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Polymer composites filled with powders as polymer graded materials

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Materials

ABSTRACT

Purpose: The goal of this paper is to present general overview of research results on Polymeric Gradient Materials (PGMs) performed in Division of Metallic and Polymeric Materials Processing of Silesian University of Technology. Achievements in research on production technologies, compositions and properties are presented.

Design/methodology/approach: Two basic technologies that were used for preparing polymeric gradient composites filled with powders are presented (centrifugal and gravity casting). Composites based on epoxy resin and filled with iron, ferrite, graphite, coal powders are characterized. Among other, the following properties were tested: surface resistivity, coefficient of friction, magnetic induction, filler particles distribution in polymeric matrix and others.

Findings: Casting methods presented in this article can successfully be used to produce polymer composites characterized by gradual distribution of powder content and by this way by gradual distribution of properties. Results show that it is possible not only to achieve but also in some extend to control gradient of filler concentration. Especially in centrifugal casting is possible to influence gradient of filler concentration and in this way gradient of many properties.

Research limitations/implications: The main problem in presented researches was to introduce higher quantities of filler. The side effect of high filler content was high viscosity. Filler particles were added to the epoxy matrix in range from 3vol.% to 50vol.% depending on filler properties, method of casting etc.

Practical implications: Elaborated PGMs may be applied in many fields such as medicine, electronics, mining industry, machine building industry and many others.

Originality/value: New type of polymeric gradient composites were achieved using centrifugal and gravity casting technique. Influence of casting parameters, concentration and type of filler on composites properties was researched.

Keywords: Polymers; Composites; Polymeric Gradient Materials; Casting

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1. Introduction

In recent years one of the main classes of high performance engineering materials, next to metals and alloys, ceramics and polymeric materials are composite materials. These engineering materials are prepared from minimum two separate substances. In ready composite these separate materials are connected by interface layer coupling two immiscible phases – matrix and reinforcement or filler. Properties of two phases, reinforcement or filler distribution in matrix and adhesion phenomena between filler and matrix determine final properties of composite. The idea of connecting two or more different constituents into one substance gives almost infinite possibilities to create new engineering materials characterized by variety of different properties. Composite materials because of these diverse properties are successfully used in almost all areas of industry and science. Especially popular are composites in automotive, electrical and electronic, aerospace and machine building industries, sport and leisure industry, civil engineering, etc. [1-3].

Almost all properties can be changed by incorporation of reinforcement or filler particles into matrix. Main classes of properties influenced by fillers and reinforcements are mechanical properties (strength, stiffness, hardness, wear resistance and other), electrical properties (surface and cross resistivity, loss, factor, permeability and so on), thermal properties and optical properties.

There are three main classes of materials applied as composites matrixes: metals (MMC – metal matrix composites), ceramics (CMC – ceramic matrix composites) and polymers (PMC – polymeric matrix composite). Types of fillers and reinforcements applied in composites are so many that it is impossible to enumerate all. Main forms of reinforcement and filler particles are powders of different shape, fibres, fabrics and mats.

The next step in composites development was to differentiate filler or reinforcement concentration in one, two or three directions. The result of this was differentiation of properties in these directions. In this way a new class of composite materials was elaborated named Functional Graded Materials (FGMs). Continuously varying filler distribution causes that graded composites become non-homogeneous and give scientists huge field of possibilities to create new generations of composites depending on requirements and future applications [4,5]. By applying gradual distribution of fillers or reinforcement in the matrix of graded composites it is possible to prevent many of basic disadvantages of composites, namely sharp boundaries between connected together substances and thermal, mechanical or/and internal stresses concentrations. Until now scientists create many definitions for FGMs. For instance Gooch et al [6] wrote that 'FGMs are a new class of composite materials for which transition from one material to another takes place in gradient layers without discrete interface boundaries'. Whereas X.F. Yao in [7] wrote that in essence FGM is a two-phase composite with graded volume fractions of its constituent phases from one end to the other. Gradation of mechanical and other properties is manifestation of gradation in composition and varies essentially in comparison with traditional composites. Dreyer et al [8] and Gasik et al [9] defines it as materials characterised by a linear or non-linear 3-D distribution of chemical composition or phase content corresponding to distribution of properties (electric or thermal conductivity, resistance, hardness, wear resistance etc). Gradually changes from one side to the other distinguishes graded materials from homogeneous and conventional composite materials. First time technical graded materials were produced in 1944 but there was no pronounced interest in them. Afterwards in 1972 Shen and Bever [10] wrote that 'structure and properties of polymeric materials can be varied over wide ranges' but in the past scientists directed very little attention to polymer gradient materials besides few of them. For instance Ferry [11] analysed some aspects of gradient in polymers. In the next years it was found that polymer gradient materials can be successfully used as semiconductors which are characterized by gradual change of dielectric strength or electric conductivity. Subsequently Japanese researchers approximately in 1987 interested in FGMs in a greater scale. Scientists formed a special group that tried widely to develop knowledge concerning this class of composites [3,12]. More and more scientific researches were undertaken on FGMs. These projects concern methods of fabrication, properties designing, properties evaluation and so on.

