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Mixing, Conveying and Injection Molding Hybrid System for Conductive Polymer Composites

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Abstract

The demand for conductive fuel cell stack components contributed to the research and development of composite materials and technologies. Significant activities were directed to the study of low-cost bipolar plates made in thermosets and thermoplastics manufactured by compression and injection molding. For the production of conductive thermoplastics carbon-polymers composites are used methods including thermokinetting, twin screw extruder, or Banbury type mixing. In this paper are presented the results of research of a technology combining the mixing of the pellets of a composite carbon black in a polymer matrix with expanded graphite and conveying the compound to the injection molding unit and then, the melt injection molded into a micro-channel bipolar plate for a proton exchange membrane fuel cell (PEMFC).

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1. Introduction

Fuel cells are electrochemical devices that convert chemical energy of fuels into electrical energy. In 1842, the first fuel cell was developed by Sir William Robert Grove, who mixed hydrogen and oxygen in the presence of an electrolyte producing electricity and water [1]. Fuel cells were used in NASA space programs to generate energy to satellites and space capsules. Today fuel cells are used to power vehicles including automobiles, forklifts, buses, boats, motorcycles or submarines. Bipolar plates are components of the fuel cell stack and must be highly electrically conductive to obtain a good voltage across the stack and highly thermally conductive to help cooling. Bipolar plates are made of graphite, stainless steel and conductive composites. In Table 1 are presented the Department of Energy 2020 targets for bipolar plates for transportation [2]. The European Union aims at reducing its greenhouse emissions by at least 20% and to increase the share of renewable energy at least 20% with a

minimum 10% in the transportation sector. Hydrogen and fuel cell technologies were identified amongst new renewable energy technologies needed to achieve 60% to 80% reduction in greenhouse gases by 2050.

Table 1. US Department of Energy – Technical Targets for Bipolar Plates [2].

Characteristic	Units	2015 Status	2020 Target
Cost	\$/kW	7	3
Electrical conductivity	S/cm	>100	>100
Area specific resistance	Ohm cm ²	0.006	<0.01
Flexural Strength	MPa	>34	>25

For the bipolar plates made of graphite are needed treatments to reduce permeability and for the stainless-steel plates special surface coatings to reduce corrosion are needed; both operations are expensive. Important research activities were directed to the development of composite polymer carbon bipolar plates as an economical alternative.

The bipolar plates represent an important component of the fuel stacks with of about 80% of the total weight and 30% to 40% of the total cost. Carbon black, carbon fibers or carbon nanotubes can be added to the graphite into the polymeric matrix to increase the conductivity and the flexural strength. It was observed that for the thermosets-carbon composites was obtained a good conductivity, for example, for a compression molded Epoxy matrix polymer with fillers graphite 80% and carbon black 4.5% it was obtained a conductivity of 150 S/cm and a flexural strength of 20 MPa [3].

Composites on polypropylene matrix with graphite were obtained by a high-speed thermo-kinetic mixer, specifically designed to handle difficult compounding in shorter times; same method was used for polypropylene-recycled carbon fiber composites for which was found out improvement in tensile and flexural strength with the weight fraction up to 20% [4].

Polymeric composites of graphite (87wt%) in polypropylene and hybrid compounds: graphite (82wt%) with secondary filling carbon black (5wt%) or carbon nanotubes (5wt%) in polypropylene were produced in a laboratory kneader compounder. The experiments on a disc of 30 mm diameter and thickness of 2 mm evidenced the influence of the carbon nanotubes to the improved electrical conductivity and the additional conductive bridges created by the carbon black and carbon nanotubes through the insulating polymer matrix (it was obtained an area specific resistance of about 10 mΩcm²). Injection molded bipolar plates were successfully assembled and tested in fuel cell stacks [5].

