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Influence of Injection Moulding Parameters on Electrical Conductivity of Polypropylene-Graphite Composite Bipolar Plates for Hydrogen Fuel Cells

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Abstract: *News on Green Energy and Green Hydrogen is spread on popular and academic media. When energy is obtained from sunlight, wind or water, we call it Green Energy. When hydrogen is obtained from electrolysis with Green Energy, we call it Green Hydrogen. Hydrogen Fuel Cells are electro-chemical devices that convert hydrogen and oxygen's chemical energy into electricity and heat energy with high efficiency and contribute to the decarbonisation of the power supply. Bipolar plates, essential components of the fuel cells, made in polymer-carbon composites, are an economical alternative to the stainless steel, titan and graphite, traditional materials. Our experiments have used a polypropylene matrix filled with graphite with a total inorganic content of 87%, which contributes to high electrical and thermic conductivity but strongly influences the viscosity, flow, pressures, temperatures, and is then challenging to process. Injection Moulding of thermoplastics is a technology widespread in all fields of activities and has considerable potential. In this paper, the experiments' design is highlighted in choosing the factors. A debate regarding the filling, packing, holding pressures, and the last decades' approach and optimisation of injection moulding parameters with the Taguchi Method is presented. Conclusions on the injection moulding process of the bipolar plate made of a polypropylene-graphite composite, the parameters' influence with direct effects on the fuel stack's performance are presented. The combined melt and mould temperatures influence most electrical conductivity by better contacting the electrically conductive particles through the polymer's melted layer. The injection pressure influences the mass and thickness of the product and the electrical conductivity by better packing. Furthermore, we suggest an adapted formula to predict the injection pressure considering the inorganic content and the process temperatures in agreement with the experiments.*

Keywords*: injection moulding, polypropylene-graphite composite, hydrogen fuel cell, Taguchi Method*

1.Introduction

The bipolar plates are components of the fuel cell stacks, representing about 60% of the total weight and 40% of total costs. The functions are to distribute the fuel uniformly (the hydrogen at anode and oxygen at the cathode) and provide the electrical and thermal connection between the cells. Good electrical conductivity is required to reduce power losses. Bipolar plates made of stainless steel, titan or graphite require expensive surface treatments to reduce corrosion and permeability. Thus, polymeric-carbon composites are an economical alternative.

A polymer may be defined as a macromolecule product built by repeating small, simple chemical units (monomers). For example, polypropylene (PP), also known as polypropene, is a thermoplastic polymer used in various applications and is produced via polymerisation from the monomer propylene, primarily based on a method now known as Ziegler-Natta catalyst [1]. Thermoplastic materials are obtained from polymers and are shaped at temperatures when they become plastics and get the final product solid configuration by cooling. Glass-transition temperature indicates the range of temperatures over which the glass transition occurs, from a brittle into a viscous state. For crystalline polymers, the glass-transition temperature is lower than the melting temperature of the crystalline state. At higher temperatures, the material can degrade.

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Thermogravimetric analysis (TGA) is a process that continuously measures sample weight when heated at a linear rate.TGA can help to evaluate thermal degradation behaviour. Thermoplastics are processed mainly by extrusion, injection moulding, vacuum forming, compression, blow moulding [2]. The proprieties of a polymer can be improved by incorporating additives like fillers, colourants, flame-retarders, anti-ageing, to name a few. A polymeric composite consists of a polymer matrix to which fillers are added. The mixing methods may vary, extrusion, Banbury mixing, roll-mill mixing, melt compounding or solution compounding. The fillers do not interact with the matrix. For example, carbon black is a powerful reinforcing filler that contributes to the composite's good thermal and electrical conductivity. Graphite fillers improve dimensional stability, thermal and electrical conductivity [1].

The majority works theoretically and experimentally evaluated the percolation threshold, thermal and electrical conductivity, aggregation, structure for composites with inorganic content up to 10%. In addition, influences of fillers like carbon nanotubes (CNT's), carbon nanostructures (CBN's), graphene and derivates, available at high costs, were evaluated. The review of conductive composites highlighted the analyses used mostly of thermosets (epoxy) matrices, thermoplastics polycarbonate, polyethylene - a maximum conductivity of 700 S/m obtained for a PPO matrix filled with 50wt% MWCNT, and 20S/m for a polypropylene filled 9wt% MWCNT (multi-wall carbon nanotubes [3]. The US Department of Energy recommends a conductivity of 100 S/cm for bipolar plates materials.

A high proportion, usually over 70% of graphite, is added to a thermoplastic polymer to obtain a good electrical conductivity of a composite for injection moulding bipolar plates at an industrial scale at economical costs. Nevertheless, in this range, there are few works disseminating results. Good electrical conductivities of 27 S/cm for bipolar plates were obtained by solution blending polypropylene, graphite and carbon black with a total inorganic content of 80% [4]. Thermogravimetry analyses on a similar polypropylene composite with high graphite content of 60% demonstrated a minor degradation step up to 480ºC; after that, a sharp weight loss was observed [4]. Derieth et al. demonstrated better results of about 100 S/cm of bulk conductivity for smaller flakes particles of graphite at a 78% load. However, they observed that spherical morphology enables a higher filling load and then conductivity. The pressure applied to the measurement sandwich influenced very little bulk conductivity, but an important influence was observed for volume conductivities [5]. Polypropylene melt-mixed in a twin-extruder with expanded graphite powder with loads from 10% to 80% demonstrated increased thermal and electrical conductivity with the filler content. For example, the electrical conductivity: 0.6 S/cm for 10wt% load to 15.9 S/cm for PP composite with 80wt% graphite. The contents were confirmed by thermogravimetric analyses [6].

The inorganic content influences the viscosity of the composite. Therefore, higher temperatures and injection pressures are required for injection moulding. Higher temperatures may concern the degradation of the product. Thermogravimetric analyses demonstrated for polypropylene that a maximum degradation rate at a recorded temperature ranges from 435 to 457ºC [7]. Chipara et al. demonstrated that the temperature at which the mass loss rate is maximum is increased with the concentration of carbon fibres dispersed within the polypropylene matrix, and it was measured in the range of 460 to 470 ºC for composites with up to 20% carbon nanofibers [8].

