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INJECTION MOLDING OPTIMIZATION IN ORDER TO IMPROVE THE DISPERSION OF THE NANOCCLAYS



Memòria i Annexos

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Abstract

Injection molding is the most commonly manufacturing process used for the fabrication of plastic parts. Different products can be manufactured using injection molding which vary greatly in their size, complexity and application. Automotive industry is the most important sector that uses this technology. A wide variety of additives are used to modify the raw polymers and achieve new properties. Nanoadditives and nanoclays specifically, are used to improve various physical properties, such as reinforcement, synergistic flame retardant and barrier.

This work is focused on the study the different parameters in the injection molding process in order to optimize the process using a specific grade of polypropylene and a specific grade of nanoclay. The main goal of the project is to improve the flexural modulus of the studied part using a lineal model taking into account the behavior the selected parameters.

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1. Introduction

Injection molding process is one of the most important technology used in the automotive industry. Three main components are required: injection molding machine (IMM), tool or mold and plastic pellets. Depends on the final part, different plastic will be selected based on the final part properties.

Additives are usually used with the aim of enhance some properties of the standard material. Nanoadditives are commonly used to enhance properties like barrier properties, mechanical properties, thermal properties, optical properties among others. Good dispersions is related directly to a high performance of these nanofiller within the polymer matrix.

All experiment carried out during this work were performed in EURECAT, a technology center in Catalonia. EURECAT-Cerdanyola has experience in plastic injection for more than 30 years. The center participates in public and private projects researching in different applications using the injection molding process as a basis.

This work is focused on study how some injection parameters may affect to the dispersion of the nanoadditives and the mechanical properties of the final part.

1.1. Polymer processing

There are many different types of plastics processed by different methods to produce products meeting many different performance requirements, including costs. The basics in processing relate to temperature, time and pressure. In turn they interrelate with product requirements, including plastics type and the process to be used. Europe plastics consumption in 2016 was 60 million tonnes and the worldwide plastic consumption was 355 million tones. Packaging is the market sector which converts 39.9% of the consumption and the automotive sector consumes 10% of the total in Europe.

All of this processes are used to fabricate all types and shapes of plastic products; household convenience packages, electronic devices and many others, including the strongest products in the world, used in space vehicles, aircraft, building structures, and so on.

Proper process selection depends upon the nature and requirements of the plastic, the properties desired in the final product, the cost of the process, its speed, and product volume. Some materials can be used with many kinds of processes; others require a specific or specialized machine. Numerous fabrication process variables play an important role and can markedly influence a product's esthetics, performance, and cost. The relative use of these methods in Europe in 2016 is shown in Fig. 1 [1].

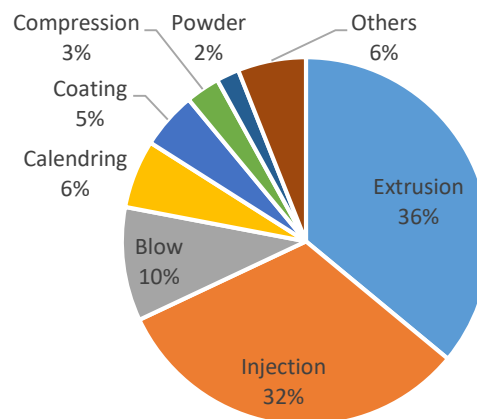


Figure 1. Plastic consumption by process. Europe 2016

Many of these variables and their behaviors are the same in the different processes, as they all relate to temperature, time, and pressure. The process depends on several interrelated factors: (1) designing a part to meet performance and manufacturing requirements at the lowest cost; (2) specifying the plastic; (3) specifying the manufacturing process, which requires (a) designing a tool 'around' the part, (b) putting the 'proper performance' fabricating process around the tool, (c) setting up necessary auxiliary equipment to interface with the main processing machine, and (d) setting up 'completely integrated' controls to meet the goal of zero defects; and (4) 'properly' purchasing equipment and materials, and warehousing the materials.

Major advantages of using plastics include formability, consolidation of parts, and providing a low cost-to-performance ratio. For the majority of applications that require only minimum mechanical

performance, the product shape can help to overcome the limitations of commodity resins such as low stiffness; here improved performance is easily incorporated in a process. However, where extremely high performance is required, reinforced plastics or composites are used.

Polymers are usually obtained in the form of granules, powder, pellets, and liquids. Processing mostly involves their physical change (thermoplastics), though chemical reactions sometimes occur (thermosets). Two of the main characteristics of the processing methods are compared in Fig. 2 [1]. One group consists of the extrusion processes (pipe, sheet, profiles, etc.). A second group takes extrusion and sometimes injection molding through an additional processing stage (blow molding, blown film, quenched film, etc.). A third group consists of injection and compression molding (different shapes and sizes), and a fourth group includes various other processes (thermoforming, calendaring, rotational molding, etc.).

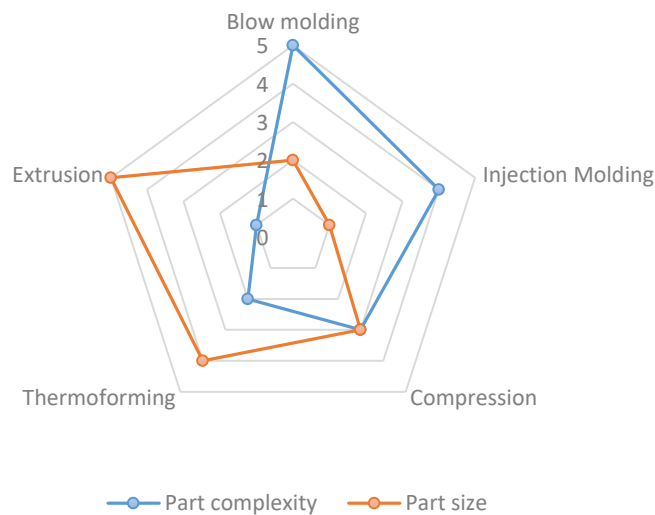


Figure 2. Process characteristics graph

The common features of these groups are (1) mixing, melting, and plasticizing; (2) melt transporting and shaping; (3) drawing and blowing; and (4) finishing. Mixing, melting and plasticizing produce a plasticized melt, usually made in a screw (extruder or injection). Melt transport and shaping apply pressure to the hot melt to move it through a die or into a mold. The drawing and blowing technique stretches the melt to produce orientation of the different shapes (blow molding, forming, etc.). Finishing usually means solidification of the melt. The most common feature of all processes is deformation of the melt with its flow, which depends on its rheology. Another feature is heat exchange, which involves the study of thermodynamics. Changes in a plastic's molecular structure are chemical.

1.2. Injection molding process

Injection molding is a repetitive process in which melted (plasticized) plastic is injected into a mold cavity or cavities, where it is held under pressure until it is removed in a solid state, basically duplicating the cavity of the mold. The mold may consist of a single cavity or a number of similar or dissimilar cavities, each connected to flow channels, or runners, which direct the flow of the melt to the individual cavities.

The process is divided in three steps: (1) heating the plastic in the injection or plasticizing unit so that it will flow under pressure, (2) allowing the plastic melt to solidify in the mold, and (3) opening the mold to eject the molded product. These three steps are the operations in which the mechanical and thermal inputs of the injection equipment must be coordinated with the fundamental properties and behavior of the plastic being processed; different plastics tend to have different melting characteristics, with some being extremely different. They are also the prime determinants of the productivity of the process, since the cycle time (Fig. 3) will depend on how fast the material can be heated, injected, solidified, and ejected. Depending on shot size and/or wall thicknesses, cycle times range from fractions of a second to many minutes. Other important operations in the injection process include feeding the injection molding machine (IMM), usually gravimetrically through a hopper, and controlling the barrel's thermal profile to ensure high product quality.