Injection and compression molding of carbon - filled polypropylene, PP, and polyphenylene sulfide, PPS, were used to fabricate two models of bipolar plates. Fillers up to 60% in weight in the form of graphite, conductive carbon black, and carbon fibers were investigated. The bipolar plates were successfully fabricated by molding the gas flow channels over aluminum plates to form a metallic/polymer composite plate or simply by direct injection molding of the conductive polymer composite. For the first design, overall plate volume resistivities of 0.2 and 0.1 Ohm·cm were respectively attained using PP and PPS based blends [6].

High Density Polyethylene pellets (with a melt flow Index of 10.0 g/10 min) were mixed with graphite nanoplatelets, GNP with a diameter of about 25 μm and a powder was obtained by cryogenic milling process. The powders with GNP 10 wt% to 60 wt% were compression molded at 190 °C and measurements indicated a good flexural strength of 28MPa for the 20wt% GNP to a maximum 50 MPa for the 50 wt% GNP incorporated platelets but not enough electrical conductivity, only 0.6 S/cm for the composite loaded with 60 wt% GNP [7].

2. Experiments

The goal of the experiments consisted in preparing low cost electrically conductive polymeric composites based on a matrix of a low-density polyethylene with filler carbon black 50% on weight, (mixed on a double screw extruder and then pelletized), to which was added expanded graphite. With an electrical activated screw, the composites were mechanical

mixed and conveyed to the hydraulic operated injection unit. A mold made in Aluminum EN 7075 was built for the bipolar plates with micro channels of a 0.13 mm² section which were injection molded in the polymeric composite's recipes.

2.1. Polymeric-Carbon-Expanded Graphite Composites

The specifications of the low-density polyethylene matrix with carbon black 50% on weight are presented on Table 2.

Table 2. Low-Density Polyethylene (PE-LD) - Carbon Black (CB) Composite.

Characteristic	Material	Property
Matrix	PE-LD	MFI=70 gr/10 min
Filler	Carbon Black	Particle size= 60-70 nm
Total inorganic content	-	48.5%-55%

The specifications of the expanded graphite added to the PE-LD-CB composite are presented on table 3. The expanded graphite powder manufactured from natural graphite increases the thermal conductivity of various compound materials. Due to the electrically conductive properties of graphite, it is also suitable for electric, antistatic and mechanical applications [5].

Table 3. Expanded Graphite SGRATHERM® GFG 600 Properties.

Typical properties	Units	GFG600
Dimension of particle D50 (ISO13320)	μm	600
Powder density (DIN51938)	g/l	100
Carbon Content (DIN51903)	%	>95
Moisture content (DIN51901)	%	<5

The PE-LD-CB pellets (as per Table 2) were mixed with expanded graphite EG (as per Table 3) with a combined system consisting in a dosing screw for the PE-LD-CB pellets and a mixer and conveying screw electrically activated (Fig.10). Compositions obtained are presented in Table 4. The pellets and expanded graphite are presented in Fig. 1.

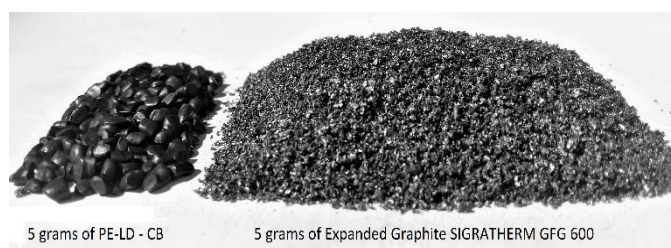


Fig. 1. Five grams of PE-LD-CB pellets and five grams of the expanded graphite grade SGRATHERM® GFG 600.

Table 4. Composites prepared by mixing PE-LD-CB with expanded graphite.

Composite	Matrix PE-LD	Filler 1 - CB	Filler 2 - EG
C1	50wt%	50wt%	-
C2	41.7wt%	41.7wt%	16.7wt%
C3	32.2wt%	32.2wt%	35.6wt%
C4	25wt%	25wt%	50wt%

2.2. The bipolar plate

The bipolar plate was designed with a double micro channel network with a section of 0.13 mm², an active surface of 676 mm² and a total surface of about 900 mm² at a thickness of 2.25 mm (Fig. 2).