In previous experiments with a compound 87% graphite in PP, the author observed on the injection moulded bipolar plates a variance of the performance when tested in fuel cell stacks. Then, we planed new experiments to explore the improvements in performance by analysing the influence of surface microstructure on the electrical contact resistance, effect of inorganic content, the hydrogen supply and presented here in this paper, optimise and effect of the injection moulding parameters.

The Taguchi approach of Design of Experiments has been the popular product and process improvement tool for engineering and scientific professionals since its introduction in the USA in the 1980s. Simulating flow software can optimise the injection moulding parameters against trial and error, statistical methods on the Design of Experiments. However, flow simulation software needs accurate rheological material data, unavailable for our experiments material. Thus, we chose a method that can be introduced to small companies at no high costs. This paper proposes a simple formula to predict the injection pressure of a highly filled polymeric composite. The formula is adapted on an experimentally developed equation for the calculus of the viscosity of a composite filled with carbon black and considers the influence of process temperatures. The Taguchi method performed to optimise the injection moulding parameters for better conductivity of a polymer composite bipolar plate and the influence of the bipolar plate on the power efficiency of the hydrogen-air PEM fuel cell are presented.

2.Materials, equipment and methods

2.1. Materials

First, the bipolar plate was injection moulded in a PP, Polypropylene grade J1100 from Rompetrol (MFR of 26,0- 30,0 g/10 min, 230ºC, 2.16 kg/ISO 1133 B) for evaluation of the injection moulding parameters: the temperature at injection moulding nozzle, the temperature of the mould cavity, injection pressure and cavity pressure.

Then, we performed the experiments of injection moulding the bipolar plates in a polypropylene - graphite composite (PP+87GR) with an 87wt% inorganic content, purchased from Centre of Fuel Cell Technology ZBT GmbH Duisburg. The material is suitable for bipolar plates for low-temperature operated fuel cells (under 120ºC). The compound is made in a twin-screw extruder and granulated in pellets form with maximum dimension as of four-millimetre diameter and 12 mm length as shown in Figure 1a. Derieth et al. evidenced the influence of the particle dimension on the bulk-conductivity: about 98 S/cm for particles of 5 µm diameter and particles of 10 µm a bulk-conductivity of about 58 S/cm [5]. An SEM analysis of the internal microstructure of the compound observed that the layer of 200 to 400 µm closed to the mould surface presented lower conductivity because the graphite flakes were oriented perpendicular to the current flow. The core presented an orientation of the graphite flakes in the sense of the current flow in the fuel cell and a better electrical conductivity [5].

Thermogravimetric analysis (TGA) of the composite PP+87GR performed at Advanced Polymer Materials Group confirmed a high rate of degradation in 430ºC to 490ºC and 86.6% inorganic content (Figure 1b).

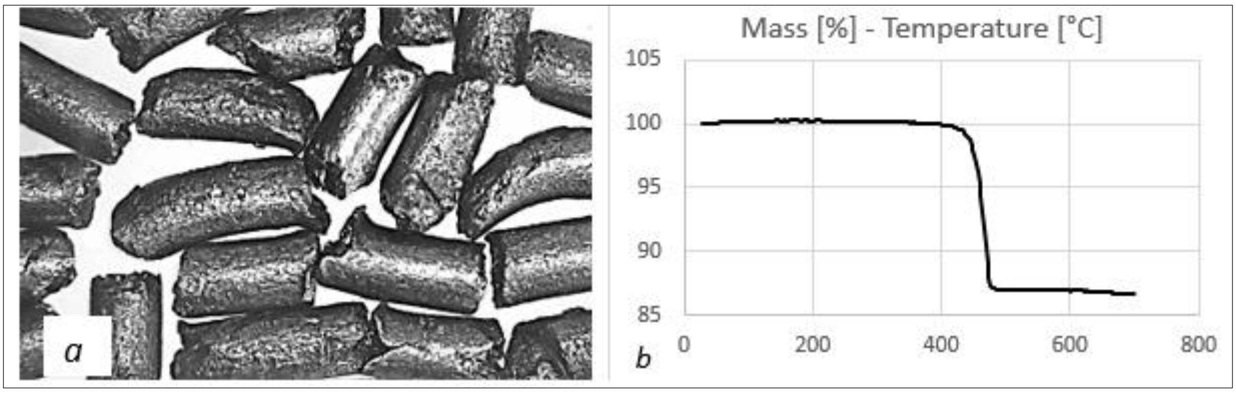


Figure 1a. Composite pellets samples; b. TGA analyse on a ten ºC / min profile

2.2. Equipment

The injection moulding machine, Arburg Allrounder 221-75-350 equipped with Polytronica Controller one-stage system with switch-over on stroke and time which can deliver the same holding pressure as the injection pressure and on which the parameters can be set as follows: maximum hydraulic ram injection pressure - p_h 135 bar, specific injection pressure - p 1090 bar, times - [s], strokes - [mm], speeds - in percentage [%], 100% corresponding to a maximum speed of 100 mm/s or 64 cm³/s [9]. The cavity pressure was measured with a Multi-Process Controller DME 4000 and a sensor DME 405C placed on the cathode side of the bipolar plate cavity mould, made in Aluminium EN 7075, and electrically heated. The model of the bipolar plate has a hydrogen circuit at the anode and an oxygen circuit at the cathode and has a size of 55 x 55 x 4 mm³. For the electrical resistance measurements, a

Direct Current Source (30 Volt, 10 Amper) was used, and each sample was measured in a stack at a load of ten daN. The voltage and current were recorded with the help of a multifunction monitor. The thickness of the bipolar plates was measured with a digital calliper. The fuel cell stack was supplied hydrogen from a hydride cartridge at 0.3 bar and forced air with a fan.

