materials consists of individual grains, and particles. Very small dimensions of structural elements and their graded spatial distribution in material volume cause that in macroscopic scale no sharp properties changes are observed.

Taking into account the profile of structure, composition and properties changes many authors [2] distinguish between ‘gradient’ materials as materials with continuous and smooth changes and ‘graded’ materials as materials with stepwise changes. To the first class assigned are materials produced for example as a result of deposition, diffusion and sedimentation processes, to the second class are assigned materials produced for example as a result of co-extrusion, lamination and powder layers compression moulding. Because smoothness is observed only in macroscopic scale it is better to classify all materials under consideration as ‘graded’ materials. In recent literature this term is applied most frequently and in the following text this designation will be applied consistently.

Many combinations of different materials, different physical states and different geometrical configurations can form FGMs. Taking into account types of combined materials metallic, ceramic and polymeric graded materials are often specified. Polymeric Graded Materials (PGMs) are in the scope of interest of present paper.

There are three main means enabling properties gradation shaping: by composition selection, by processing parameters control and by post manufacture parts treatment. In the present paper chosen method of PGMs manufacture are shortly described and technological parameters influencing graded structure formation discussed.

2. Methods of PGMs manufacture

2.1. General remarks

There are two main classes of technological processes of FGMs manufacture. The first class comprises method of new material forming by sequential addition of layers or unit volumes. Such technologies as laminating, coextrusion, pressing, deposition or solid freeform fabrication belong to this class. The second class consists in modification of initially homogeneous system. To this class belong such technologies as centrifugal casting, heat treatment, surface treatment or infiltration. Another classification proposed Kieback, Neubrand and Riedel [6]. They classified gradation processes into constitutive, homogenizing and segregating. Constitutive processes consist in stepwise build-up of graded structure from precursor materials. In homogenizing processes sharp boundary between different materials is softened and graded region is formed by material transport phenomena. In segregating processes homogeneous systems are converted into graded material by material transport processes.

It is not possible to present in detailed manner all technologies of PGMs production. Only chosen, the most frequently applied technologies will be shortly described.

2.2. Compression moulding

Compression moulding is one of the oldest technologies of polymeric materials processing [7]. In this technique processed material in the form of powder, granules or pills is first placed in a cavity of heated open mould. In closed mould the material is molten and formed under the action of pressure at elevated temperature. For thermosetting materials (the most frequently processed) heat and pressure are maintained to cure the moulded material. For thermoplastic materials after part formation the polymer is cooled. Finally ready parts are removed from the mould cavity with ejectors.

In this technology composition gradation is achieved by pressing sequential layers with changing content of one or more components. Successive layers are compressed one by one or all layers are compressed together. With modern powders feeding systems it is possible to achieve material consisting of thin layers with almost continuous composition gradation.

In this process four physical phenomena determine strong joining of layers and sharp interfaces elimination. First, short

range particles transport phenomena takes place during powder compaction. Second, short range mixing takes place after polymer melting and molten material deformation. Third, in molten state diffusion is possible at the interfaces. Fourth, curing process across interfaces forms strong chemical bonds joining adjacent layers. As a result, very thin transient interlayer is produced between successive compressed layers.

In the compression moulding the main factors allowing graded structure shaping are the following:

- Materials used;
- Thickness of layers;
- Composition changes in successive layers;
- Mould and materials temperatures;
- Pressure of compression.

2.3. Gravitational casting

Gravitational casting is mainly applied to process liquid curable resins. Bulky parts and complicated products combining metallic and ceramic components with polymeric curable resins are manufactured with this technology.

This technology is applied to produce PGMs out of liquid resins filled with solid particles. Filler content gradation is achieved due to sedimentation of solid particles. Also other types of gradation such as foaming degree or crosslinking degree are possible but rarely applied. Sedimentation process results in particle concentration gradation but also in particles segregation with respect to their size and shape. Velocity of particle in sedimentation motion in gravitational casting is mainly influenced by particle diameter, particle shape and surface characteristics, densities difference, fluid viscosity and nature [8-10]. Many additional factors have to be taken into account such as particles interactions, particle size and shape distribution, viscosity changes due to polymerization process and temperature changes, rheological properties of Non-Newtonian fluids, convective and counter flows [10,11]. Interesting but very difficult to apply manner of controlling particles motion is to utilize viscosity increase during resin curing. For example it is possible to delay composition pouring into the mould after components mixing [12].