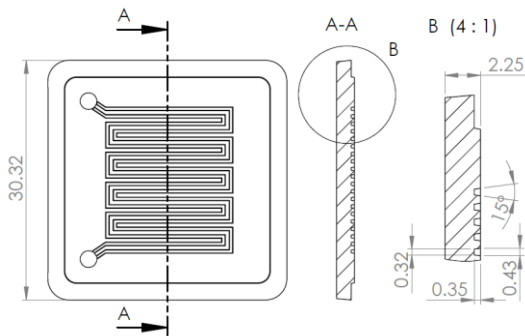


Fig. 2. The bipolar plate drawing (units mm).

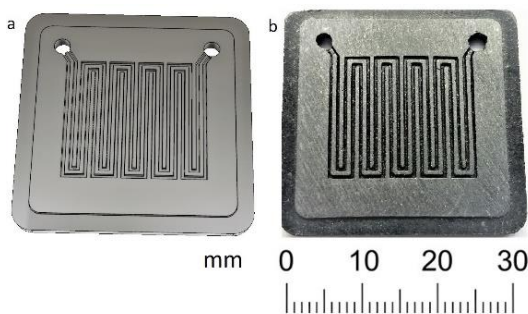


Fig. 3 a) The 3D model and b) the molded bipolar plate.

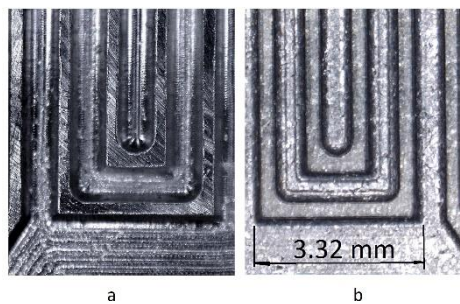


Fig. 4. a) Detail of micro-milled cavity and b) detail of molded part.

The mold was made in aluminum EN 7075, on a standard mold base 100 mm x 130 mm. The cavity was micro-milled with a pocket strategy for roughing with a tool of 1 mm diameter and finishing was done with a (rest milling) pocket strategy followed by a contour with a tool of 0.5 mm diameter at 24,000 rotations per minute, a feed speed of 150 mm/min and depth of cut of 0.02 mm (detail of micro-milled cavity in Fig. 4, a) on a vertical machining center ZPS LMG 1000 with a SELCA 3045 P controller and equipped with direct measuring system. Minimum retraction of tool and smooth profiles of acceleration/deceleration were considered for the optimizations of the CNC paths.

2.3. Injection Molding of Polymeric-Carbon Composites Experiment nr. 1

In a previous experiment, E1, dedicated to compression and injection molding electrically conductive polymer composites, a family injection mold was built for ISO 527-2 compliant samples and one part simulating a bipolar plate with 3 sections flow channels network on 3 different thicknesses of the plate: 4, 2.5 and 1.5 mm. For measuring the cavity pressure was used a controller DME CP 3000 with a DME 405C pressure sensor [8].

Table 5. Injection Molded Composites; CB-Carbon Black, GR-Graphite, PE-LD-Low-Density Polyethylene, PP-Polypropylene [8].

Composite	Matrix Polymer	Filler 1	Filler 2
	Polyolefins	CB	GR
P6	PE-LD 50wt%	CB 50wt%	-
P7	PE-LD 45wt%	CB 45wt%	GR 10wt%
P8	PP	-	-

On experiment nr.1 were molded composites P8, P6 and P7 (recipes as per Table 5) on an injection molding machine Arburg Allrounder 221-75-350 with Polytronica controller; the set-up of parameters was based on available data from raw material suppliers and were optimized on the hypothesis that higher melt temperature, injection pressure & speed could help filling the part.