2.3.Estimate the injection pressure method

Dobrescu et al. [10] developed formula (1) for composites low-density polyethylene – carbon black:

$$\eta_k = \eta_p(1 + ac^b) \tag{1}$$

where: η_k is the viscosity of the composite [Pas]; η_p is the viscosity of the matrix polymer [Pas]; *a, b* are coefficients experimentally developed, and *c* represents the parts of filler. Viscosity is not a direct parameter the operator can set on the equipment controller; therefore, based on equation (1), here we introduce an adapted formula (2) by considering the influence of melts and mould temperatures for the estimation of the hydraulic injection pressure:

$$p_{hk} = p_{hp}(1 + ac^b/d^f) \tag{2}$$

where: $p_{hk}$is the hydraulic injection pressure of the composite, p_{hp} the matrix polymer's hydraulic injection pressure, $a = 0.297$ and $b=1.3$, are experimentally evaluated by Dobrescu et al. [10], $f=2.5$, coefficient experimentally evaluated by considering the influence of the combined temperatures of the melt at the nozzle and mould temperature, *d*, calculated with equation (3):

$$d = (T_{Nk} + T_{Ck})/(T_{Np} + T_{Cp}) \tag{3}$$

where: T_{Nk} is the (nozzle set) temperature of the composite, T_{Np} is the (nozzle set) temperature of the polymer, T_{Ck} is the mould cavity temperature for the composite, and T_{Cp} is the mould cavity temperature for the polymer, as recommended by suppliers. It is the place to clarify the terms regarding pressures related to the injection phases. The pressures set on machine controllers: maximum injection pressure controlled by speeds, p_h-hydraulic pressure or *p* - specific pressure on modern controllers, hydraulic or specific holding pressures controlled by time. Moreover, we have the pressures related to the mould cavity and mentioned by literature, papers, flow simulation software: (mould) filling pressure, (mould) packing pressure measured on sensors placed into the mould cavities. The cavity pressure might differ with the sensor's position, lower at the end of the flow. In our experiment, we use the terms hydraulic injection pressure p_h, specific injection pressure p (as the hydraulic pressure multiplied with the intensification ratio) and mould cavity pressure p_c (as measured with the DME sensor placed in the mould manufactured for the injection moulds tests), as shown in Figure 2a. We consider packing pressure controlled by time as holding pressure, and when not mentioning control, we consider it the second stage phase injection pressure.

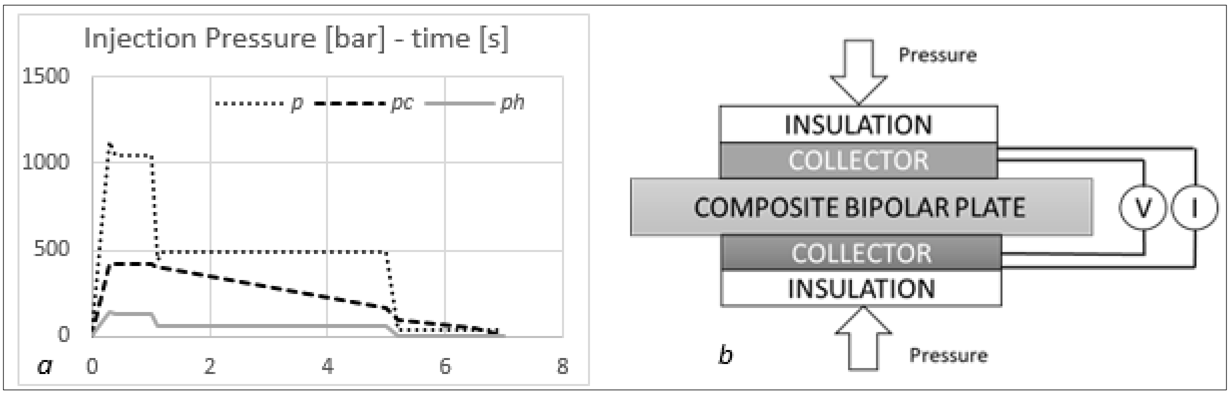


Figure 2a. Hydraulic pressure (set) – p_h, cavity mould pressure (measured) -p_c, specific pressure p; b. measuring electrical resistance layout

2.4. Measuring the electrical conductive proprieties of the moulded bipolar plates

We measured the electrical resistance through-plane of the bipolar plates in an assembly to compare the results shown in Figure 2b at a ten daN load. Then, four bipolar plates of each experiment were assembled in a hydrogen-air (forced) fuel cell stack and tested at room temperature; hydrogen supplied from an AB_5 metal hydride cartridge at 0.03 MPa pressure and forced air with a fan help. The measurement of the fuel cell efficiency equipped with the bipolar plates of the four experiments directly indicates the influence of the injection moulding parameters.

2.5. Taguchi process optimisation method

The Taguchi Method utilises the conventional tools, simplifying them by identifying the guidelines for the experiment layout and the result analysis. The Taguchi method consists of (a) Select Project and Form Team, (b) Conduct Experiment Planning Discussion, (c) Design Experiment (Layout/Test Plan), (d) Carry Out Planned Experiments and Collect Results, (e) Analyse Results, (f) Observation Summary, (g) Validate Improvement. The concepts are: (1) quality should be designed into the product and not inspected into it, (2) quality is best achieved by reducing the deviation from a target, (3) the cost of quality is appreciated as a function of the deviation from the standard, and (4) the losses should be measured system-wide [11]. In the injection moulding process, quality characteristics such as reject rate, flash, or porosity have traditionally been measured Taguchi method uses Smaller-the-Better, Nominal-the-Better and Larger-the-Better [11,12].

2.5.1. Select Project and form team

Project: Optimisation of injection moulding parameters of a bipolar plate for a Proton-Exchange Membrane (or Polymer Electrolyte Membrane - PEM) hydrogen fuel cell. The study's goal consisted of analysing the influence of the injection moulding parameters on the electrical conductivity of the bipolar plate and the performance of the PEM hydrogen fuel five cell assembly.

Form Team: Any Design of Experiments (DOE) procedure must be backed by a complete knowledge of the technology underlying principles, which helps understand the phenomena and is essential in interpreting the analysis. The team should have between 2 and 15 members. The machine operator and the production staff should be part of the team.

Team, 3 Members: Machine Operator, The Author (Leader and Facilitator) and we considered as a third "member" the References (Injection Moulding Machine Controller Polytronica Operation Manual, Literature, Taguchi Papers, open-access Flow Simulation Software documentation).

2.5.2. Experiment planning discussions

Objective: To investigate the interaction between packing and electrical conductance of the bipolar plate and its influence on the PEM hydrogen fuel cell's performance.

Identify the quality characteristics: measured the parts' weight, the resistance (calculate conductance), and the fuel cell efficiency performance; strategy: Larger -the-Better.