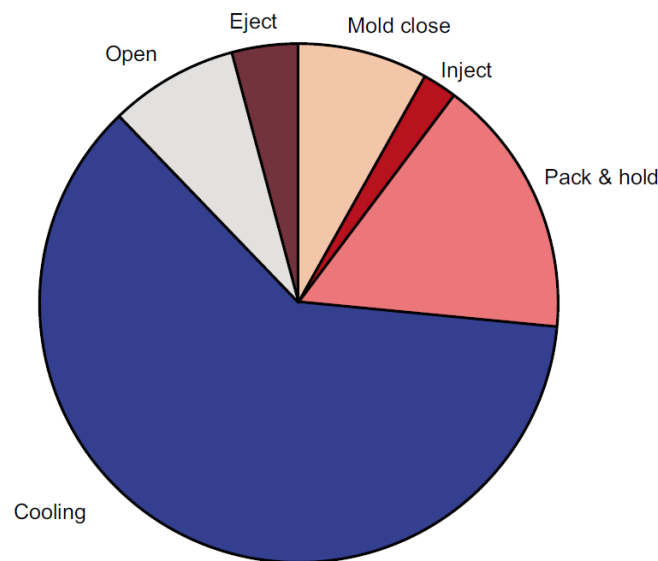


Figure 3. Typical cycle time break-down

IMMs are characterized by their shot capacity and their clamping force. A shot represents the maximum volume of melt that is injected into the mold. It is usually about 20 to 80% of the actual available volume in the barrel. Injection pressure in the barrel can range from 15 to 400 MPa. The characteristics of the plastic being processed determine what pressure is required in the mold to obtain good products. Given

a required cavity pressure, the barrel pressure has to be high enough to meet pressure flow restrictions going from the barrel into the mold cavity or cavities.

Otherwise, the clamping force on the mold halves required in the IMM also depends on the plastic being processed. A specified clamping force is required to retain the pressure in the mold cavity. It also depends on the projected area of any melt located on the parting line of the mold, including any cavities and mold runner(s) that are located on the parting line. By multiplying the pressure required to inject the part and the projected area, the clamping force required is determined. To provide a safety factor, 10 to 20% should be added.

Many thousands of different plastics (also called polymers, resins, reinforced plastics, elastomers, etc.) are processed every year. Each of the plastics has different melt behavior, product and cost. To ensure that the quality of the different plastics meets requirements, tests are carried out on melts as well as molded products. There are many different tests to provide all kinds of information. Important tests on molded products are mechanical tests.

There are basically two types of plastic materials molded: 1) thermoplastics (TPs), which are predominantly used, can go through repeated cycles of heating/melting usually at least to 260°C and cooling/solidification. The different TPs have different practical limitations on the number of heating-cooling cycles before appearance and/or properties are affected. Thermosets (TSs), upon their final heating [usually at least to 120°C, become permanently insoluble and infusible. During heating they undergo a cross-linking process. Certain plastics require higher melt temperature, some may require 400°C. Most of the literature on injection molding processing refers entirely or primarily to TPs; very little, if any at all, refers to thermoset TS plastics. At least 90% of all injection-molded plastics are TPs.

1.3. Thermoplastic nanocomposites

Extensive compounding of different amounts and combinations of additives (colorants, flame retardants, heat and light stabilizers, etc.), fillers (calcium carbonate, etc.), and reinforcements (glass fibers, glass flakes, graphite fibers, whiskers, etc.) are used with plastics.

Thermoplastic nanocomposites are the combinations between a nanostructured inorganic or organic filler with size typically between 1 and 100 nm in at least one dimension, and a polymeric matrix. The main advantage of use this fillers over the conventional composite material is the extremely high surface area, which have proportionally more surface atoms than their micro-scale counterparts, thus allowing intimate interphase interactions and conferring extraordinary properties to the polymer. The size of the nano-fillers favors the use of small amount of them and a more effective transfer to the polymer matrix of their unique molecular properties.

Typical nano-fillers include nanoclays, carbon nanotubes (CNT), nanoparticle silver, nanoalumina, among others. Nanocomposite materials exhibit unique material properties, such as improved barrier properties, flame retardant, and mechanical properties, depending on the choice of filler. This materials have application for lighter weight structural parts, barrier materials for improved packaging (e.g MREs), EMI shielding, and antimicrobial performance.

Compound processing of polymers is mainly performed via extrusion. Extrusion allows melting a polymer with a high energy input during short time. Due to the supply of heat and energy input caused by friction between the screws, the mass melts, becomes formable and is pressed through the extruder die [2]. During the whole process the mass can be compressed, mixed, plasticized, homogenized, chemically transformed, degasificated or gasificated [3], [4]. It is also possible to incorporate nanoparticles in a compounding process, in the last years different types of nano-composites are available. In case of processing exfoliated nano-composites, the dispersion quality mainly depends on the extruder and screw configuration [5]. Exfoliation is favored at high shear rates [6], while longer residence time favors a better dispersion [5]. Also, the location where the nano-clay is introduced has been shown to be an important factor [7]. However, the major factor whether a good dispersion or exfoliation is possible is the thermodynamic affinity between the nanoclay/nanoparticle and the polymer matrix [8]. When attractive interactions between matrix and nanoclay are not sufficient, intercalation is acquired, while exfoliation can be obtained when strong attractive interactions are present [9]. Figure 4 shows how exfoliation can be achieved via extrusion/melt processing [8].

The nanocomposite performance depends on number of nanoparticles features such as the size, aspect ratio, specific surface area, volume fraction used, compatibility with the matrix and dispersion. In fact, although a long time has gone in the nanocomposites' era, the dispersion state of nanoparticles remains the key challenge in order to obtain the full potential of properties enhancement at lower filler loading than for microcomposites. Not only the nanoparticles themselves can explain the observed effects, the impact of the interface between the matrix and particle also play a very important role. Indeed, the extremely high surface area leads to change in the macromolecular state around the nanoparticles (e.g. composition gradient, crystallinity, changed mobility, etc.) that modifies the overall material behavior [10].

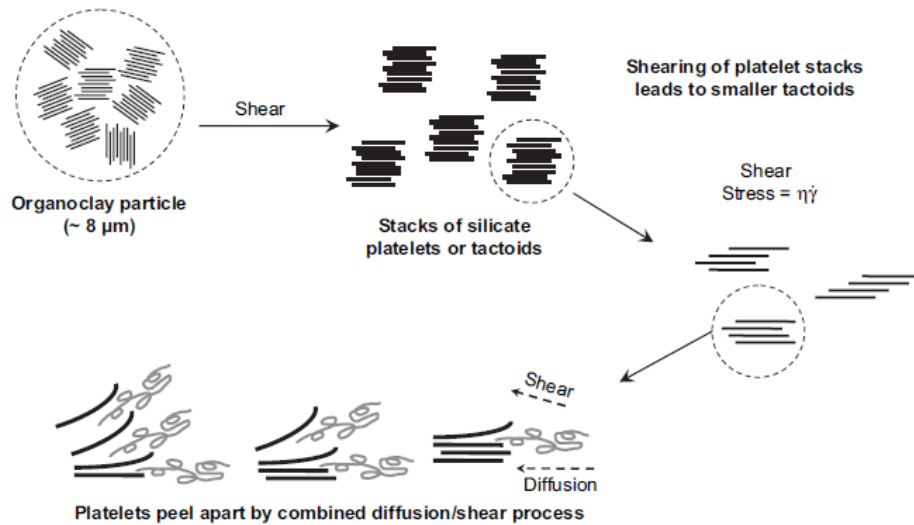


Figure 4. Mechanism of organoclay dispersion and exfoliation during melt processing [50, 52]

The nanoparticles dispersion can be characterized by different states at nano-, micro- and macroscopic scales. For example, nanoclay based composites can show three different types of morphology: immiscible (eg. microscale dispersion, tactoid), intercalated or exfoliated (miscible) composites [8]. The affinity between matrix and filler increases from tactoid over intercalated to exfoliated clays [6].