Many of PGMs production were developed. The most widely used up till now are: spraying processes, corona discharge, powder metallurgy methods, selective laser sintering, gravitational or rotational casting and other. Gradients of many classes of properties were searched: mechanical, thermal, electrical or magnetic and other.

Polymer Graded Materials (PGMs) is a special class of graded materials wherein at least one compound is polymer, usually thermosetting or thermoplastic resin used as a matrix. PGMs are searched in less extend than other classes of graded materials. Generally polymer matrix in composites are use inter alia because of their: low density, resistance to atmospheric influences and resistance to aggressive environments, electric and thermal properties, high specific mechanical strength compared with their mass [3,13,14]. Several investigations have been reported producing PGMs: epoxy resin – triglycidyl phosphate [15], PVC/PMMA [16], epoxy-TiO_2 [17], PP-PA6 [18], epoxy/ferrites [19] epoxy/graphite [20, 21], glass-fibre mat/PMMA [22] etc.

Up to now a variety of distinct non-homogeneous properties of FGMs and PGMs were studied e.g.: electric properties in an FGM were discussed in [20,21,23,24], mechanical properties in an FGM were studied in [22,25,26], and magnetic properties in FGM were treated in [4,27].

Some methods of PGMs preparation are the same as for other functionally materials, for example gravitational and centrifugal casing, spraying, pressing, selective laser sintering. There are also methods specific for polymers only such as in situ polymerization, selective polymerization, radiation hardening.

In this paper, researches on PGMs with different amount and sort of fillers are presented. They were designed and then fabricated by pressing, gravity and centrifugal casting methods. Properties such as electrical surface resistivity, magnetic induction, coefficient of friction were tested and analyzed. Additionally distribution of filler particles in polymeric matrix was investigated. It is worth to underline that these problems are not often reported in literature. Especially magnetic properties of PGMs are rarely discussed.

2. Experimental

2.1. Materials and methods of research

Materials

As matrixes of all searched composites different types of epoxy resin were used. The following epoxy resins were applied: Epidian 100 Epidian 6 and Epidian 6011. All resins were produced by Organika- Nowa Sarzyna (Poland). Main properties of these resins are given in Tables 1 and 2. Epoxy resins were cured using Z1 triethylenetetramine (Z1) or curing agent ET also produced by Organika- Nowa Sarzyna (Poland). Selected properties of curing agents are given in Table 3. Additionally in order to decrease viscosity some of mixtures contained also thinner (xylene). Different types of powders were used as fillers in different research projects: copper powder (A-53SS), anisotropic ferrite powder (AMM), ferrites ($BaFe_{12}O_{19}$, $SrFe_{12}O_{19}$ both received from ZAM Trzebinia – Poland), graphite powders (PV60/65, SV94, GK3), two types of coal were used anthracite coal (Kuznetsk Basin) and hard coal ("Zofiówka" coalmine Poland). Selected characteristics of these powders are presented in Tables 1-8.

Table 1.
Main characteristics of epoxy resin Epidian 100

Form	Flake
Density (20ºC) [g/cm³]	1.18-1.19
Viscosity (25ºC) [mPa·s]	-
Softening point [ºC]	70-80
Ignition temperature [ºC]	> 250
Autoignition point [ºC]	> 500

Table 2.
Main characteristics of Epidian 6 and Epidian 6011

Properties	**Epidian 6**	**Epidian 6011**
Density (20ºC) [g/cm³]	1.17	1.13
Viscosity (25ºC) [mPa·s]	10000-15000	200-400
Boiling point [ºC]	> 200	> 150
Ignition temperature [ºC]	> 200	120
Autoignition point [ºC]	> 300	460

Table 3.
Specification of curing agents – triethylenetetramine (TETA) and ET

Trade name	**Z-1**	**ET**
Form	colourless liquid	pale yellow liquid
Density (25ºC) [g/cm³]	0.98	1.02-1.05
Viscosity (25ºC) [mPa·s]	20-30	-
Amine value [mg KOH/g]	min. 1100	-