2.5.3. Factors

We analysed the literature content (period 1982 - 2020, in Table 1) and the Taguchi method applied to injection moulding (2004 - 2020, in Table 2) by counting the number of times a parameter is mentioned. When the pack pressure was mentioned as the second stage, it was considered an Injection pressure - fill & pack, and when the pack was referred to as the third stage controlled by time, it was considered a holding pressure.

Table 1. Quantitative analysis of the literature content - The number of times a parameter related to the injection unit and mould mentioned in literature [1, 14-20]

Parameters (term)	Nr.	Nr.	Nr.	Nr.	Nr.	Nr.	Nr.	Nr.	**Total**	**Rank**
Mould temperature	46	37	65	300	140	89	8	89	774	3

Injection pressure - fill	73	6	120	280	85	83	36	184	867	2
Cooling / cure time	29	5	29	104	37	25	66	18	313	7
Packing/holding pressure	8	0	26	145	165	82	126	84	636	4
Melt / barrel temperature	152	40	59	375	53	120	158	85	1042	1
Back pressure	72	3	51	109	64	40	15	68	422	5
Injection speed	69	3	13	91	76	23	29	107	411	6
Packing / holding time	2	0	6	29	8	43	32	3	123	9
Injection time	13	3	8	34	20	6	28	11	123	10
Reference	[14]	[1]	[15]	[16]	[17]	[18]	[19]	[20]		
Year of publication	1982	1989	1996	2000	2004	2010	2013	2020		

Table 2. Quantitative analysis of the parameters related to the injection unit and mould - factors contribution rank according to Taguchi analysis works [12, 13, 21-24]

Parameters (Factors)	Rank	Rank	Rank	Rank	Rank	Rank	AV	N/AV	**Rank**
Mould temperature	1	3	4	3	1	4	2.67	2.25	1
Injection pressure – fill & pack			1		3		2	1	5
Cooling / cure time	4	2				3	3	1	5
Packing/holding pressure	6	1		4		1	3	1.33	2
Melt / barrel temperature	5		2	2	4		3.25	1.23	4
Injection speed	3		3	1			2.33	1.28	3
Packing/holding time	2					2	2	1	5
Injection time					2		2	0.5	6
Noise Factors				2					
Levels	3	2	3	2	2				
Measurements	3	2	2	2	1				
Reference	[12]	[13]	[21]	[22]	[23]	[24]			
Year of publication	2004	2010	2011	2013	2016	2020			

The coefficient N/AV representing Sum of apparitions of the term/ Average Rank, presented in Table 2, do not confirm the Ranks according to the literature presented in Table 1, the packing/holding, overpasses the injection/filling pressure and mould temperature overpasses the melt temperature. Injection pressure is the fifth, injection speed is the third. It shows the approach of the last decade, influenced by the flow simulation software analyses.

Filling pressure and packing pressure terms in injection moulding technology

Literature. *Filling:* the injection unit delivers a pre-set amount of molten polymer to the mould tool; *Packing and Solidification:* Under pressure, once the material is in the tool, it fills the cavity (mould packing), then the part cooled and is finally ejected. The packing stage aims to add extra material to compensate for the shrinkage caused by the decreasing density of the solidifying polymer [17]. During the mould cavity filling, high injection pressures maintain the desired filling speed. Once the mould cavity is complete, this high pressure may not be necessary or desirable; a lower, second stage pressure may follow a high first stage pressure. At a certain point in the injection moulding stroke, when the mould is almost complete or the gate freezes, the resistance to flow becomes high and, it becomes difficult for the screw to maintain the desired rate. The Velocity Pressure Transfer (VPT) is when control shifts from velocity to pressure [1]. Seres claims that the transition from filling the mould cavity to the packing (also known as the transition from the first stage to the second stage) is performed differently in injection with a material cushion versus without a material cushion (switch-over on the maximum stroke). The packing phase starts with the end of filling and ends with the gate freezing point [2]. A three-stage system introduces the terms filling (first stage), packing (second stage) and holding (third stage). The first injection pressure completes the filling and packing phases; the holding pressure executes the third stage.

Flow simulation software. When comparing the pressures between the moulding machine and the simulation, the plastic pressure should be measured directly and not calculated as the hydraulic pressure multiplied by the intensification ratio whenever possible. Differences between simulated and real pressure can appear when data is not dependent on viscosity [25]. Eventually, accurate rheologic data are a must; data collection is a hard and expensive job.

For the polypropylene - graphite composite is not available rheologic data for a reliable flow simulation. Therefore, we have chosen the L4 orthogonal array with a Larger-the-Better strategy to optimise the process and an adapted formula for estimating the injection pressure. We used the terms hydraulic injection pressure p_h, specific injection pressure p (as the hydraulic pressure multiplied with the intensification ratio) and mould cavity pressure p_c (as measured with the DME sensor placed in the mould manufactured for the injection moulds tests).

Machine controllers. In modern injection moulding machines, the operator can set multi-stage pressures, maximum injection pressure, injection speeds, holding pressures, and times. The switch-over point (Velocity Pressure Transfer) can be set on screw position, hydraulic pressure or specific pressure, cavity pressure (optional), or time [26-28]. Machine Constructors like Fanuc use the terms maximum injection pressure and maximum pack pressure [29].

2.5.4. Levels

Material supplier recommendation guideline for injection moulding of composites with high graphite content: the shot weights: 30-70% of the maximum available on the injection unit, generous open machine and mould nozzle, large cross-section runners and gate, high injection speed, holding pressure: 2/3 of the maximum injection pressure, holding Time: 1.25 s/mm of thickness, temperatures: mould 70-90ºC, barrel 220 to 360ºC (to the nozzle of the injection unit). This study indicates the equipment, injection unit cylinder and mould temperatures and not of the compound melt. In Figure 3 are presented the injection moulding parameters and the location where they are set or measured. No polymer is infinitely stable at the processing temperatures, so that it may concern changing proprieties and degradation [14]. TGA analyses performed at Advanced Polymer Materials Group on our experiments material observed the composite degradation high rate above 430ºC. Results are confirmed by Halasz et al. [7] or Chipara et al. [8] on polypropylene–carbon compounds TGA. Our tests with injection moulding the bipolar plate in polypropylene evidenced the maximum hydraulic injection pressure, p_{hp} of 30 bar, a specific pressure of 242.22 bar and a measured (average) cavity pressure p_c 207.6 bar at a barrel nozzle temperature set 220ºC, mould temperature 30ºC.