Finally in the gravitational casting the main factors which may be applied to control structure, composition and properties gradation are the following:

- particles size and shape distribution,
- particle surface characteristics,
- fluid and particles densities,
- fluid viscosity other rheological properties and their changes during curing time.

2.4. Centrifugal casting

Centrifugal casting as previously described technology is applied mainly to process liquid curable resins. Centrifugal casting is also used to produce polymeric graded materials manufacture out of curable resins filled with solid particles. Properties gradation is achieved mainly due to sedimentation resulting in filler concentration gradation and filler size segregation. The physical laws describing particles motion and their final distribution are the same as in the gravitational casting process.

The main difference is that gravitation is the driving force of particles radial motion. Velocity of particle is influenced by the same factors as in gravitational casting and in addition by rotational velocity [8-10]. All previously mentioned additional factors, like particles shape and size characteristics, Non-Newtonian and viscoelastic nature of polymeric fluid have influence on properties gradation.

Summarizing, the following factors determine composition gradation achieved in centrifugal casting process:

- rotational velocity,
- rotation axis position (mainly for non-axi-symmetric parts),
- particles size, shape and surface characteristics,
- fluid and particles densities,
- fluid viscosity and viscosity changes during curing,
- rheological nature of fluid.

2.5. Co-extrusion

Co-extrusion is used among others in production of multilayer films, multi-component profiles, multilayer pipes and blow moulded multilayer containers. This technology allow to combine layers and profile sections with different strength, barrier, antistatic, antioxidant and other properties. For the best joining of different materials their mutual mixing and formation of thin graded interlayer is highly desirable. Convection and shear controlled mixing enable graded layer formation.

Convective mass transport is the sum of advective and diffusive transport components. Diffusion is the most probably for low molecular-weight additions and little probably for large macromolecules. Advection is possible for low and high molecular weight fluids.

Diffusion is the process of concentration equalization due to random motion of particles. The time dependence of mass transfer from regions of higher to regions of lower concentration is described by the diffusion equation, proposed by A. Fick [13]. The first Fick's law determines the diffusive flux in steady state conditions. This flux is proportional to the concentration gradient and occurs from regions of high concentration to regions of lower concentration. The main material characteristic controlling the process is diffusion coefficient. It depends on particles size, temperature and fluid viscosity. The second Fick's law describes concentration change with time.

Advection is a transport mechanism due to the fluid's bulk motion. Advection requires currents in the fluid, and because of this is little probably in polymeric melts in extrusion processes. More probably in extrusion is macromolecules shear induced mixing. A flow evokes mixing by shear induced separating of initially neighboring fluid particles [14,15].

Gradient in shear rate causes also a gradient in the elastic strain energy of molten, viscoelastic polymers. There are theories that due to this effect the smaller chains migrate toward the channel wall [15]. This shear induced mixing effect increases as the shear gradient increases.

Taking into account all described phenomena the following means may be applied to influence properties gradation:

- composition of co-extruded streams;
- temperatures of materials being in contact;
- time of mutual contact;
- rate at co-extruded streams interlayer.

2.6. Foaming

Polymeric foams consist at least of a solid polymer matrix and a gaseous phase. Solid phase may be more complex consisting eg. of polymer blends, interpenetrating polymer networks, crosslinked polymer networks and many types of polymer composites [16]. Polymeric foams with graded content of gaseous phase are known as integral or structural foams for many years. These materials are typical PGMs even though they were no called as graded materials.

Commonly applied methods of gaseous phase formation are thermal decomposition of blowing agent, mechanical whipping, volatilization of liquids by boiling, gases educing during polymerization or crosslinking, expansion of gases dissolved in polymer, incorporation of hollow beads into polymer matrix and expansion of gas filled beads by heat [16]. Widely used technologies of production of foamed parts are [16,17] continuous pouring or impinging, compression moulding, reaction injection moulding (RIM), casting, spraying, extrusion and injection moulding of materials with expandable beads, rotational moulding, frothing, laminating, production of foam composites and precipitation foam processes. Three main technologies applied to manufacture of graded foams are casting, RIM and extrusion.

To control foaming process in graded materials production, fundamentals of bubbles creation are to be known [16]. Lowering the surface tension (e.g. by addition of surfactant) decreases energy needed to disperse the gas in the liquid and aids fine cells formation. The gas pressure in the bubble is larger than the in liquid around it. The gas pressure is greater in small bubble than is greater one. Because of this gas diffuses from small bubbles to larger and small bubbles disappear and large bubbles grow. Once more lowering surface tension reduces the pressure differences between bubbles of different sizes and stabilizes small average cell size. While bubbles expand the concentration of surfactant at the interface decreases. Two phenomena counteracts this and stabilizes foam. Shearing during flow cause deeper and surfactant reach layers to go to the interface ('Maragoni effect') and diffusion equalizes concentration of the surfactant across membrane wall ('Gibbs effect') [16].