Table 4.
Main characteristics of barium ferrite and strontium ferrite powder

	Chemical formula	$BaFe_{12}O_{19}$	$SrFe_{12}O_{19}$
	Form	powder	
	Fe_2O_3 [mol] BaO [mol]	5.6-6.2	-
	Fe_2O_3 [mol] SrO [mol]	-	5.6-6.2
	Humidity % max	0.5	
	Density (20ºC) [g/cm³]	5.3	4.9±0.2
	Melting point [ºC]	1315.6	-
	Formula weight [g/mol]	1111.46	1061.77
	Solubility	water-insoluble	
	Smell	inodorous	
	Grain size [µm]	<100	
Component %	Fe	58.6-59.6	61.4-62.4
	Ba	12.7-13.7	-
	Sr	-	8.6-9.6
	Mn max	0.5	
	$BaSO_4$ max	1.0	-
	$SrSO_4$ max	-	1.0
	SiO_2	0.3-0.6	

Table 5.
Specification of graphite powders: PV60/65, SV94 and GK3

Properties	**PV60/65**		**SV94**		**GK3**	
Carbon, min [%]	64.8		94.23		94	
Ash, max [%]	35.2		5.77		5	
Moisture, max [%]			0.34		1	
Degree of fineness [%]/[µm]	10	125	0.1	>500	90	38
			42.0	<160	50	15
			11.0	<100	10	10

Table 6.
Characteristics of anthracite coal

Carbon contents	87.9 %
Ash contents	3.37 %
Specific surface	0.146 m²/g
Range of grain size	$d_{10\%}$ = 20.12 µm $d_{50\%}$ = 132.64 µm $d_{90\%}$ = 358.36 µm
Density	1.37 g/cm³

Table 7.
Characteristics of hard coal from "Zofiówka" coalmine

Carbon contents	88.5 %
Ash contents	16.78 %
Specific surface	0.939 m²/g
Range of grain size	$d_{10\%}$ = 2.92 µm $d_{50\%}$ = 17.93 µm $d_{90\%}$ = 64.25 µm
Density	1.40 g/cm³

Table 8.
Characteristics of copper powder A-53SS

Cu %	99.58
Pb %	0.005
P %	0.025
O_2 %	0.27
Particles below 53 μm [%]	99.8
Particles 75-53 μm [%]	0.3
Density (25°C) [g/cm³]	8.933
Surface resistance (25°C) [Ω]	$1.7 \cdot 10^{-8}$

Method of graded composites manufacture

Three different PGMs preparation technologies were used: powder pressing, gravitational and centrifugal casting. Powders pressing and gravity casting allowed to produce flat composites with gradient of composition in the thickness direction. Centrifugal casting was used to manufacture samples in pipe form with radial gradient of composition. These methods were selected because they were successfully used by researchers for manufacturing FGMs in works. In this works chosen methods allowed obtain gradual distribution of powder particles what was possible by changing of size, shape and amount of particles, time and rate of casting and also by controlling process of filler sedimentation.

At the beginning of all mixture preparation processes suitable amounts of components were calculated and weighted in order to achieve suitable amounts of composites with prescribed filler concentrations. In the next stage epoxy resins and filler powders were mixed together in a manner allowing to achieve homogeneous solid particles distribution in matrix and deaeration of mixture. After that curing agent was added and intensively mixed with prepared composition (besides pressed composites).

Details of graded composites that were prepared are followed:

1. Composites that were filled by graphite powder (SV94, GK3, PV60/65) or coal filler (anthracite coal and hard coal) prepared by pressing or casting methods. They were build by four layers with 15%vol., 10%vol., 5%vol. and 0%vol. of graphite powder (or 12%vol., 9%vol., 6%vol. and 3%vol. of coal powder);
2. Composites filled with ferrite powders were pressed and cast (centrifugal and gravitational). Volume fraction of inclusions were from 5%vol. to 50%vol. for gravitational casting, 30%vol. for centrifugal casting and even 60%vol. for pressed composites;
3. Composites filled with 10%vol. of copper powder were centrifugal cast.

2.2. Results and discussion

Different properties were search in different projects. Results will be presented separately for different projects and tested properties.

Fillers particle distribution in polymeric matrix

In every research filler particle distribution was tested. Exemplary photograph of sample cross section is presented in Fig. 1. Exemplary quantitative analysis is presented in Fig. 2.