Valero et al. [20] recommend for PP melt temperature of 200 to 290ºC and affirm that melt temperature results from screw rotation speed, back pressure and injection unit temperature. Seres [2], Whelan [14], Rosato et al. [16] indicate a lower effect of the injection rotational speed and a significant effect of the shear rate heating and barrel temperatures. Goodship recommends for PP an ascending profile of cylinder temperatures from 220 to 290ºC [17].

The decision on choosing the factors and level

To optimise the process and analyse the influence of the injection moulding parameters on the resistance of the bipolar plate (and on the fuel cell performance), on a minimal design of experiments, a Taguchi L4 orthogonal array, three factors with two levels was chosen.

Table 3. Procedure on choosing the levels of the factor's temperature and pressure

Factor	Composite Supplier Recommendation	Observation
Set Temperature at Nozzle (T_N)	T_N = 300÷360ºC AVERAGE T_N= 330 ºC	For polypropylene, the AVERAGE Barrel's Nozzle Temperature for PP is of about 220ºC;
Mould Cavity Temperature (T_C)	T_C = 70÷80 ºC AVERAGE T_C =75ºC	For polypropylene, the AVERAGE Mould Temperature is of about 30ºC;
Injection Pressure (p_{hk}) [bar]	High pressure. It was chosen, $p_{hk} \pm 15\ bar$, 100 and 130 bar	Applying formula (2) $p_{hk} = p_{hp}(1 + ac^b/d^f)$ For values of $a = 0.0295$ and $b=1.3$ [10], $d= (330+75)/ (220+30)$, $f=2.5$, p_{hp} $=30$ bar results $p_{hk=}$ *115* bar.

From 30 experiments, we analysed the representative 20 experiments (5 samples for each experiment). Table 3 is presented the procedure for choosing the levels of factors: T_N – barrel nozzle set temperature, 320-340 [ºC] & T_C - mould temperature, 70-80 [ºC], p_h- hydraulic injection pressure 100 – 130 bar, and t_H- holding time 4-8 s. Table 4 presents the order of experiments, factors and levels. Pressures are indicated in bars as they can be set and measured.

2.6. Measurements concept

We considered simple methods for evaluating the influence of the injection moulding parameters on the electrical conductivity of the bipolar plates: measuring the performance of the fuel cell stack, the product and standard available equipment. The units are indicated as they can be set or read on equipment controllers.

3. Results and discussions

3.1. Results, Taguchi and ANOVA analyses

The Taguchi method uses a statistical measure of performance called signal-to-noise SN, for Larger-The-Better, calculated with formulas (3) and (4) a function of Mean Sum of Squares Deviation of the measured values of the experiment (y_i), MSD. The Taguchi and ANOVA analyses calculations were made with a standard commercially licenced spreadsheet software.

$$MSD = n^{-1} \sum_1^n \frac{1}{y_i^2} \tag{3}$$

$$SN = -10 \log (MSD) \tag{4}$$

Table 4. Order of experiments, L4 orthogonal array, 3 factors, 2 levels, SET on controller values

		3 FACTORS – 2 LEVELS					
Exp. No.	Order No.	T_N+T_C [ºC]		p_h - Hydraulic Pressure [bar]		t_H-Holding Time [s]	
		T_N 320 + T_C 70	T_N 340 + T_C 80	100	130	4	8
1	1	320 + 70		100		4	
2	2	320 + 70		130		8	
3	3	340 + 80		100		8	
4	4	340 + 80		130		4	

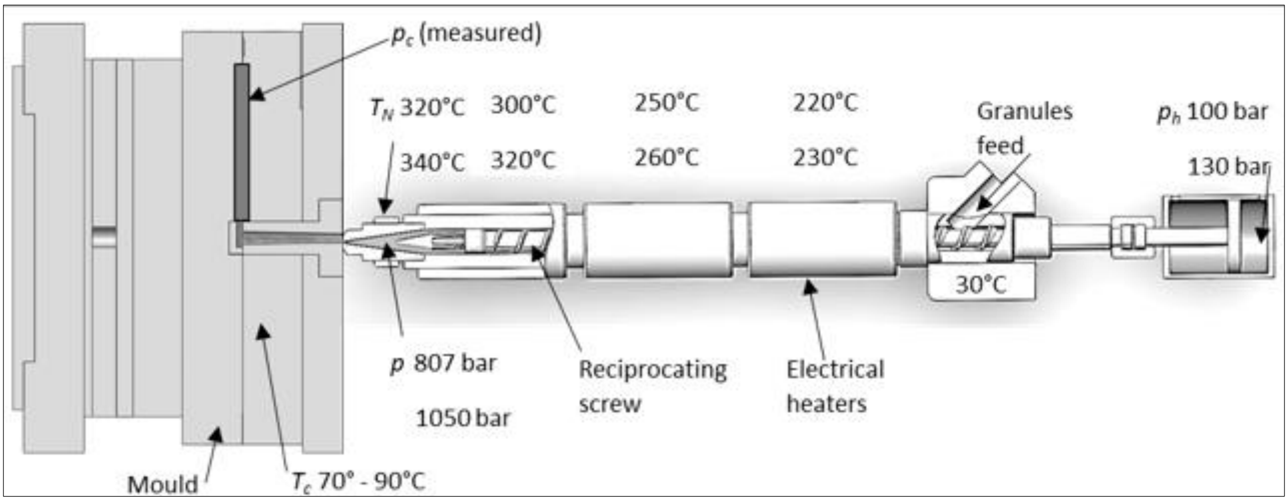
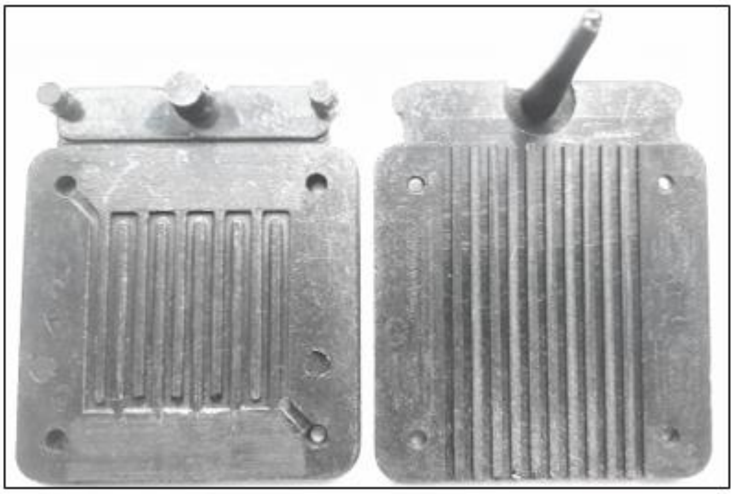