Additionally temperature plays important role in foaming. The higher is the temperature the lower is the viscosity and the surface tension what results in bubble walls thinning and even collapse. More over low viscosity facilitates liquid drainage from bubbles walls due to gravity and capillary effect action. On the other hand to low temperature and high viscosity influence gas evolution and crosslinking reaction. Apart from temperature control the balance between viscosity and gas evolution can be achieved by application of proper type and concentration of blowing agents, surfactants, catalyst and nucleating agents [16].

Summarizing, the following factors influence foaming process and its gradation:

- polymeric matrix composition,
- additives concentration (blowing agent, surfactant, nucleating agent, fillers, etc.),
- pressure and temperature,
- fluid viscosity and viscosity changes during curing,
- other technological parameters depending on foam production technique.

2.7. In situ polymerization

Preparation of graded composites by in situ polymerization is carried out gradually by manufacturing in reactor filled prepolymers and then bound them with a polymer matrix which is also obtained in situ [18]. As polymerization in situ is new and developing technology in polymer processing it is not widely used for obtaining graded materials. This method is, therefore, a modern alternative to traditional methods.

In situ polymerization as a method of manufacturing graded polymer composites brings solutions to many problems encountered during the producing composite by other methods.

This method provides a good homogeneous dispersion of filler in polymer by appropriate choice of filler particles. By using in situ polymerization of the polymer good vaccination of filler particles is obtained, and its mixing with the free polymer chains. Filler particles (especially coal) should be modified to obtain good polymer macromolecules adsorption on their surface. Modification could be carried by non-covalent or covalent bonding of filler particles and polymer [19-23]. Non covalent modifications concerns the physical adsorption and /or wrapping of polymers to the surface of the filler particles. Preparation of graded polymer composites via in situ polymerization allows the production of composites with insoluble and thermally unstable polymers, which cannot be processed using other methods. Its creation depends on continuously varying the chemical reaction conditions (such as temperature, exposure time or light intensity in the case of a photoreaction) along the gradient direction. The introduction of functional groups- as on macromolecules or small molecules, including monomers-can be achieved by either a "grafting to" or "grafting from" approach. "Grafting to" approach involves a synthesis of polymer with precise molecular weight, chain densities, nanoarchitectures. Chains are terminated with reactive groups or radical precursor. A typical instance is the preparation of a gradient surface using macromolecules with a functional end group, such as halogen, mercapto, organosilane, vinyl etc. This is based on gradually depositing the macromolecules. In such gradient surfaces, the gradually varying concentration of macromolecules on the surface produces gradients in wettability, thickness, and other physicochemical properties. Polymer chain is attached to the surface of filler by addition reactions. This method is limited by low reactivity of long polymer chains and high steric hindrance of molecules but can be used for pre- formed commercial polymers. Gradient polymers can also be easily produced by "grafting from" with the help of using "living" or controlled chain-growth polymerizations that proceed without irreversible chain transfer or termination. Recently, advances in "living" polymerization techniques have led to a number of methodologies that can be used to produce surfaces exhibiting spatial and temporal polymer distributions which couldn't be obtained by traditional methods. "Grafting from" involves growing polymers from filler surface via in situ polymerization of monomers initiated by chemical species on the filler particles. The advantage of this method is that high reactivity monomers makes efficient, controllable, designable, and tailored grafting feasible. In this approach following mechanism of reaction are used: cationic/anionic polymerization, condensation polymerization. metallocene catalysis polymerization, electrochemical grafting, atom transfer radical polymerization, ring opening polymerization, free radical

polymerization, polymerization with shift chain of polymer, photopolymerization, polycondensation. Using a different functionalized filler it is possible to create a polymer gradient material [19, 24-27] To produce polymer materials with a gradient in mechanical properties, instead of taking advantage of the concentration gradient generated by diffusion, a gradient of light intensity was recently used to induce photopolymerization and photo-crosslink reactions. By irradiation from one side of the sample, the properties of the sample become asymmetric, dissimilating the front and back sides of the samples [28-29]. Also modern technique such as plasma polymerization can be used for manufacturing gradient polymer.