Due to the very aggressive influence of the inorganic content to the flow, for the parameters tuning was considered an increase of the combination of the three parameters (melt temperature + 5°C and injection pressure + 0.5 MPa and injection speed + 5% for one new test set, as shown in Fig. 9).

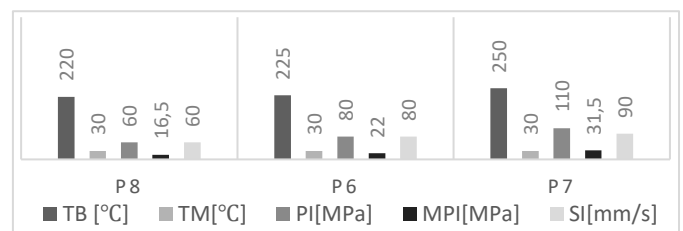


Fig. 5. Experiment nr. 1 Parameters; TB – Temperature of barrel; TM – temperature of mold; PI – Injection pressure; MPI- Measured injection pressure into the cavity; SI- Injection speed.

The experiment nr. 1, composite P7 evidenced the difficult fill of the 1.5 mm thickness section of the plate and poor replications of the 0.5 x 0.5 mm² section channels; poor flow was confirmed by the studies of the influence of the carbon black on the flowability of conductive composite materials injection molded into a mold spiral with section 3 mm x 1.5 mm and it was observed that the flow decreases with the increasing inorganic content, for example: from 251.6 mm (20wt% CB , 60wt% total fillers) to 16 mm (for 20wt% CB, 80wt% total fillers) [10]; the observations on E1-C7 indicated a first stage associated to the thermoplastics flow model, explained by Bodini and Pessani [11] , Goodship [12], Seres [13], followed by a second stage with a different behavior due

to a very fast cooling and transition to solid phase of the high inorganic content (Fig. 6); the poor replication of the channels $0.5 \times 0.5 \text{ mm}^2$ could be assimilated to a “record groove effect” caused by high cooling velocity, melt and mold wall temperature too low injection speed too low (Fig. 7), or to an “air streak behind an engraving” caused by air streaks [12] but the “copy-paste” like shape of the channels with a step of about 0.3 mm on the flow direction may lead to a third explanation according to which the solidified front was moved and compressed with the force given by the packing pressure applied on the central stream (probably still melted on the thick zone of the plate).

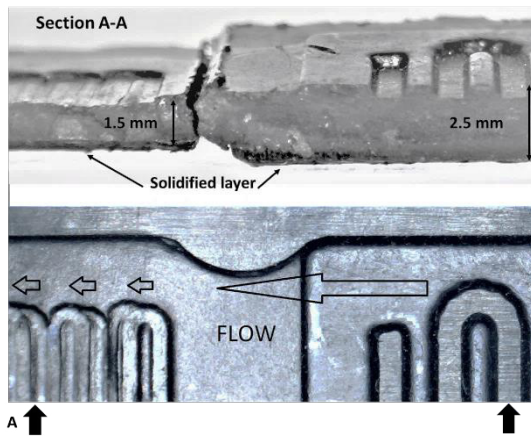


Fig. 6. Flow of the polymeric-carbon black composite; poor flow on the thickness 1.5 mm and solidified layer well evidenced [8].

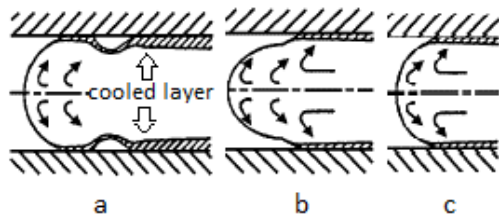


Fig. 7. “Record Groove Effect”: a) flow front reaches the mold wall again; b) cooled down peripheral layer impedes frontal flow to the wall; c) front flow cooled down near the wall, according Goodship [12].