Figure 3. Process parameters. Profile of temperatures set on the injection barrel. Set hydraulic pressure in the installation - p_h, calculated specific pressure in the front of the screw - p, measured pressure in the cavity - p_c



a b

Figure 4. Samples of Experiment no. 3, a) complete injection anode side view, b) complete injection cathode side view including sprue, runner and gate

Process parameters are presented in Figure 3, and injection moulded samples of experiment no. 3 are shown in Figure 4.

3.2. Analyses of mass and thicknesses measurements

In Figure 4 are presented samples of experiment no. 3; the mass has been measured on a complete injection shot, including sprue, runner and gate (to not influence the results by different gate cuts). The bipolar plates have 55 mm x 55 mm - 4.2 mm with a 32 mm x 32 mm gas active area at the anode and eleven channels 55 mm x 1.5 mm - 1 mm at the cathode. Figure 5 are presented the mass and thickness measurements. Analyses results of injection moulding experiments Tables 5, 6, 7 confirm the dominant influence of injection pressure (Rank 1) on mass and thickness.

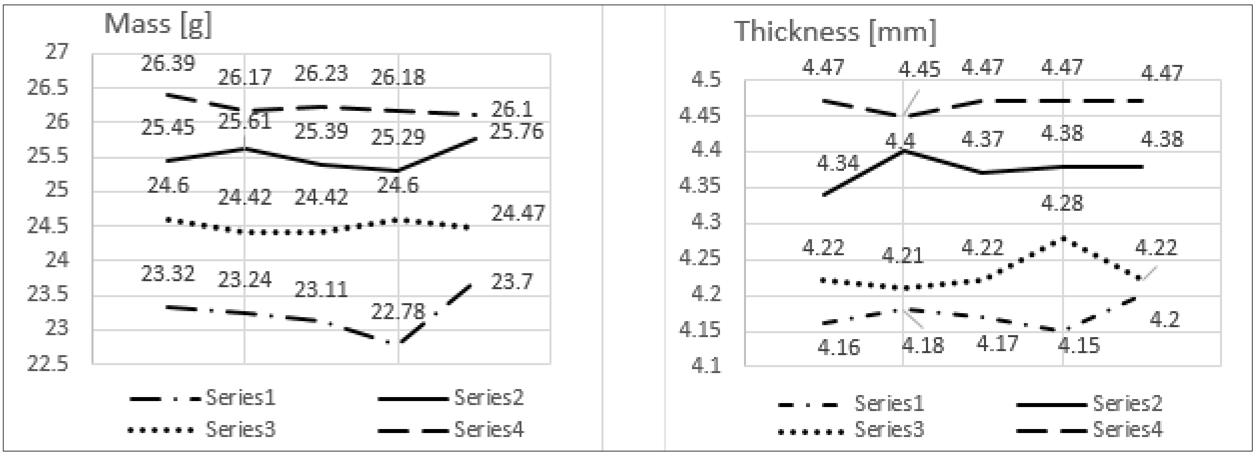


Figure 5. Mass and thickness measurements

Table 5. Mass measurements, mean sum of squares deviation, *SN* ratio for larger-the-better

No.	$T_N + T_C$ [ºC]	p_h [bar]	t_H [s]	Mass Measurements (y_i) [g]					*MSD*	*SN* Ratio
				1	2	3	4	5		
1	320+70	100	4	23.32	23.24	23.11	22.78	23.7	0.00185403	27.318833
2	320+70	130	8	25.45	25.61	25.39	25.29	25.76	0.001538066	28.13025068
3	340+80	100	8	24.6	24.42	24.42	24.6	24.47	0.001665757	27.7838847
4	340+80	130	4	26.39	26.17	26.23	26.18	26.1	0.001455296	28.3704872

Table 6. Taguchi analyse on SN ratio for larger-the-better, mass measurements

Factors		Temperatures $T_N + T_C$ [ºC]		Injection Pressure p_h Bar]		Holding time t_H [s]	
Exp.	*SN* Ratio	320 + 70	340 + 80	100	130	4	8
1	27.3188	27.3188		27.3188		27.3188	
2	28.1303	28.1303			28.1303		28.1303
3	27.7839		27.7839	27.7839			27.7839
4	28.3705		28.3705		28.3705	28.3705	
Sum of *SN* at level		55.4491	56.1544	55.1027	56.5007	55.6893	55.9141
Factor Effect at level		27.7245	28.0772	27.5514	28.2504	27.8447	27.9571
Factor Effect		0.3526		0.6990		0.1124	
Rank		**2**		**1**		**3**	

Table 7. ANOVA analyse of sum of squares (SS), factors contribution, factor influence on mass

Factors	Level 1	Level 2	*SN* at L1	*SN* at L2	SS	Contribution	Influence
$T_N + T_C$ [ºC]	320+70	340+80	27.72454184	28.07718595	0.124357871	19.9%	DOMINANT
p_h [bar]	100	130	27.55135885	28.25036894	0.488615105	78.1%	DOMINANT
t_H [s]	4	8	27.8446601	27.95706769	0.012635466	2.0%	Negligible

3.3 Electrical conductivity

The electrical resistance is a direct indicator of the electrical conductivity, and on the layout presented in Figure 2, the resistance was calculated with Ohm's law. For the composite polypropylene-graphite-carbon black bipolar plates, the packing pressure influence on the conductivity was anticipated by reducing the graphite particles' gaps. The carbon black and graphite contribution were recorded. Nevertheless, in this particular situation, from Tables 8, 9 and 10, it can be observed a more considerable influence on the electrical conductance of the combined factor material temperature – mould temperature (Rank 1) versus the influence of the injection pressure (Rank 2). The temperature favours the contact between the graphite conductive particles penetrating the polymer layer, creating more electrically conductive circuits.