Plasma polymerization is a way to obtain the specific polymeric materials, which cannot be obtained by other methods. Plasma created polymer differs greatly from the polymer formed from the same monomer, obtained by other methods. For the plasma polymer is not possible to determine the individual mere's. All organic compounds and large number of inorganic compounds undergo plasma polymerization. Chemical reactions extending during the polymerization in the plasma are complicated, and their mechanism has not yet been fully known. The advantage of this method is the possibility to obtain ultra-thin plasma polymer films in a pure form (in the absence of an oxidant in the reaction), often highly branched and cross-linked and therefore insoluble [30]. This method has been also used for preparing a functionally graded polymer materials. Investigation carried by Ogumi et al [31] results with preparing graded polymer electrolytes 2-[2-(2-Ethoxyethoxy)ethoxy]ethoxydimethylvinylsilane (EDVS) containing 10 wt% LiCF_3SO_3 polymerized by use of plasma polymerization.

3. Experimental

Division of Metallic and Polymeric Materials Processing of Silesian University of Technology in Gliwice, Poland for several years is engaged in the research of polymeric graded materials using casting technologies (gravitational and centrifugal).

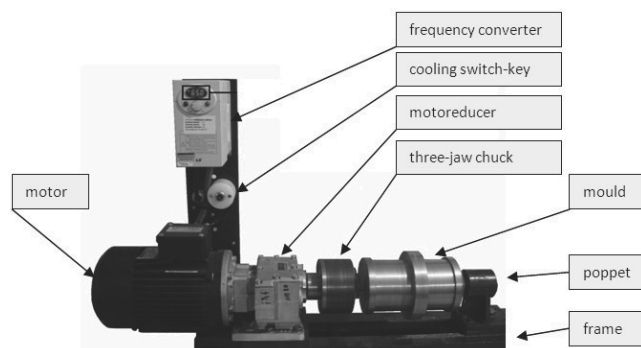


Fig. 1. Photograph of centrifugal casting device

The work was already presented in many original publications on this topic [28-39]. The aim of this study was to produce a material with a variable electric and magnetic properties on specimen's cross section. To change these properties to the polymer matrix

was introduced a hard coal and iron as powder filler. Properly prepared mixture was poured into a mold which was then in the case of centrifugal casting propelled rotary with specified constant speed. The photograph of centrifugal casting device and the form is shown in the Fig. 1. The resulting specimens had a cylindrical shape with dimensions: diameter of 80 mm, length of 150 mm and wall thickness of 9 mm (Fig. 2).

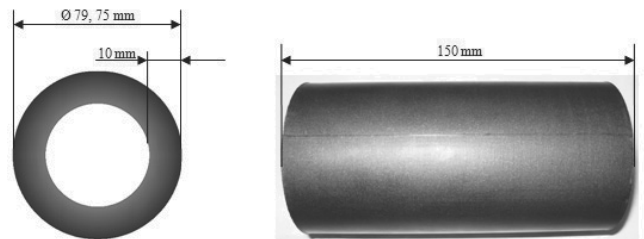


Fig. 2. Specimen of gradient material (cured epoxy resin with hard coal filler) made by centrifugal casting method

The photograph of gravitational casting mould is shown in the Fig. 3. However, in the case of gravity casting samples had the shape of discs with a diameter of 100 mm and a height of about 8.5 mm (Fig. 4).

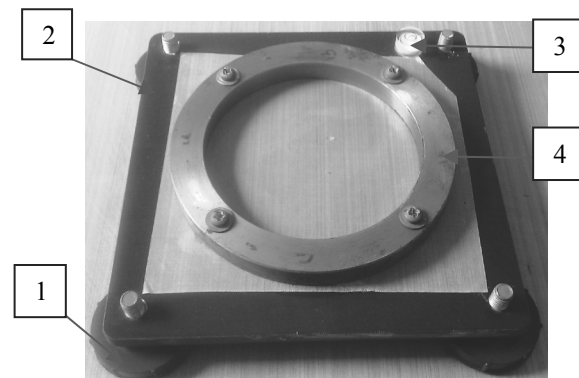


Fig. 3. Gravitational casting mould; 1 - mould levelling foot, 2 - bottom plate, 3 - level line, 4 - steel ring