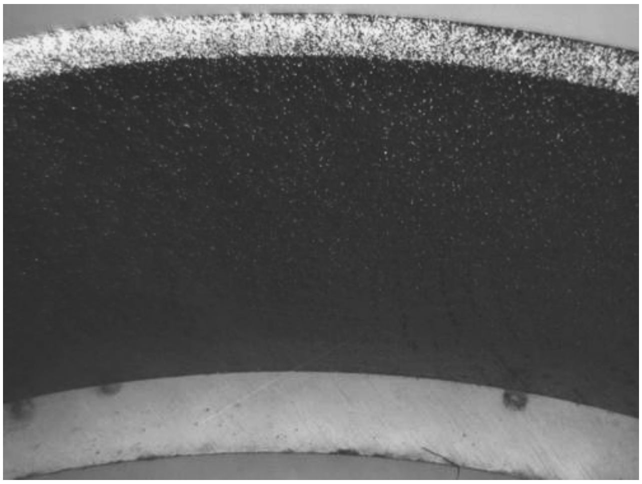


Fig. 1. Copper particle distribution in epoxy-copper composite cast in centrifugal process

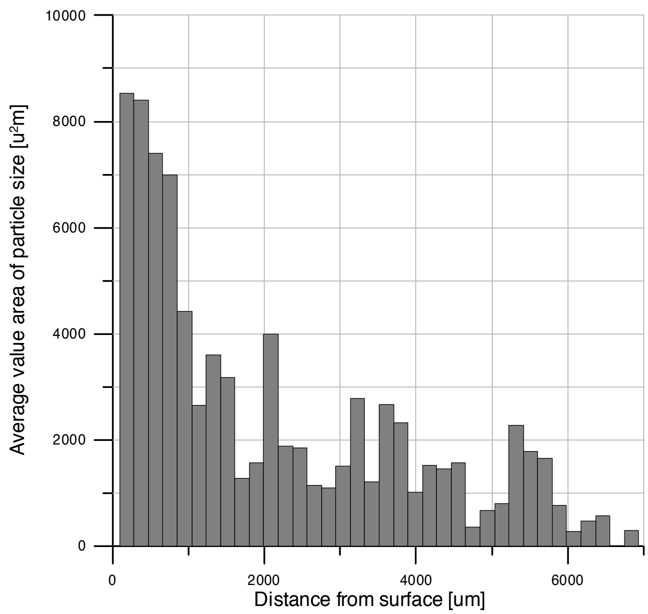


Fig. 2. Average value of area of particle in cross section depending on distance from surface – composite filled with copper powder centrifugal cast at 300 rpm

Results of particle distribution on samples cross sections allowed to draw two main conclusions:

- applied technologies allow to produce composites with concentration gradient;
- it is possible to control the gradient in some extant by changing filler properties, matrix properties and casting parameters.

Wear properties

In project concerning wear properties coefficient of friction was tested. Composites with graphite as filler were searched. Results are presented in Fig. 3 to Fig. 6.

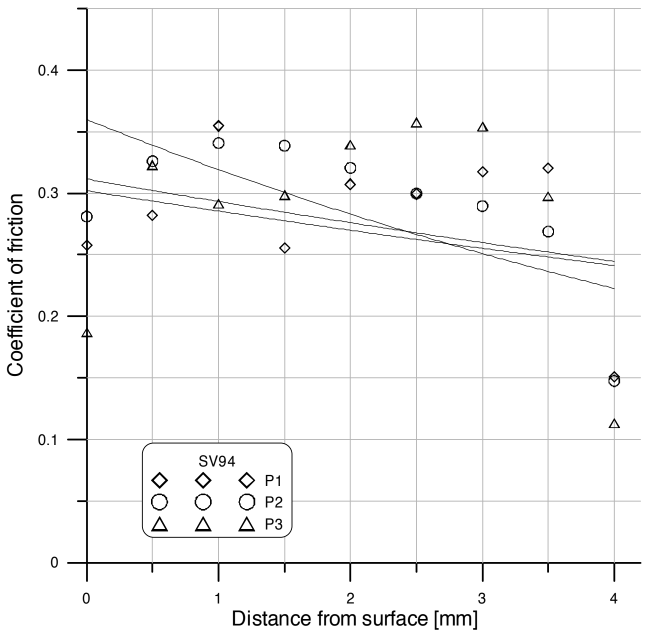


Fig. 3 Average values of coefficient of friction for pressed composites filled with graphite SV94