Table 8. Conductance G (calculated as 1/R), mean sum of squares of reciprocals, SN ratio

No.	$T_N + T_C$ [ºC]	p_h [bar]	t_H [s]	Conductance, *G=1/R* [S]					*MSD*	*SN* Ratio
				1	2	3	4	5		
1	320+70	100	4	1.96	2.56	2.78	3.33	3.03	0.14814	8.2933
2	320+70	130	8	2.78	3.33	3.03	3.70	3.23	0.0995	10.0218
3	340+80	100	8	3.70	4.17	4.17	4.76	4.17	0.05796	12.3687
4	340+80	130	4	4.17	4.76	4.76	5.00	4.55	0.04684	13.2938

Table 9. Taguchi analyse on *SN* Ratio for larger-the-better, conductance (*G=1/R*)

Factors →		Temperature $T_N + T_C$ [ºC]		Injection Pressure p_h [bar]		Holding Time t_H [s]	
Exp.	SN Ratio	320 + 70	340 + 80	100	130	4	8
1	27.3188	8.2933		8.2933		8.2933	
2	28.1303	10.0218			10.0218		10.0218
3	27.7839		12.3687	12.3687			12.3687
4	28.3705		13.2938		13.2938	13.2938	
Sum of *SN* at level		18.3150	25.6625	20.6620	23.3156	21.5871	22.3905
Factor Effect at level		9.1575	12.8313	10.3310	11.6578	10.7936	11.1952
Factor Effect		3.6738		1.3268		0.4017	
Rank		1		2		3	

Seres indicated the effect of temperatures on the specific volume and the product's packing [2]. Rosato et al. mentioned that melt temperatures help molecular knitting and entanglement, and mould temperature elevation promotes slow cooling, more time for packing, allowing the molecules to entangle [16]. On the other hand, with higher temperatures, the polymer permits conductive particles to create more conductive network chains, therefore better conductivity. Further experiments demonstrated a variance of the electrical resistance with the load and the contact surface quality.

Table 10. ANOVA analyse, sum of squares (SS), contribution, influence on conductance *G*

Factors	Level 1	Level 2	*SN* at L1	*SN* at L2	SS	Contributio	Influence
$T_N + T_C$ [ºC]	320+70	340+ 80	9.157522895	12.83127368	13.49644486	87.5%	DOMINANT
p_h [bar]	100	130	10.33099641	11.65780016	1.760408191	11.4%	DOMINANT
t_H [s]	4	8	10.79355387	11.19524271	0.161353929	1.0%	Negligible

3.4. Fuel cell performance

The measurement of the fuel cell efficiency equipped with the bipolar plates of the four experiments directly indicates the influence of the injection moulding parameters. Four bipolar plates of each experiment were assembled in a hydrogen-air (forced) fuel cell stack, as shown in Figure 6. The fuel cell stack was tested at room temperature.

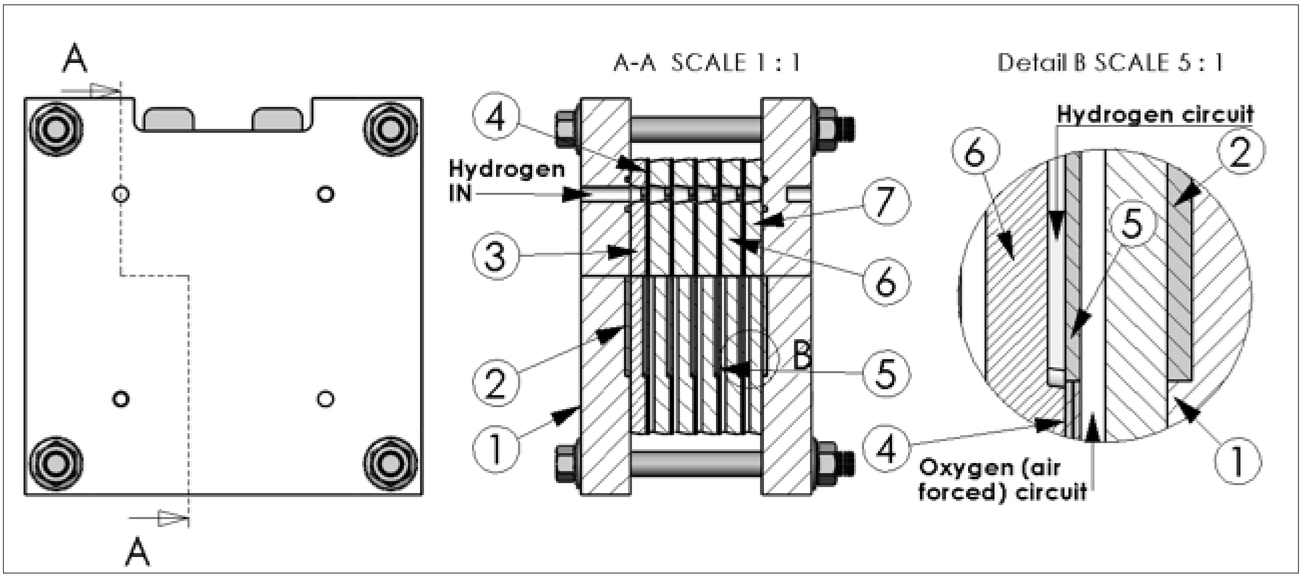


Figure 6. PEM (Proton-Exchange Membrane) Fuel cell test assembly: 1) Endplate Anode side; 2) Copper Collector; 3) Anode Endplate; 4) Gasket; 5) Polymer Membrane Electrode Assembly; 6) Bipolar Plate; 7) Cathode Endplate

Table 11. The power efficiency of the fuel cell with each of the four experiments bipolar plates

Nr.	$T_N + T_C$ [ºC]	p_h [bar]	t_H [s]	Voltage [V]	Current [A]	Power [W]	Power Efficiency
1	320 + 70	100	4	2.6855	0.8738	2.3466	100.00%
2	320 + 70	130	8	2.6457	1.0108	2.6895	114.61%
3	340 + 80	100	4	2.8053	1.0221	2.8642	122.06%
4	340 + 80	130	8	2.8495	1.0994	3.1408	133.84%