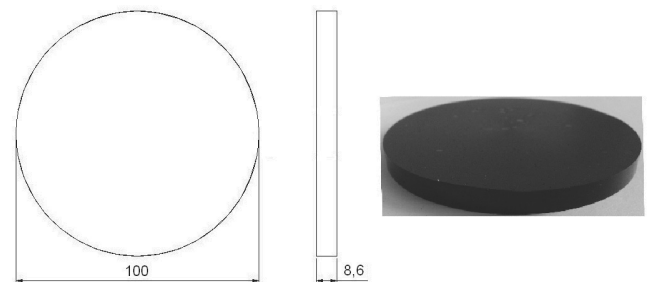


Fig. 4. Shape of the disk specimen

In order to verify the presence of the properties gradient in the obtained materials, electrical properties (surface resistivity) and magnetic properties were searched and the specimen's cross-sections were observed using optical microscope. Many factors affect the sedimentation velocity of the powder introduced into the polymer matrix and hence the width of the layer in which the filler occurs. One of the main factors is viscosity of polymer matrix and another essential factors are the density of the powder, the size and shape of the filler grains and the rotational speed of

the mould in which a specimen is cast. Appropriate selection of these parameters allows to an intentional and controlled production of polymer graded materials. Achieved results confirm the existence of the properties gradient across wall thickness of cast specimens and the possibility to control this gradient by mentioned factors. In Figures 5-8 are shown exemplary images of specimen's cross-sections. Graphs presenting surface resistivity changes depending on the depth position of the tested surface are shown in Figures 9-11.

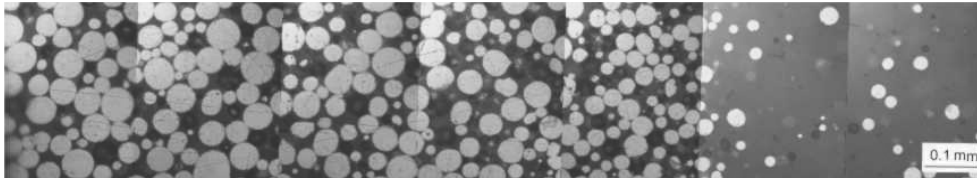


Fig. 5. Panorama photograph of structure of the specimen containing 10% vol. of copper manufactured by centrifugal casting at the velocity of 300 rpm

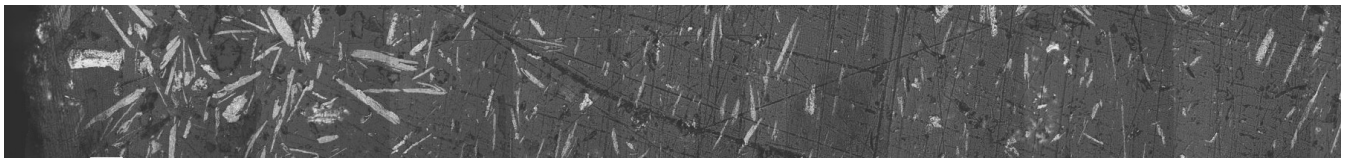


Fig. 6. Panorama photograph of structure of a specimen containing 12% vol. of graphite PV 60/65, manufactured by centrifugal casting at the velocity of 535 rpm

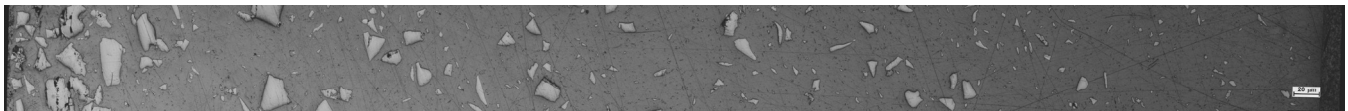


Fig. 7. Panorama photograph of structure of a specimen containing 12% vol. of anthracite coal, manufactured by centrifugal casting at the velocity of 577 rpm

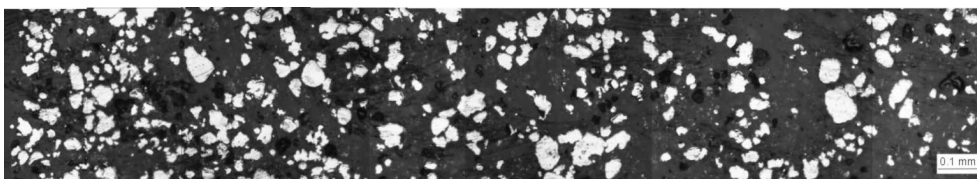


Fig. 8. Panorama photograph of specimen's cross section of epoxy resin filled with mixture of iron powders 50% vol. ASC200 and 50% vol. ASC300 manufactured by centrifugal casting at the velocity of 1820 rpm