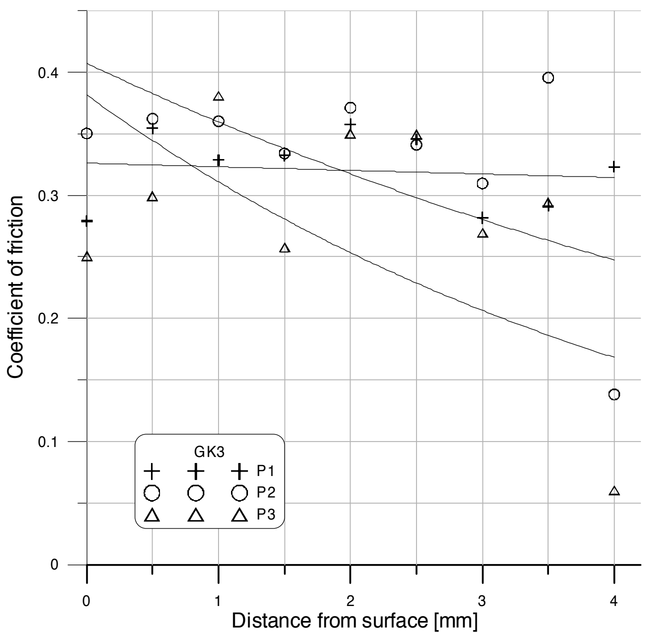


Fig. 4. Average values of coefficient of friction for pressed composites filled with graphite GK3

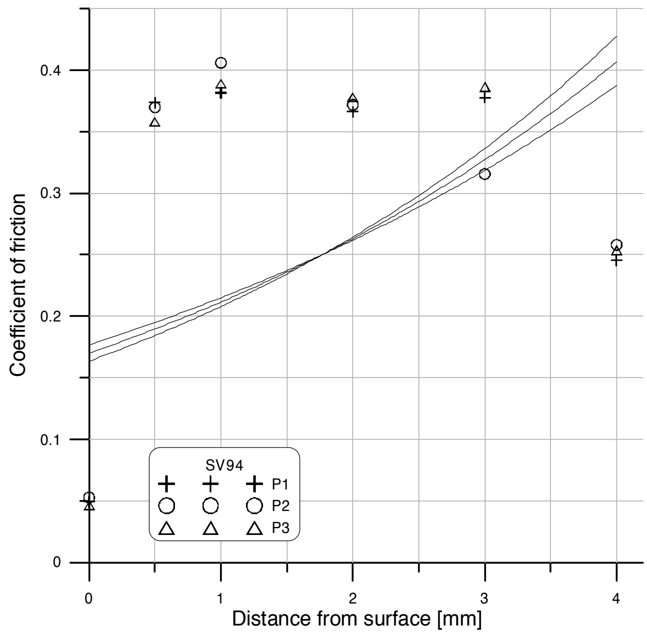


Fig. 5. Average values of coefficient of friction for cast composites filled with graphite SV94

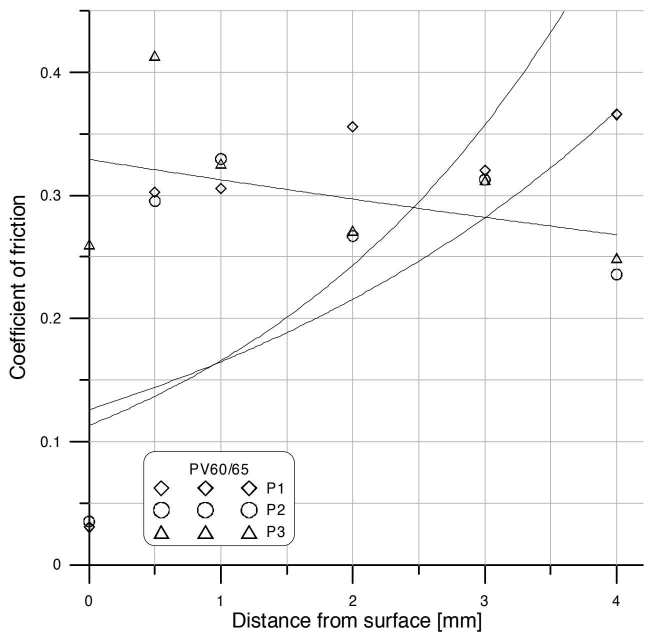


Fig. 6. Average values of coefficient of friction for cast composites filled with graphite PV60/65

Achieved results are not univocal. For most composites coefficient of friction on surface was higher on surface where more graphite particles were incorporated. As can also be observed for some sorts of graphite powders coefficient of friction increased together with distance from the surface. Graphite powders are used in polymer composites to lower the coefficient of friction but in this study in some cases higher amount of graphite increased coefficient of friction. That unexpected behaviour can be explained poor adhesion between matrix and filler particles.