As shown in Table 11, the power efficiency measurements confirmed the influence of melt and mould temperatures on the bipolar plates' performance and the fuel cell stack accordingly. According to our knowledge, not many works have been analysing process temperatures affecting the conductivity of a product injection moulded in a polymeric composite with high inorganic filler content. The dominant influence of temperatures on the electrical resistance shown in Table 10 agrees with Lellinger et al. [30], Chandra et al. [31], Rios et al. [32], all confirmed the significant effect of increasing melt temperature on decreasing the electrical resistivity. For example, Chandra et al. found the electrical conductivity 3.84 E-06 S/cm of an injection moulded composite CNT 1.8wt% / PC at low injection speed and low process temperature and 1.81 E-05 S/cm at high injection speed and high level of process temperature [31]. On injection moulding of polycarbonate filled with 5% carbon nanotubes, Rios et al. demonstrated an increase in the processing temperature from 280 to 310ºC led to a decrease of about two orders magnitude the volumetric resistivity [32].

3.5 Analyses of inorganic content influence on viscosity and injection pressure

As presented in 2.3 with Dobrescu et al. formula (1), for values of *a = 0.0295* and *b=1.3* [10] can be estimated a relative composite's viscosity η_k:

$$\eta_k = \eta_p(1 + ac^b) = \eta_p\ (1 + 0.0295\ \cdot 85^{1.3}) = 10.705 \cdot \eta_p \tag{5}$$

To estimate the injection pressure, we used the formulas (2) and (3) proposed in this paper, considering the values recorded on the Polypropylene injection moulding experiments (set hydraulic injection pressure p_{hp} of 30 bar, cavity pressure 220 bar, nozzle temperature of 220ºC and a mould temperature of 30ºC):

$$p_{hk} = p_{hp}\left(1 + \frac{ac^b}{df}\right) = p_{hp}\left(1 + \frac{0.0295 \cdot 85^{1.3}}{(\frac{330+75}{220+30})^{2.5}}\right) = 3.846 \cdot p_{hp} \tag{6}$$

$$p_{hk} = 3.846 \cdot p_{hp} = 115.389 \text{ [bar]} \tag{7}$$

The equation fits the results if conditioned by an influence of the combined temperatures. It could be used as an estimated injection pressure level (hydraulic installation pressure multiplied by the intensification factor) in the design of the experiment, as shown in Table 3. Analysing the results, we noted that the cavity pressure is complex influenced by injection pressure, melt and mould temperatures and inorganic content, as shown in Table 12. The inorganic content negatively influences the flow, higher pressures, and necessary temperatures (experiment 5 / 1,2,3,4). Increasing the melt and mould temperatures reduces the injection pressure (experiment 2/4).

Table 12. Set and measured hydraulic injection pressure - p_h , calculated specific injection pressure - p, measured cavity pressure - p_c , average mass and average *G* for injection moulding of composite PP+87GR and polypropylene PP, at different temperatures of barrel's nozzle T_N and mould cavity T_C

Exp. No.	Material	$T_N + T_C$ [ºC]	p_h [bar] Set & measured	p [bar] calculated	p_c [bar] measured	Average mass [g]	*Av. G* (*=1/R*) [S]
1	PP+87GR	320 + 70	100	807.41	98.6	23.23	2.733
2	PP+87GR	320 + 70	130	1049.63	189	25.5	3.214
3	PP+87GR	340 + 80	100	807.41	187.75	24.502	4.193
4	PP+87GR	340 + 80	130	1049.63	300.125	26.214	4.647
5	PP	220 + 30	30	242.22	207.6	10.8	-

Increasing the melt and mould temperatures helps obtain better replication by obtaining higher cavity pressure at the same injection pressure level (experiment 3/1. Results confirm that an accurate rheologic description of the composite is a must for an appropriate flow simulation, and the process temperatures influence the product's proprieties. When not available, or optimising the process parameters through simple design experiments, the suggested formula might help.

Brydson demonstrated the melt viscosity is a function of the difference between the polymer's processing temperature and glass transition temperature $(T - T_g)$ and claimed an increase in pressure with 1000 bar is equivalent to a drop in temperature in the range of 30-50ºC [1]. As shown in Table 12, at the same injection pressure p_h of 100 bar, specific pressure p of 807.41 bar respectively, a combined increase of temperatures with 30ºC increased the mould cavity p_c from 98.6 to 187.75 bar (Experiment 1/3), and at pressure p_h of 130 bar, p of 1049.63 bar, a combined increase of 30ºC increased the mould cavity p_c from 189 to 300 bar (Experiment 2/4). The polypropylene injection moulding has a different flow behaviour than the polypropylene-graphite composite, with a lower cavity pressure drop.

Electrical conductivity can be predicted on a complex model considering the content, dimensions, and orientation of the conductive particles in the polymeric matrix. Table 12 results indicate that the process temperatures and the cavity pressure, which contribute too, can be considered for an estimation.

4.Conclusions

The Taguchi and ANOVA analysis on an L4 orthogonal array demonstrated a dominant influence of injection pressure on the mass and thickness of the bipolar plate, a situation that was anticipated. Furthermore, an adapted formula has been introduced here for estimating the injection pressure by considering the influence of the combined temperatures of the melt (at the barrel nozzle) and mould temperature. The bipolar plates were tested in a PEM hydrogen fuel cell stack, a direct indication of the influence of injection moulding parameters on the performance. The Taguchi Method does not require high-level mathematics and, backed by a complete knowledge of the technology underlying principles, can be integrated even by small companies.

The electrical resistance analysis evidenced a significant influence of composite and mould temperatures, explained by better contact of the electrically conductive particles through the polypropylene's melted layer. In addition, higher process temperatures contributed to increased cavity pressure and better packing and conductivity by improving the conductive network chain. The electrical conductivity can be predicted by a model considering the process temperatures influence.

The material's excellent proprieties are not a guarantee that the manufactured product will correspond to the requirements. Moreover, the experiments demonstrated the need to optimise the injection moulding parameters to get the best performance of the composite recipe. The efficiency of a hydrogen-air fuel cell stack assembled with each of the four bipolar plates demonstrated the dominant temperature's (rank 1) and injection pressure's (rank 2) effect for better performance.

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