Different techniques can be used to study the dispersion quality of nano-particles within the polymeric matrix: XRD, SEM, TEM, infrared spectroscopy (IR) and atomic force microscopy (AFM). Figure 5 shows the different states of dispersion for a nano-composite prepared with nano-clays and a polymer matrix, using TEM and XRD and its correspondent illustration.

Widely performed melt processes specialized in packaging and automotive are injection molding, film extrusion and extrusion coating. Since many different process parameters have a direct influence on the processed materials, Taguchi methods are commonly used in plastic injection molding industry as a robust optimization technique for applications from product design to mold design; and from optimal material selection to processing parameter optimization. Pötschke et al. (2008) studied the influence of injection molding parameters on the electrical resistivity of nanocomposite formed by PP/CNT using a four-factor factorial design with keeping pressure, injection velocity, mold temperature and melt temperature. Sample with lower melt temperature and higher injection velocity shown a better dispersion compared with injection molded at low velocity and high melt temperature [11]. Chandra et al. (2007) summarized their research on PC and CNT nanocomposite in order to achieve homogeneous distribution of CNT and to obtain high electrical conductivity the nanocomposites should be processed at high melt temperatures and low injection speeds to ensure proper and uniform electrical conductivity [12]. Recently, the F. Stan group has made a study about the influence of the process parameters in the nanocomposite (PP/CNT) to improve the mechanical properties. The injection molding parameters affect the degree of crystalline morphology of the molded polymers. Therefore, these effects could affect the physical and mechanical properties of the injection molded parts. On the other hand, the effect of crystallinity on the mechanical properties is less important than the effect of the carbon nanotubes. Their research work, concluded that the most significant injection molding parameter is the injection pressure [13].

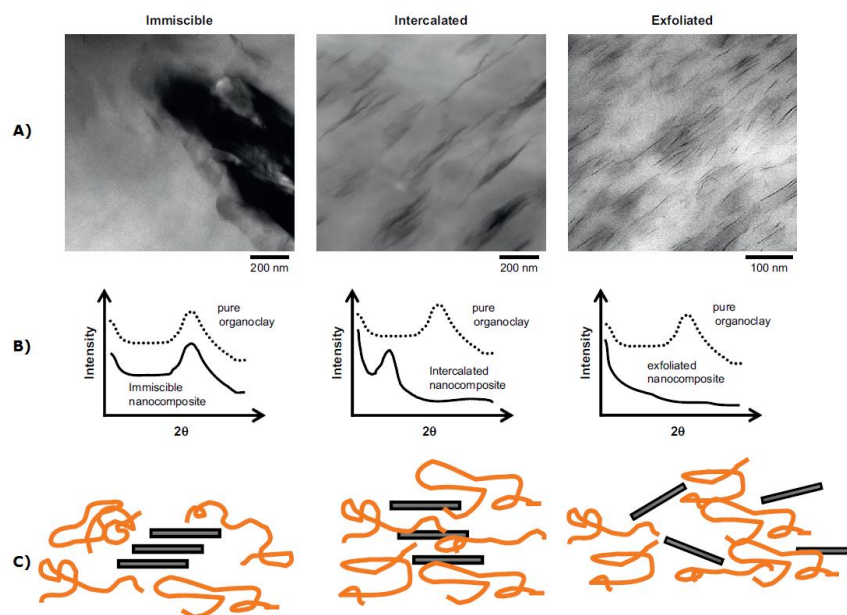


Figure 5. Different states of nano-additive's dispersion. a)TEM, b) XRD.

Additionally, the use of compatibilizers can change the optimal parameters to the process. P. Constantino et al. studied the microstructure of the same nanocomposites PP/nanoclay produced by a non-conventional method of extrusion, SCORIM (Shear Controlled Orientation in Injection Molding). This method is based on the concept of in-mold shear manipulation of the melt during the polymer solidification phase. The degree of clay exfoliation not only depends on the affinity and compatibility of the organoclay with the matrix, but also on the shear stress which is an extrinsic factor dependent on processing conditions and clay loading. High shear rate induced a thicker skin, while high temperature induced a thinner skin [14]. An interesting work was made by P.F. Rios, comparing the behavior of different polymers with the same nanofiller. He studies the influence of injection molding parameters in HDPE, PA6, PA66, PBT and PC with carbon nanotubes. The main objective was to evaluate the electrical resistivity, thermal conductivity and the mechanical properties. The literature reveal how the different parameters of the injection molding process might affect directly in the quality of the part injected and their properties. The formulation is important, but the process parameters show a relevant importance [15].

1.4.Nano-clays

From the end of the last century, the discovery of various clays and their use in a variety of applications resulted in a continuous developments in polymer science and nanotechnology. The term 'clay' is referred to a class of materials generally made up of layered silicates or clay minerals with traces of metal oxides and organic matter. Clay minerals, usually crystalline, are hydrous aluminum phyllosilicates, sometimes with variable amounts of iron, magnesium, alkali metals, alkaline earths, and other cations.

As a low cost inorganic material, clays are used in industrial, engineering and scientific fields. In science, these are commonly also used as catalysts, decoloration agents and adsorbents and in industrial and engineering fields, these are used in oil drilling, ceramics and the paper industry.

Generally, clay particles have lateral dimensions of centimeters, micrometers in one dimension and the thickness of a single clay platelets in order of nanometers. These layered clays are characterized by strong intralayer covalent bonds within the individual sheets comprising the clay [16]. This is the reason why dispersion of them in a polymer matrix is very difficult during the preparation of polymer nano-composites, generally requiring modification of the clay.

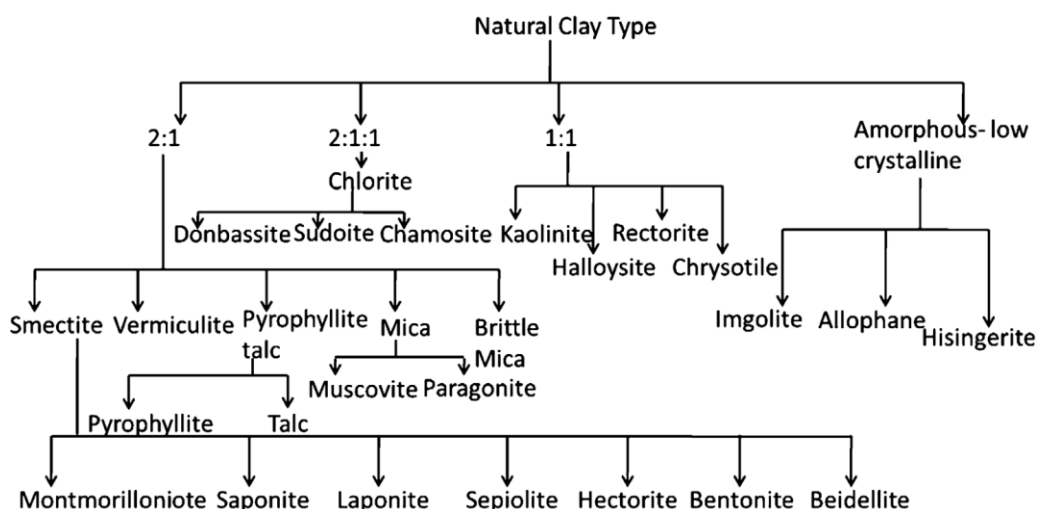


Figure 6. Classification of natural clay

The modification of the space between layers of clay by intercalating long chains or by grafting with different functional groups results in a change from hydrophilic to hydrophobic character, and a wide range of new and fascinating properties. Therefore, nowadays the modification of clay has a lot of interest in the preparation of polymer-clay nanocomposites [17], [18]. However, the nanolayers of the clay tend to stack face to face leading to agglomerated tactoids in nanocomposites, which may work again the properties of the individual components. The dispersion of the tactoids into discrete monolayers is related to the intrinsic incompatibility of hydrophilic clay and hydrophobic engineering polymers. Since proper dispersion of these nanostructures in a polymer matrix is essential for the improvement of material properties compared with pristine polymer or conventional micro- and macro-composites [19], [20].