Electrical properties

Different electrical properties were tested in different projects. As an example surface resistivity will be presented. Surface resistivity was measured on subsequent layers. After each measuring surface layer was removed in grinding process. Results are presented in Figs.7 to 9.

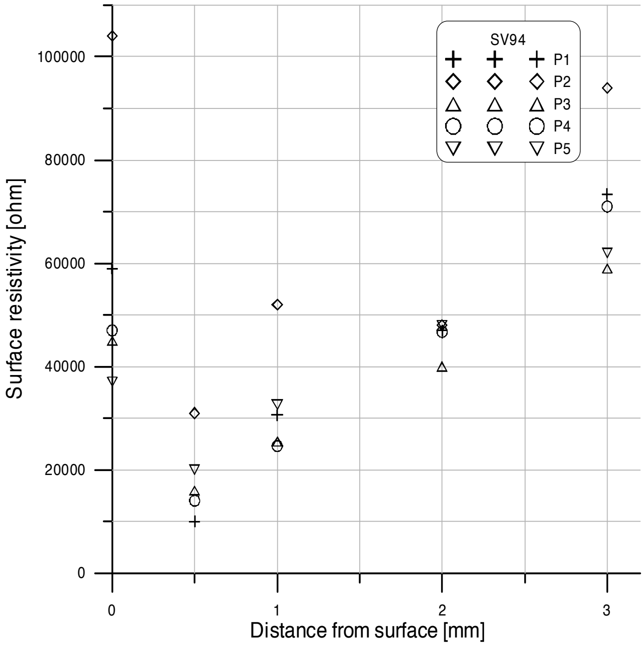
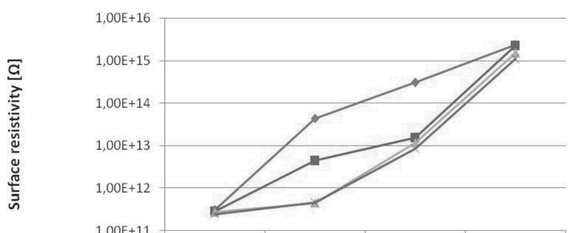


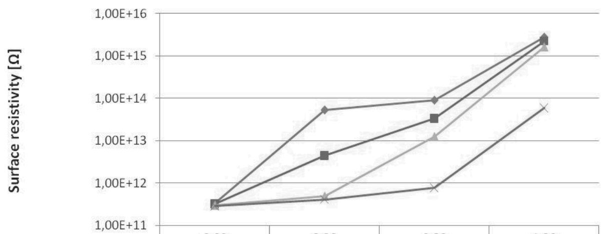
Fig. 7. Relationship between surface resistivity and distance from surface of centrifugal cast composites filled with SV94 graphite powder



	0,00	0,30	0,80	1,30
3%vol of anthracite coal	3,11E+11	4,41E+13	3,07E+14	2,38E+15
6%vol of anthracite coal	2,89E+11	4,43E+12	1,57E+13	2,27E+15
9% vol of anthracite coal	2,76E+11	4,52E+11	1,20E+13	1,52E+15
12%vol of anthracite coal	2,46E+11	4,60E+11	8,67E+12	1,10E+15

Depth of the layer [mm]

Fig. 8. Relationship between surface resistivity and depth of the layer for specimens containing 3-12%vol of anthracite coal



	0,00	0,30	0,80	1,30
3%vol of hard coal from Zofiówka coalmine	3,44E+11	5,36E+13	9,05E+13	2,80E+15
6% vol of hard coal from Zofiówka coalmine	3,26E+11	4,50E+12	3,34E+13	2,25E+15
9%vol of hard coal from Zofiówka coalmine	3,02E+11	4,97E+11	1,26E+13	1,63E+15
12% vol of hard coal from Zofiówka coalmine	2,87E+11	4,16E+11	7,74E+11	5,96E+13

Depth of the layer [mm]

Fig. 9. Relationship between surface resistivity and depth of the layer for specimens containing 3-12%vol of hard coal from "Zofiówka" coalmine

Results of electric properties searches allowed to draw the following conclusions:

- gradient of electro-conducting filler manifested in gradient of surface resistivity. Lowest resistivities were observed on surface of all composites;
- the higher was mean initial content of electro-conducting filler the lower surface resistivity was observed;
- It is possible to decrease surface resistivity to values preventing electrostatic discharges.