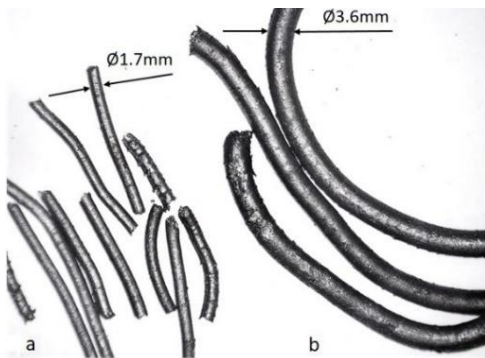


Fig. 8. a) Free melt injected into atmosphere – E1 and b) after increasing the opening of the injection unit nozzle from 1.7 mm to 3.6 mm diameter – E2.

For the experiment nr. 2 the mold was electrically heated to help flow and high-speed injection speed was considered to avoid the fast transition to solid phase of the polymeric composite. When composite P7 was injected in atmosphere was observed a poor injection rate and was decided to increase the diameter of the openings of the injection unit and mold nozzle in order to reduce pressure loss and to help injection rate (Fig. 8).

Experiments nr. 1 evidenced that higher inorganic contents negatively influenced the flow and the composite melt cooled fast; In an optimal situation, 50% of the heat energy comes from the screw shear (in the compression zone) and 50% from the conductive heat delivered by the heater bands around the screw barrel [14], [15]. Considering the description of the thermoplastics granules transit from solid to melt phase on the screw compression zone [13], it was estimated the hypothesis that the expanded graphite, at a density of 100 grams/liter, will be compacted with no significant shear - no energy and the thermoplastic composite pellets dispersed into the graphite will not profit as normal from the heat produced by the shear; it was decided to set higher temperatures for the screw barrel and high screw rotational speed (resulting in high shear rates) as mentioned by Whelan and Goff [15]. A screw with a high compression ratio profile could be considered for future tests.

It was noted that even well mixed into the hopper, due to different density, the pellets dropped first to the center of the hopper and graphite powder second, observation confirmed by Olmsted and Davis in *Practical Injection Molding* [14]. Feeding problems could be encountered when are used two different forms of the materials (especially for powders) [15]. It was observed that the expanded graphite was stacking into the feeding throat of the injection unit. To solve the problem, for the experiment nr. 2 was added a feeding and mixing screw to convey the mixture polymer-carbon black-expanded graphite to the injection unit closed to the reciprocating screw and in a second stage, for a good homogenization was foreseen a feeding screw for the PE-LD-CB pellets (Fig. 10).

2.4. Injection Molding of the Bipolar Plates-Experiment nr.2

The E2 process parameters were configured on the basis of the E1 [8] observations, analyses and conclusions and the parameters optimization flow chart are presented in Fig. 9.

Tests were performed on same machine Arburg Allrounder 221-75-350 with Polytronica controller (with a clamping force unit of 350 kN and an injection unit with a 30 mm diameter reciprocating screw developing a maximum 110 MPa pressure into the melted material). Revolving the mixing and conveying screw the PE-LD-CB pellets were mixed with the expanded graphite EG and conveyed to the metering zone of the reciprocating screw and then the resulting melt was injected into the mold, with parameters as per Table 8. For an improved homogenization was added a dosing screw for the PE-LD-CB pellets and to avoid the EG powder to stack (Fig. 10). Future work will be directed to the control optimization of dosing the composite materials for a repeatable process.