Different methods have been developed in order to improve the clays dispersion, based on two main methods of modification: (1) physical absorption and (2) chemical modifications, such as grafting functional polymers or functional groups on to the surface of clay or ion exchange with organic cations or anions [17]. First method is based on thermodynamics which improves their physical and chemical properties for composite and the structure of the clays remain unaltered. In this case, exists a weak force between the adsorbed molecules and the clay is an important disadvantage. Otherwise, the second method improves the interaction force between clays and modifiers, controlling and tuning their properties.

Generally, clay can be classified into two categories: natural and synthetic clays. Figure 6 shows the classification of natural clays. They are basically composed of alternating sheets of SiO_2 and AlO_6 units in ratios of 1:1 (kaolinite), 2:1 (montmorillonite and vermiculite) and 2:2 (chlorite) [21]. Modification of clay minerals such as organoclay and organo-modified clay is a new path of clay mineral research.

2. State of the art: Automotive Sector

The basic trends that nanotechnology enables for the automobile are

- lighter but stronger materials (for better fuel consumption and increased safety)
- improved engine efficiency and fuel consumption for gasoline-powered cars (catalysts; fuel additives; lubricants)
- reduced environmental impact from hydrogen and fuel cell-powered cars
- improved and miniaturized electronic systems
- better economies (longer service life; lower component failure rate; smart materials for self-repair)

The use of polymer nanocomposites in the manufacturing chain started in 1991 when Toyota Motor Co., in collaboration with Ube Industries, introduced nylon-6/clay nano composites in the market to produce timing belt covers as a part of the engine for their Toyota Camry cars [22]. Then, Japan introduced nylon-6 nanocomposites for engine covers on Mitsubishi GDI engines [23] manufactured by injection moulding. The product is said to offer a 20% weight reduction and excellent surface finish. In 2002, General Motors launched a step-assist automotive component made of polyolefin reinforced with 3% nanoclays, in collaboration with Basell (now LyondellBasell Industries) for GM's Safari and Chevrolet Astro vans, followed by the application of these nanocomposites in the doors of Chevrolet Impalas [24], [25].

The important increase in the commercialization of nanocomposites production occurred over the last years. In 2009, a one-piece compression moulded rear floor assembly was manufactured by General Motor for their Pontiac Solace using nano-enhanced Sheet Moulding Compounds (SMCs) developed by Molded Fiber Glass Companies (MFG), Ohio. This technology is also in use on GM's Chevrolet Corvette Coupe and Corvette ZO6. The nano-filled SMCs exhibit significantly lower density than conventional SMCs resulting in improved fuel efficiency [26]. At this point, the automotive industry can benefit from this material in several applications such engines, suspension, break systems, frames and body parts, paints and coatings, tires and electric and electronic equipment.

In the latter part of the 1980s and the beginning of the 1990s, a research team from Toyota Central Research Development Laboratories (TCRDL) in Japan reported a work on a Nylon-6/clay nanocomposite and disclosed improved methods for producing nylon-6/ clay nanocomposites using in situ polymerization similar to the Unichika process [27] [28] [29] [30].

he research findings demonstrated a significant improvement in a wide range of physico-mechanical properties by reinforcing polymers with clay on the nanometer scale [31] [32]. The Toyota research team also reported various other types of clay nanocomposites based on polymers such as polystyrene, acrylic, polyimides, epoxy resin, and elastomers using a similar approach [33] [34] [35] [36] [37]. Since then, extensive research in nanocomposites field has been carried out worldwide. Figure 7 shows timeline for the commercialization of products by automotive players.

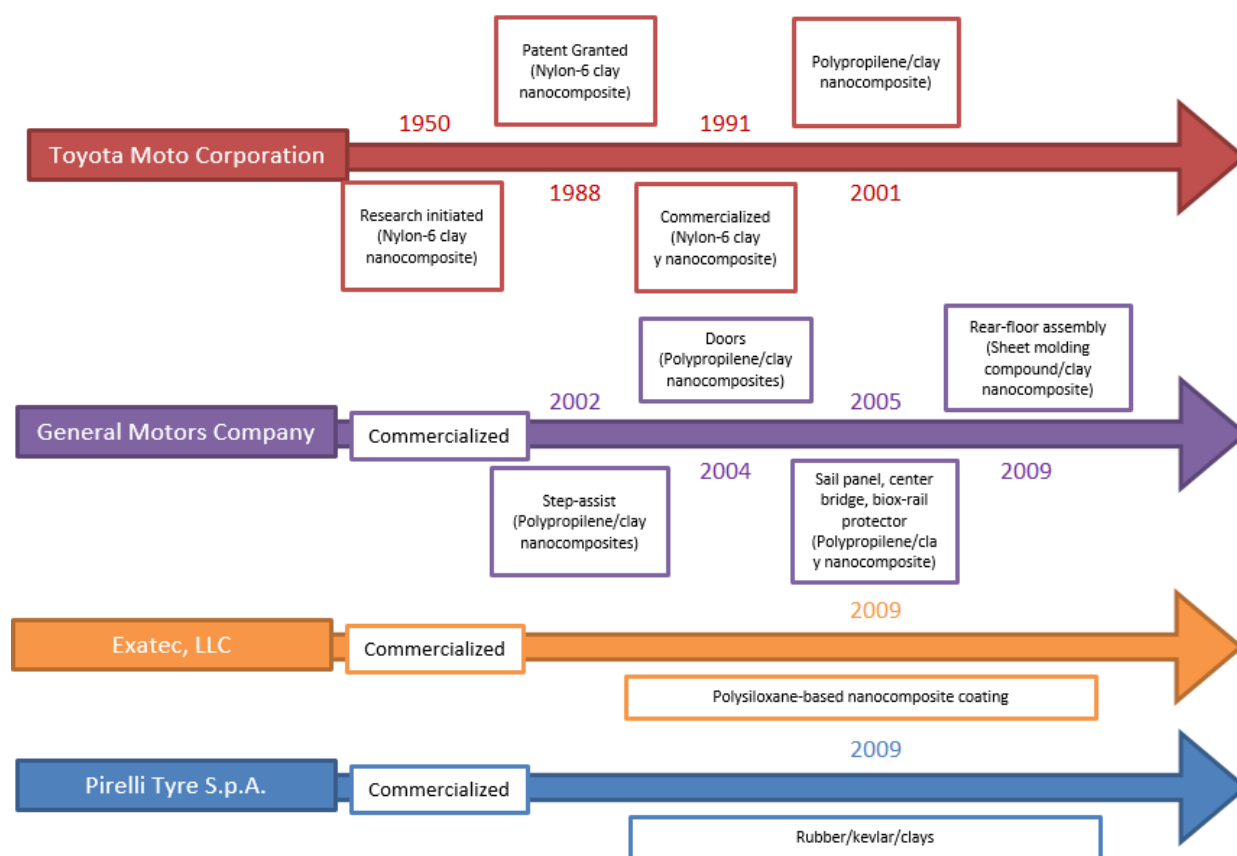


Figure 7. Timeline for the commercialization of products by automotive players.