Magnetic properties

Composites with magnetic particles were magnetized after casting and hardening of samples. In researches concerning magnetic properties different magnetic characteristics were measured. As an example magnetic induction results will be presented graphically. Chosen dependences are shown in Figs. 10 to 14.

Achieved results allowed to draw the following conclusions:

- gradient of magnetic particles concentration leads to gradient in magnetic properties;
- magnetic induction gradient on samples cross sections is not the same as gradient of particles concentration. It is the result of magnetic phenomena taking place on cross section of every magnetic object;
- maximum of magnetic induction is proportional to maximum of magnetic particles concentration;
- maximum of magnetic induction is dependent on type of magnetic particles used as fillers;
- as could be expected higher initial contents of ferrite powders in polymer composites resulted in higher magnetic induction.

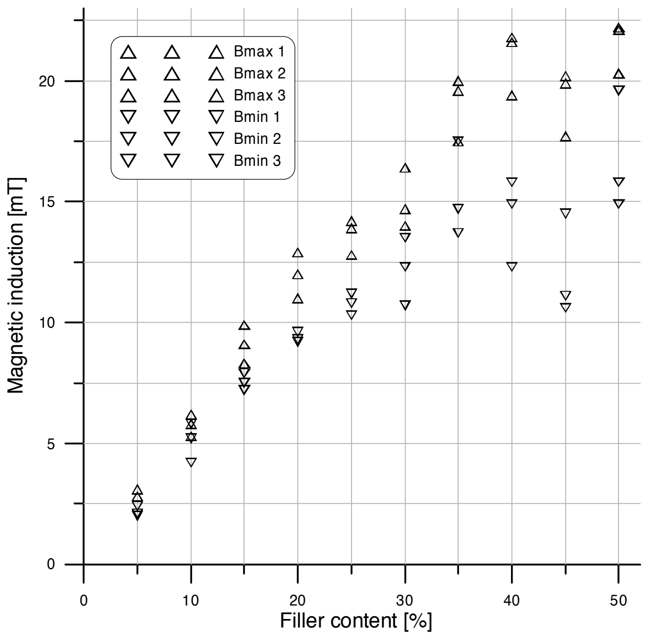


Fig. 10. Relation between magnetic induction and filler content of gravitational cast composites filled with anisotropic ferrite

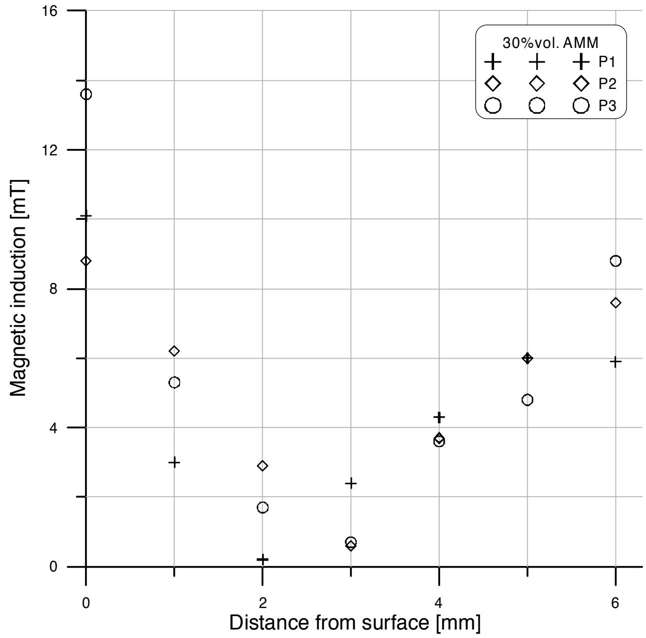


Fig. 12. Relation between magnetic induction and distance from surface of pressed composites filled with 30%vol. of anisotropic ferrite