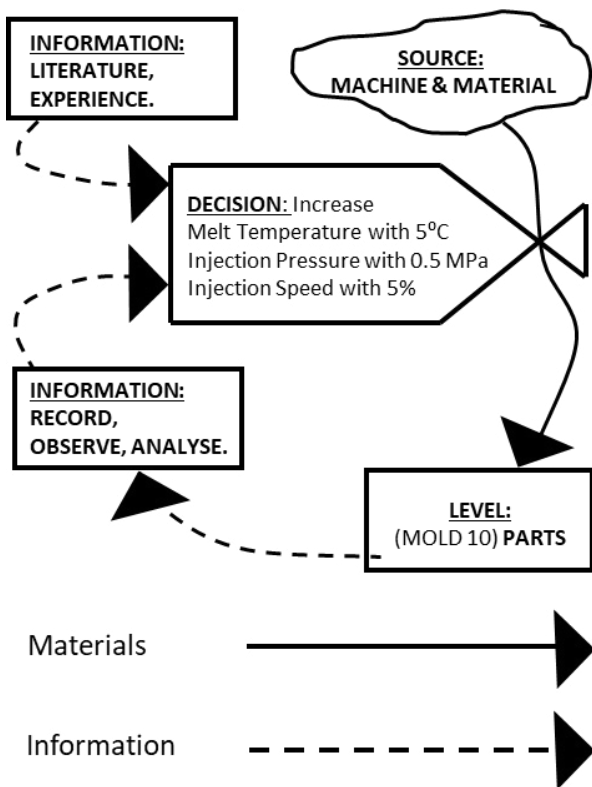


Fig. 9. Tuning injection molding parameters *Closed Loop*; Symbols as per J. W. Forrester in *Principles of Systems* [9].

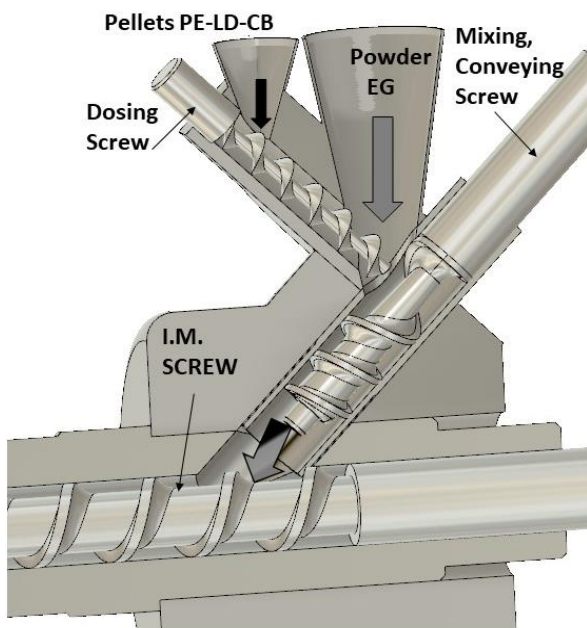


Fig. 10. Lay-out of the mixing-conveying and dosing system; the screw for dosing the pellets of PE-LD-CB with a double function, to feed and to avoid the stacking of the expanded graphite EG powder to stack; then, with the mixing and conveying screw the pellets and powder were dropped to the machine screw.

The observations, analyzes, decisions for the set-up parameters (Table 8) and design of the injection molding system (machine, mold, mixing, feeding material and part changes) are presented in Table 6 and Table 7. To be mentioned that the bipolar plate channels were designed with the length on the injection flow direction.

Table 6. Observation, analyze and decision for the set-up of injection molding parameters for PE-LD-CB - EG composites. TB- temperature of barrel-temperature of mold, PI- injection pressure, SI- injection speed, SRS - screw rotation speed, E1 – experiment nr.1.

Observation E1	Physical Cause	Mentioned in literature	Decision
Poor flow	Inorganic Content reduced the flow	[10]	Increase TB, TM, PI
Poor replication of details	Material cooled fast, low temperature	[12]	Increase TB, TM, SI
Difficult transition to melt phase	Low temperature transfer	[14],[15]	Increase TB, SRS

Table 7. Observation, analyze and decision for the design of the part and of the injection molding system.