Among nanomaterials, nanoclays are the most commonly used commercial additive for the preparation of nanocomposites, accounting for nearly 80% of the volume used. Carbon nanofibers, carbon nanotubes (mainly MWCNTs), and Polyhedral Oligomeric Silsesquioxanes (POSS) are also being used commercially in nanocomposites, gaining ground fast with improvements in cost/performance and processability characteristics.

The OEMs/Tier I, Tier II, Tier III, raw materials/nanointermediates manufacturers, researchers and technologists are realizing that other than clays, nanomaterials like graphene, carbon nanofibers, nanofoams, multiscale hybrid reinforcement and graphene-enabled rubber nanocomposites could drive the market dynamics.

The price and performance advantages of graphene are challenging carbon nanotubes in polymer nanocomposites applications due to its intrinsic properties and it is predicted that a single, defect-free graphene platelet could have an intrinsic tensile strength higher than that of any other material [38].

In June 2010, a U.S. Patent was granted to The Trustees of Princeton University for functional graphene-rubber nanocomposites [39], which can be produced at a much lower cost than carbon nanotubes and exhibits excellent mechanical strength, superior toughness, higher thermal stability and electrical conductivity. This graphene-rubber nanocomposite can be employed in all the areas for gas barrier applications including tires and packaging.

Another patent was granted in 2011, for a composite material of nanoscale graphene and an elastomer for vehicle tire application [40]. The multiscale hybrid reinforcement is another potential polymer nanocomposite material for the automotive industry due to its enhanced load transfer at the reinforcement/matrix interface, i.e. by tailoring the interfacial shear strength, which is made of micro sized carbon-fibre yarns and fabrics coated with carbon nanostructures. The high performance racing cars and high-end sports cars require excellent properties such as structural stiffness, heat shielding, impact and compressive strength, and many others.

Otherwise, different works has been carried out regarding to the surface properties of the produced parts in order to enhance their properties. In 2009, viscoelastic properties and scratch morphologies were studied using various amounts of nano silica [41]. Different nano-silica particles were incorporated in an automotive OEM clear-coat based on acrylic/melamine chemistry in order to study their effect in the scratch/mar resistances using nano-indentation hardness measurements [42]. In 2014, H. Yari, et. al. studied the influence of OH-functionalized polyhedral oligomeric silsesquioxane(POSS) nano-structure in the same clear coat [43].

In 2015, the impact behaviour of hybrid nano-/micro-modified composite was investigated in Glass Fiber Reinforced Plastics (GFRP). The hybrid nano-/micro fillers chosen were Cloisite® 30B nanoclay and 3M™ Glass Bubbles iM16K [44].

3. Objective

The aim of this project is to optimize the injection molding process to achieve the best nano-additive dispersion in order to improve mechanical properties of the injected part.

A good dispersion of the nano particles and their compatibility with the matrix polymer are the two critical points to assure the improvement of the properties comparing with the raw polymer. This work will be focused on the dispersion of the nano additives during the injection molding. A study of the interaction between some injection parameters and the dispersion will be carry out.

First of all, the injection molding process needs to be optimized taking into account the most relevant injection parameters during the process, using Scientific Injection Molding (SIM). Once the process is optimized for the selected thermoplastic composite, injection tool and injection molding machine, four injection parameters will be selected to study their behavior related to the dispersion of the nanofiller.

A mathematical model will be used to study how each parameter affect to the dispersion of the composite and determine which parameter combination enhance the selected mechanical property.

In this work, Flexural Modulus is selected as an output of the linear model. Considering the Flexural Modulus of the raw polypropylene, the goal of the project will be to increase this value as much as possible.

4. Experimental

In order to characterize the material within the project, a dog-bone specimens were produced using a special mold. Standardized specimens were tested and this data was used as an input to carry out a mathematical model.

First step was to select the most important injection parameters related to the nano-additive dispersion and then to set up a design of experiments to study their behavior related to the dispersion.

4.1. Materials

Plastic used to carry out this work is made up of two commercial grades: polypropylene and nanoclay additive. The formulation is composed by 8 wt. % of nanoclay.

4.1.1. Polymer matrix

Polymer used during the whole work was polypropylene, in particular ISPLEN PP080G2M from Repsol. This is a homopolymer grade characterised by good flow properties that enables to fill the mould easier and by short cycle times with big articles. Parts manufactured with this grade have excellent chemical resistance, are easily decorated and can accept different colouring systems.

Recommended melt temperatures range from 190 to 250°C. Main properties are shown in Table 1:

PROPERTIES	VALUE	UNIT	METHOD
General			
Melt flow rate (230°C/ 2,16 kg)	20	g/10 min	ISO 1133
Density at 23°C	905	kg/m ³	ISO 1183
Mechanical			
Flexural modulus of elasticity	1600	MPa	ISO 178
Charpy impact strength (23°C,notched)	3	kJ/m ²	ISO 179
Thermal			
HDT 0,45 MPa	85	°C	ISO 75
Others			
Shore Hardness	70	-	ISO 868

Table 1. Matrix polymer properties

This material should be stored in a dry atmosphere, on a paved, drained and not flooded area, at temperatures under 60°C and protected from UV radiation. Regarding to the pre-treatment of the material, it is not necessary to pre-dry the material due it not contains mineral additives.

4.1.2. Nanoclay additive

The nanoclay used during this work was Cloisite 20 from BYK. This grade is bis(hydrogenated tallow alkyl)dimethyl, salt with bentonite. In Table 2 are shown the typical properties of this grade:

PROPERTIES	VALUE	UNIT
Moisture	<3	%
Typical Dry Particle Size	<10	μm (d_{50})
Color	Off White	
Packed Bulk Density	175	g/l
Density	1.77	g/cm^3
X Ray Results	3.16	nm (d_{001})

Table 2. Nanoclay main properties

Using this material as an additive with the matrix, a pre-drying was needed in order to avoid processability problems during the injection process.

4.2. Injection molding machine

An ENGEL E-motion 200/55 full electric was used in Eurecat to inject the dog-bone specimens and therefore to test the mechanical properties of the samples. Technical specifications of the machine used are shown in Table 3 and a picture of the machine in the Figure 8.

	VALUE	UNIT
Clamping unit		
Clamping force	550	kN
Opening stroke	270	mm
Ejector stroke	100	mm
Ejector force	23	kN
Injection unit		
Screw diameter	25	mm
Max swept volume	59	cm ³
Screw speed max	400	r/min
Screw speed max current	400	r/min
Injection rate	109	cm ³ /s
Injection rate increased	109	cm ³ /s
Spec. Injection pressure	2400	bar
Spec. Injection pressure increased	2400	bar
Nozzle stroke	225	mm
Nozzle cont. pressure	28	kN

Table 3. Injection machine specifications

The election of this machine was determined by the mould used to inject the samples. There are some advantages of using fully electric injection moulding machines:

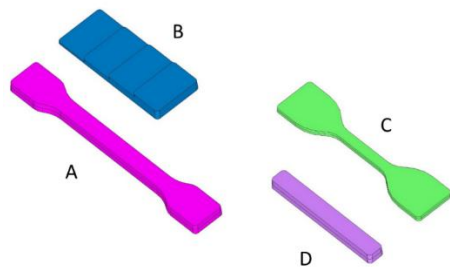
- Electric machines are digitally controlled and mechanically driven. Their processes do not vary over time since they have no hoses to expand, no valves to potentially stick and no hydraulic fluid to heat up or compress.
- Electric machines turn injection moulding into a more predictable operation. With a more consistent machine, the same process setup can be used repeatedly, without affecting part consistency or quality. For example, screw position for fill and pack is controlled with digital precision, eliminating over-packing and greatly reducing moulded-in stress. Consistent machine performance also allows labour cost reductions with unmanned shifts at night or on weekends. Utilization of skilled labour is greatly enhanced.
- From the day the machine starts up, it reduces cost per part. All-electric machines produce faster cycle times because of independent clamp/injection functions. Their precision shot control saves material and prevents using more resin, colorant or additive than the part needs.