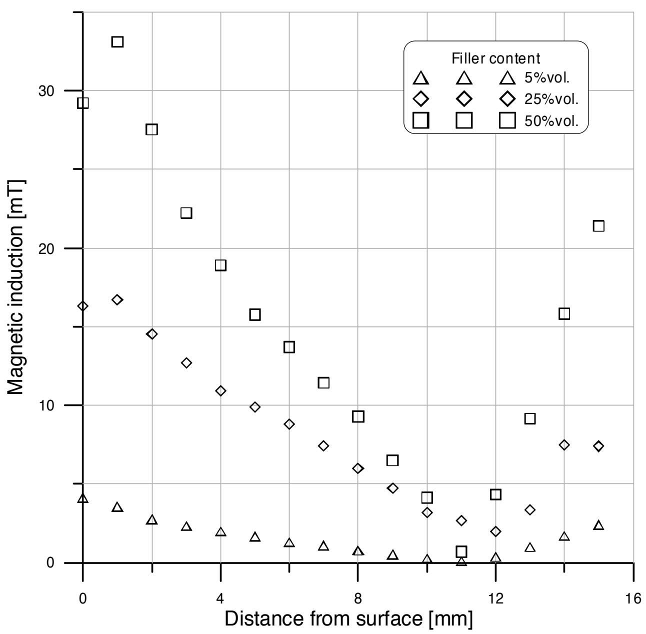


Fig. 11. Relation between magnetic induction and distance from surface of gravitational cast composites filled with anisotropic ferrite

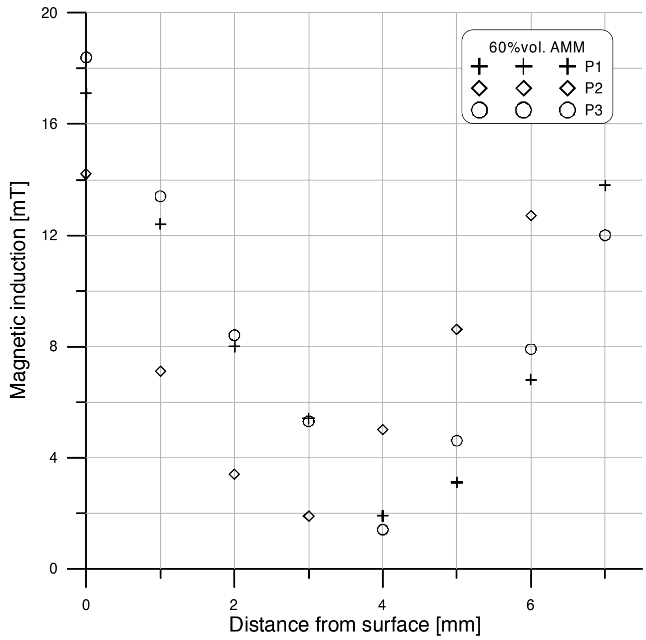


Fig. 13. Relation between magnetic induction and distance from surface of pressed composites filled with 60%vol. of anisotropic ferrite

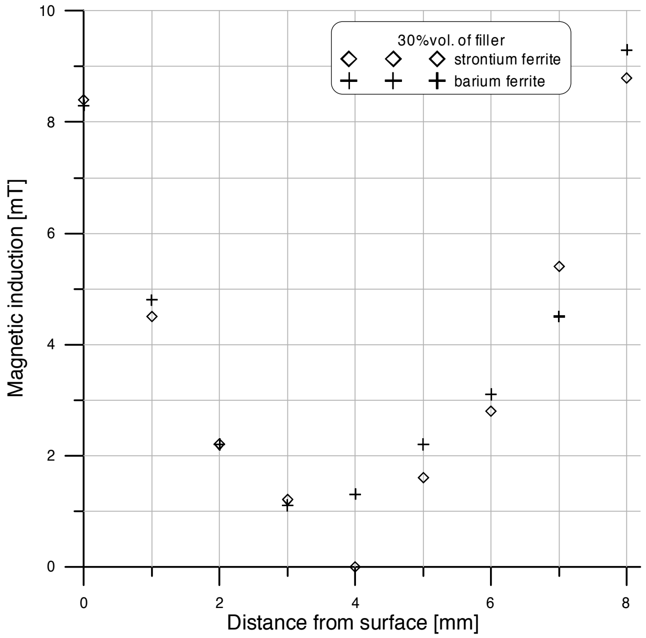


Fig. 14. Relation between magnetic induction and distance from surface of rotational cast composites filled with 30%vol. of ferrite powder

3. Conclusions

Performed studies were carried out in order to determine structure and properties of polymeric gradient composites. Basing on the obtained results the following conclusions were drawn:

- Pressing, gravitational and centrifugal casting are enable to produce graded composites which are characterized by spatial distribution of particles concentration and properties.
- It is possible to prepare compositions that contain up to 50%vol. of filler powders depending on the manufacturing method. Higher amount of fillers increased viscosity, which did not allowed to cast and prepare acceptable samples.
- It is possible to control gradient of particles concentration and in this way gradient of properties by proper selection of matrix properties, particles properties and technological parameters of casting.
- Wear, electrical and magnetic properties are dependent on initial and final filler particles concentration.
- Further researches on PGMs are planned in future. Especially interesting are polymeric graded materials with gradient of magnetic properties.

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