Observation E1	Physical Cause	Mentioned in literature	Decision
Poor flow	Inorganic Content reduced the flow	[10]	Increase Opening Diameter of machine and mold nozzles
Poor replication	Material cooled fast, low temperature	[12]	Add heating to the mold cavities
Poor replication	Small wall thickness, position of channels	[12]	Increase wall thickness from 1.5 mm to 2.25 mm; Design of channels on the direction of flow
Difficult feeding with material	Different density of materials	[14],[15]	Design a system with one dosing screw for the pellets and one mixing and conveying screw

Table 8. Injection Molding Parameters for PE-LD-CB-EG composites. A forward movement of the screw with an injection speed of 100 mm/s corresponds to a melt volume of 82 cm³/s injected into the atmosphere.

Composite	Mold Temperature	Maximum Barrell Temperature	Injection Pressure	Injection Speed
C1	30 °C	230 °C	65 MPa	75 mm/s
C2	50 °C	260 °C	75 MPa	80 mm/s
C3	70 °C	270 °C	90 MPa	85 mm/s
C4	75 °C	275 °C	95 MPa	90 mm/s

2.5. Resistivity Measurements

Volume Resistivity ρ was measured for the polymeric-carbon composites using formula (1):

$$\rho = RA/T \text{ [}\Omega\text{cm]} \quad (1)$$

where R is the resistance in [ohms], A is the common surface of the electrodes in [cm^2] and T is the thickness of the sample.

Table 9. Resistivity for PE-LD-CB - EG composites.

Composite	Area A [cm^2]	Measured Resistance [ohm]	Thickness [cm]	Calculated Resistivity [Ωcm]	Calculated Conductivity [S/cm]
C1	0.2	6	0.23	5.22	0.19
C2	0.2	0.5	0.23	0.43	2.33
C3	0.2	0.3	0.23	0.26	3.84
C4	0.2	0.2	0.23	0.17	5.88

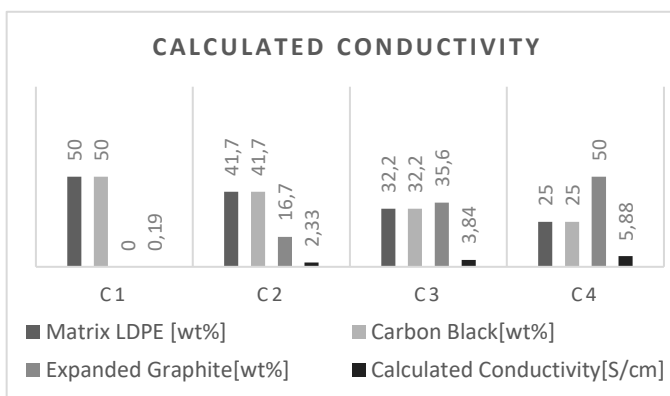


Fig. 11. Composites C1, C2, C3, C4 : Matrix PE-LD, Carbon Black, Expanded Graphite [wt%] and Calculated Conductivity [S/cm].

The expanded graphite loading positively influenced the conductivity of the polymeric composites PE-LD-CB - EG. The measurements on the injection molded samples on experiment nr. 2 are presented in Table 9 and Fig. 11.

3. Conclusions

The experiments evidenced:

- The dosing, mixing and conveying system was working properly for composites on which the content of expanded graphite was up to 30-40 wt %. An additional powder agitator could improve the repeatability of the process;
- The flow was improved by increasing the openings of the mold and injection unit nozzle;

The expanded graphite loading positively influenced the conductivity of the polymeric composite PE-LD-CB - EG;

Higher loading of the expanded graphite influenced the porosity of the bipolar plate on the areas not completely filled; the defect was fixed setting higher temperature of mold and barrel, higher injection pressure and screw rotational speed and very high injection speed to avoid the material cooling.

A molding system with a special configuration screw for the compression zone, nitrogen accumulators for higher injection speeds, reduced length of runners, an improved dosing, mixing and conveying device and with an injection-compression molding option could be considered a good platform for processing the conductive polymer composites.

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