Figure 8. IMM used for this work

4.3. Injection molding tool

A mould was manufactured in order to obtain samples to carry out mechanical characterization. Four different standardized specimens can be injected as shown in Figure 9:



- A. Tensile strength
- B. Hardness
- C. Tensile strength for thermoplastic elastomers
- D. Impact

Figure 9. Standardized specimens which can be manufactured with injection

The mould was designed with selectors to choose what part/s could be injected. Figure 10 shows the ejection side with the four parts and the sprue selector and the injection side. Injection side was equipped with a hot runner in order to ease the injection and to reduce the waste of material.



Figure 10. Ejection side (left) and injection side (right).

Only the A specimen were injected within the frame of the project. A variety of specimen shape can be used for this test, but the most commonly used specimen size for ASTM is 3.2mm x 12.7mm x 125mm and for ISO is 10mm x 4mm x 80mm. Figure 11 shows the dimensions of the standard sample used:

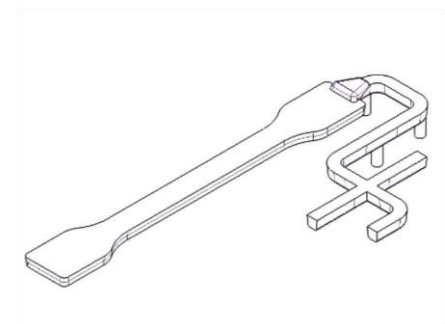
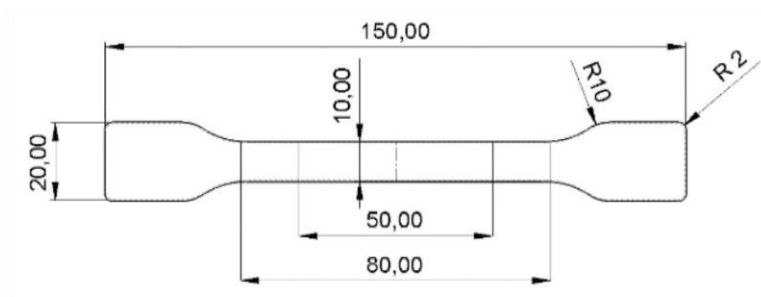


Figure 11. Left: Standard sample dimensions. Right: 3D model of the sample

4.4.Characterization methods

Different methods were used to characterize the material used within the work. Regarding to the mechanical properties, a Flexural Modulus test was carried out. On the other hand, two rheology properties were measured. Rheology properties are important when processing the material. Using additives may cause variations in some properties that can cause problems during the injection molding process.

Following are shown the methods used, equipment used and test conditions:

4.4.1. Density

Density is the mass per unit volume of a material. Specific gravity is a measure of the ratio of mass of a given volume of material at 23°C to the same volume of deionized water. Specific gravity and density are especially relevant because plastic is sold on a cost per kilogram basis and a lower density or specific gravity means more material per kilogram or varied part weight.

Equipment: Electronic Densimeter METROTEC MD300S

Test conditions:

- Standard: UNE EN ISO 1183-1 (2004)
- A method: Immersion method for solid plastics (except dust).
- Sample preparation: standardized test section 4 x 10 mm
- Immersion liquid: Distilled water

Test atmosphere:

- Test temperature: $20 \pm 1^{\circ}\text{C}$

4.4.2. Flow rate determination (MFR)

Melt Flow Rate measures the rate of extrusion of thermoplastics through an orifice at a prescribed temperature and load. It provides a means of measuring flow of a melted material which can be used to differentiate grades as with polyethylene, or determine the extent of degradation of the plastic as a result of molding. Degraded materials would generally flow more as a result of reduced molecular weight, and could exhibit reduced physical properties. Typically, flow rates for a part and the resin it is molded from are determined, then a percentage difference can be calculated. Alternatively, comparisons between "good" parts and "bad" parts may be of value.

Approximately 7 grams of the material is loaded into the barrel of the melt flow apparatus, which has been heated to a temperature specified for the material. A weight specified for the material is applied to a plunger and the molten material is forced through the die. A timed extrudate is collected and weighed. Melt flow rate values are calculated in g/10 min. At least 14 grams of material is needed.

Equipment: CEAST Modular Flow Index

Test conditions:

- Standard: EN ISO 1133-1 (2011)
- Method: procedure B of the standard
- Amount of material in the cylinder: 7 g
- Test temperature: 230°C (for PP) and 190°C (for PE and PHB)
- Weight: 2.16 Kg
- Filter size: 8 mm
- Filter diameter: 2,095mm
- Number of readings: minimum 40
- Drying of the sample prior minimum 2 h at 90 ° C in convection oven

4.4.3. Flexural strength test

The flexural test measures the force required to bend a beam under three point loading conditions. The data is often used to select materials for parts that will support loads without flexing. Flexural modulus is used as an indication of a material's stiffness when flexed. Since the physical properties of many materials (especially thermoplastics) can vary depending on ambient temperature, it is sometimes appropriate to test materials at temperatures that simulate the intended end use environment.

Most commonly the specimen lies on a support span and the load is applied to the center by the loading nose producing three point bending at a specified rate. The parameters for this test are the support span, the speed of the loading, and the maximum deflection for the test. These parameters are based on the test specimen thickness and are defined differently by ASTM and ISO. For ASTM D790, the test is stopped when the specimen reaches 5% deflection or the specimen breaks before 5%. For ISO 178, the test is stopped when the specimen breaks. If the specimen does not break, the test is continued as far as possible and the stress at 3.5% (conventional deflection) is reported.

Equipment: Universal Testing Machine INSTRON 6025

Test conditions:

- Standard: UNE EN ISO 178 (2013)
- Cell load: 50 KN
- Type test: standard Section 4 x 10 mm
- Distance between supports 64 mm
- Calculation of modulus of elasticity:
 - Preload: 2N 1 mm / min
 - Measuring Range: 0:05 to 12:25%
 - Speed: 2mm / min
- Speed trial: 10mm / min
- deformation maximum 10%
- Num. specimens 5

Test atmosphere:

- Temperature: 23 ± 2 °C
- Relative Humidity: $50 \pm 10\%$

4.4.4. Material properties comparison

In order to ensure the good processability of the composite injected in this work, a comparison between raw polymer and the nano composite was carried out using the methods described above:

Material	MFI (2,16kg 230°C) cc/10"	MFI (2,16kg 230°C) g/10"	Density theory g/cm ³	Density measured g/cm ³
Raw PP	25,0	22,6	0,905	0,906
NCC	-	-	1,770	-
Compound	28,5	26,3	0,928	0,920

Table 4. Comparison between raw polymer and the nanocomposite

4.5. Injection molding process optimization

4.5.1. Scientific Injection Molding (SIM)

Several parameters determine a successful molding process. There are various speeds, pressures, times, and temperatures to be considered. Scientific processing encompasses an understanding of the underlying scientific principles of each parameter and the application of these principles to achieve a robust process and consistency in part quality. Scientific processing covers the complete molding process, from the time the plastic enters the facility to when it leaves as a finished product.