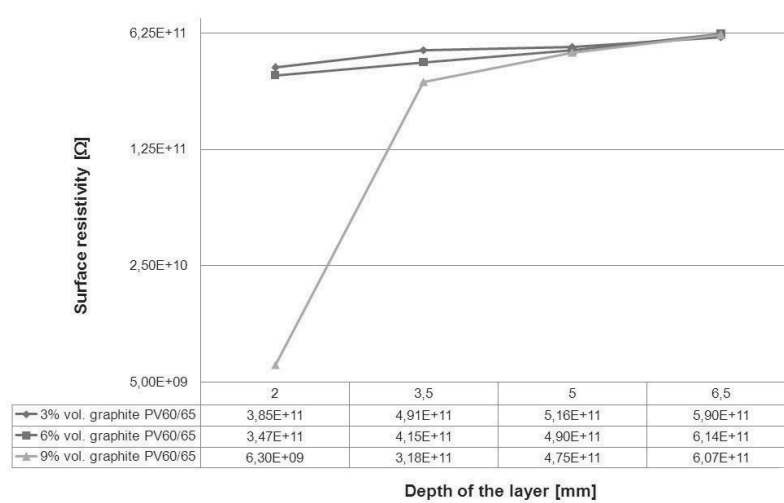


Fig. 9. Surface resistivity dependence on the depth position of the tested surface for specimens produced by gravitational casting with the addition of respectively 3 - 9% vol. of graphite PV60/65

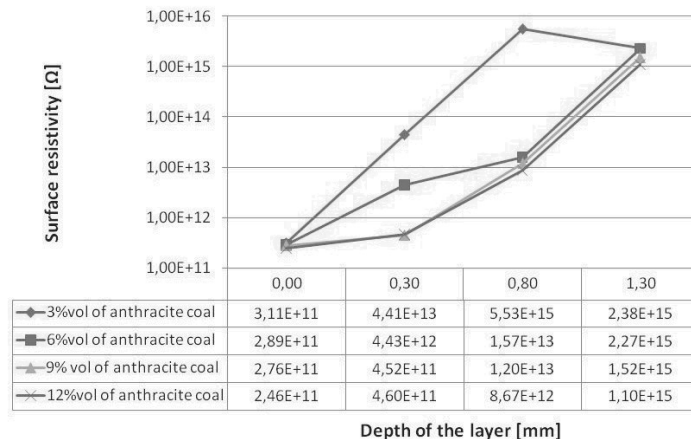


Fig. 10. Relationship between surface resistivity and depth of the layer for specimen containing 3-12%vol of anthracite coal

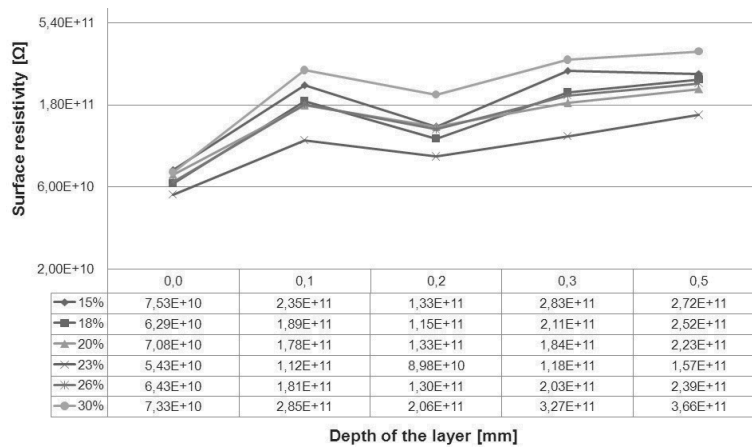


Fig. 11. Graphs of surface resistivity changes depending on the depth position of the tested surface for gravitational casting specimens with the addition of respectively 15 - 30% vol. of anthracite coal

4. Summary

The examples of the use of polymeric materials processing techniques to produce graded materials indicate that by appropriate control of processing parameters, the composition of processed materials and the proper selection of tools, it is possible to design features of gradient structures and. Of course, any technology is subject to the constraints of the range of parameters, geometrical characteristics of machines and tools and in this way also possibilities to control properties and their gradients are limited.

In the paper not all technologies were discussed which allow to receive graded materials. The paper presents only those technologies that are used by the authors or are searched by the authors. Others, worth mentioning are multi-injection, integral foam injection, deposition of multilayer coatings of different technologies, or rotational molding of multi-walled tanks.

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