A robust process is one that can accept reasonable natural variations or a small purposeful change in an input but still delivers consistent output. The term consistency means molding parts with the least variation in the quality part. The quality of the part can mean its dimensions, appearance, part weight, or any other aspect that is important for the form, fit or function of the part. The variation should be from special cause variations and not from natural cause variations. Special cause variations are variations that are caused by an external factor. For example, if the chiller unit shuts down, the mold temperature will change causing a change in the quality of the part. Natural cause variations are inherent to the process. Their effect can be minimized but not eliminated. For example, a part is injected with PP which contains 30% of fiber glass, in every molded shot the amount of glass will not be exactly 30%, it will be slightly more or less. This variation cannot be eliminated, but the mixing process can be optimized in order to reduce this variation.

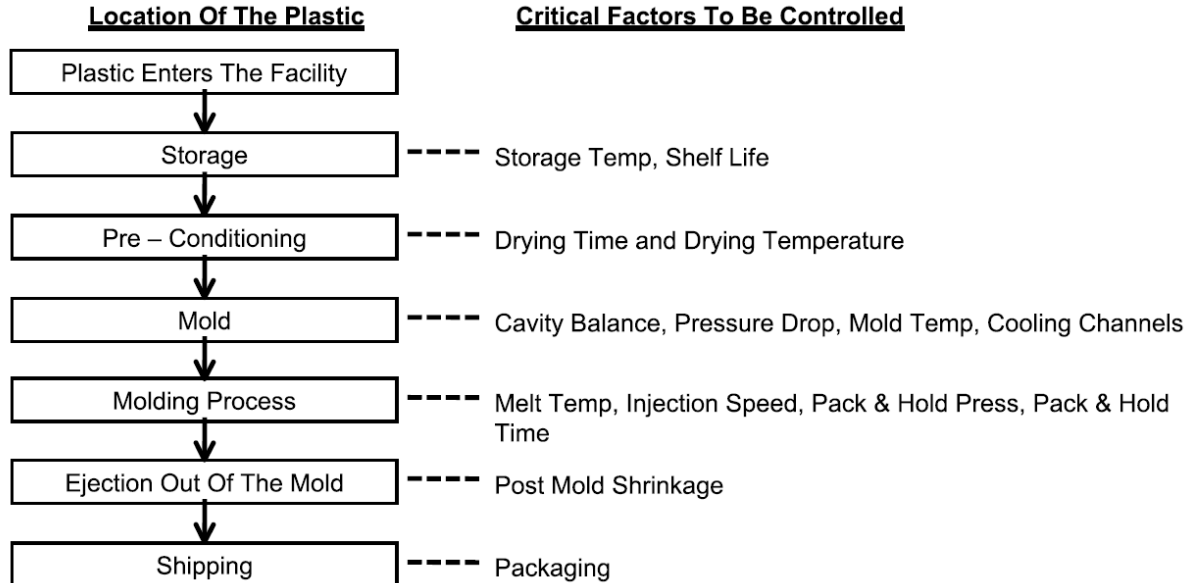


Figure 12. The journey of the pellet and the critical factors that need to be controlled

The term Scientific Molding was coined by two pioneers in the field of injection molding, John Bozzelli and Rod Groleau. Their principles and procedures are widely used today and are industry standards. Scientific molding deals with the actual plastic that enters the mold during the molding operation at the molding machine. The term introduced here is Scientific Processing, which is defined as the complete

activity the plastic is subjected to from the storage of the plastic as pellets to the shipping of the plastic as molded parts. Scientific processing is applying scientific principles to each of the steps involved in the conversion the plastic to the final product. Figure 12 shows critical points during the injection process.

4.5.2. Process optimization – The 6-Step study

The optimization process consists in 6 steps shown below:

- Step 1: Optimization of the Injection Phase – Rheology Study
- Step 2. Determining the Pressure Drop – Pressure Drop Studies
- Step 3. Determining the Process Window – Process Window Study
- Step 4: Determining the Gate Seal Time – Gate Seal Study
- Step 5. Determining the Cooling Time – Cooling Time Study
- Step 6. Determining the Screw Speed and Back Pressure – Dosing Phase Study

Step 1: Optimization of the Injection Phase – Rheology Study

All plastic melts are non-Newtonian. This means that their viscosity does not remain constant over a given range of shear rates. In the strict sense, the rheological behavior of a plastic is combination of non-Newtonian and Newtonian behavior. At extremely low shear rates, which are rarely encountered in injection molding, the plastic is Newtonian; but as the shear rates increases, the plastic tends to show non-Newtonian behavior. Interestingly, as the shear rates increase further, the plastic tends to act more and more Newtonian after an initial steep drop in viscosity.

On a linear scale graph it can be seen that the change or drop in viscosity is much greater at low shear rates as compared to higher shear rates. This happens because with increasing shear rate, the polymer molecules start to untangle from each other and start to align themselves in the direction of the flow. This reduces the resistance to flow (viscosity). The plastic tends to get more Newtonian at higher shear rates. Although there is still a continuing drop in viscosity, the change is no as significant as at the lower rates. Figures 13 shows this phenomenon.

During the injection molding process, the material is subjected to high shear forces during the injection phase. The shear rate is proportional to the injection speed. If the shear rates are low and are set in the initial non-Newtonian region of the curve, the small variations in the shear rate will cause a large shift in viscosity. Since there is always some natural variations, the mold filling will be inconsistent and will therefore result in a shot-to-shot inconsistencies. However, if the injection speeds are set to a higher values, the viscosity tends to be consistent. At high injection speeds, the shear rates are higher and the effect of shear rate on the viscosity is not as significant as it was at low injection speeds. Small changes in injection speeds result in small or almost no change in the viscosity of the melt.

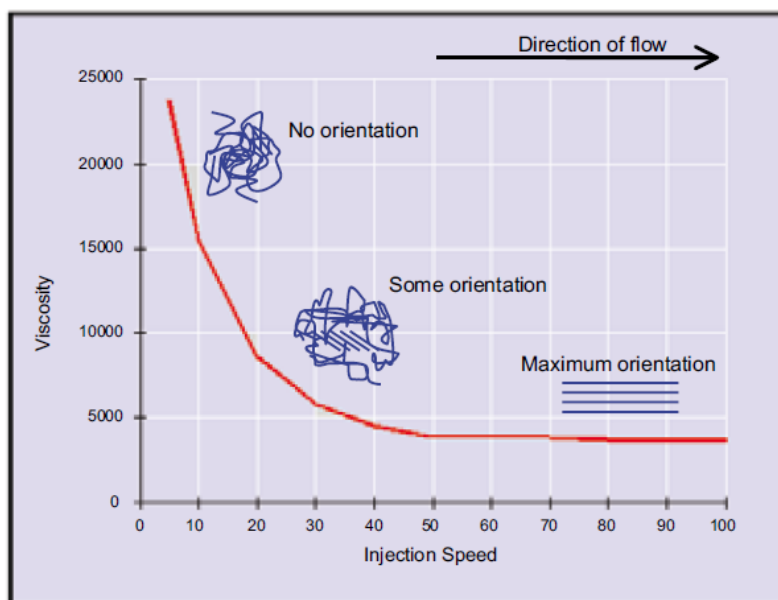


Figure 13. Orientation of the molecules in the direction of flow at different injection speeds

Any natural variation in the speed will not have a significant effect on the cavity fill in the Newtonian region of the curve and it is therefore important to find the region of the curve and set the injection speed, and with that the shear rate.

The procedure to determine the viscosity curve was first developed by John Bozzelli. The basic principle is based on the melt rheometer that is used to study the viscosity of plastics (MFR determination). The injection molding machine can also be treated as a rheometer, where the nozzle orifice is the die of the rheometer and the screw is the piston. The hydraulic pressure is applied to the molten plastic with the help of the screw. The pressure required to move the screw at a set speed is recorded.

The table below (Table 5), was obtained varying the injection rate and recording the peak of specific pressure (bar) and the filling time (s).

Injection rate (mm/s)	Filling time (s)	Peak spec. Pressure (bar)	Shear rate (1/s)	Relative viscosity (P)
5	5,00	150	0,20	750
10	2,51	183	0,40	459
15	1,68	206	0,60	346
20	1,27	228	0,79	290
25	1,02	241	0,98	246
30	0,86	257	1,16	221
35	0,74	266	1,35	197
40	0,65	279	1,54	181
45	0,59	290	1,69	171
50	0,53	297	1,89	157

55	0,48	305	2,08	146
60	0,44	312	2,27	137
65	0,41	321	2,44	132
70	0,39	328	2,56	128
75	0,37	335	2,70	124
80	0,34	342	2,94	116
85	0,33	346	3,03	114
90	0,32	354	3,13	113
95	0,30	362	3,33	109
100	0,29	367	3,45	106
105	0,28	371	3,57	104
110	0,26	374	3,85	97
115	0,26	380	3,85	99
120	0,25	386	4,00	97
125	0,24	389	4,17	93

Table 5. Viscosity curve worksheet

The optimal injection rate will be closer to the 'knee' part of the curve which in this case is 2.5 1/s of shear rate. Using the worksheet this shear rate corresponds to a 65 – 70 mm/s of injection rate. This is where a shift in the viscosity and greater consistency can be observed.

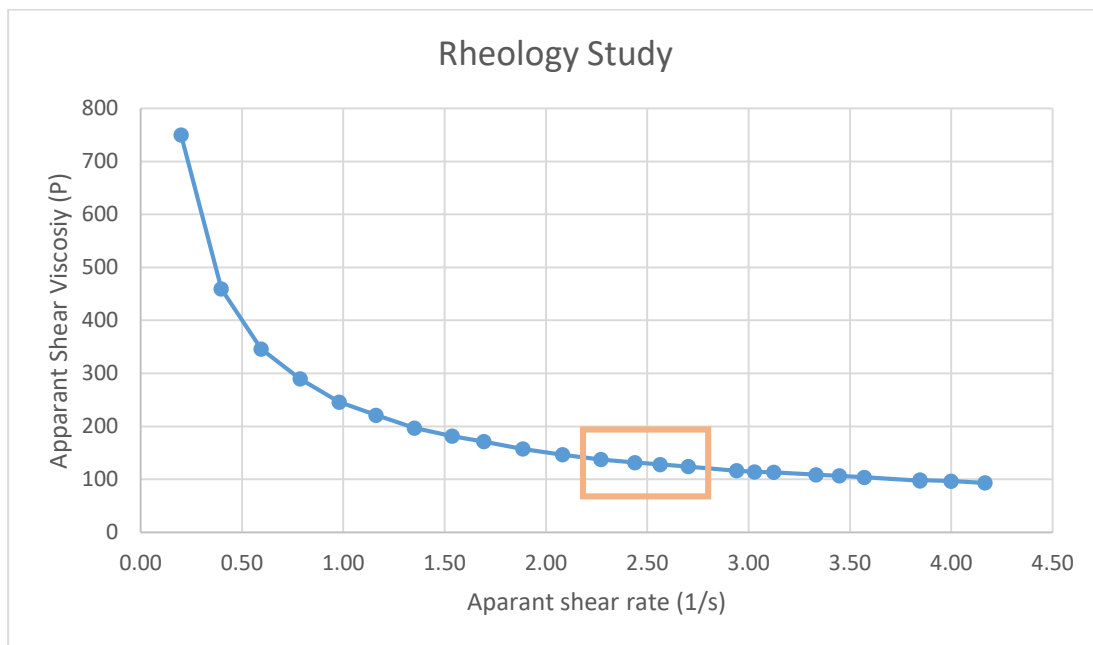


Figure 14. Viscosity curve of composite used

Step 2. Determining the Pressure Drop – Pressure Drop Studies

As plastic flows through the different sections of the nozzle and the mold, the flow front of the plastic experiences a loss of applied pressure because of drag and frictional effects. Additionally, as the plastic hits the walls of the mold, it begins to cool, increasing the viscosity of the plastic, which in turn requires additional pressure to push the plastic. The skin plastic that is formed on the internal walls of the runner system decreases the cross sectional area of the plastic flow, which also results in a pressure drop.

Measurement zone	Weight (g)	Peak pressure (bar)	% of total pressure	Drop pressure (bar)	Drop pressure (%)
Nozzle	n/a	50	2.3	50	2.3
Sprue/Hot sprue	3.64	170	7.7	120	5.5
Gate	4.73	195	8.9	25	1.1
95% of filling part	10.32	318	14.5	123	5.6
Max. pressure of the machine	-	2200	100.0		
Reserve pressure on the machine		1882	85.5		

Table 6. Pressure Drop Worksheet

Depending on the pump capacity of the molding machine, there is a limited maximum amount of pressure available to push the screw at the set injection speed. The required pressure to push the screw at the set injection speed should never be more than the maximum available pressure. If the pressure required is higher, the screw will never be able to maintain the set injection speed throughout the injection phase and the process is considered pressure limited. Initially the set speed may be reached, but as soon as the process becomes pressure limited, the screw slows down.

In order to determine the pressure drop during the whole injection process, several pressure data were recorded. Table 6 shows the data recorded during the experiments. Additionally, the different peak pressures are shown in Figure 16.

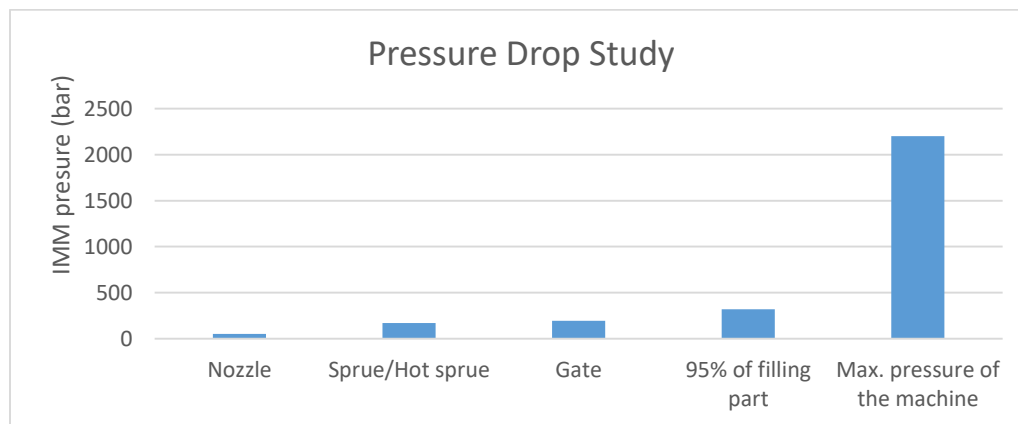


Figure 15. Pressure Drop Graph

Step 3. Determining the Process Window – Process Window Study

Injection molding process is divided in two phases: the first phase in injection and the second phase is packing and holding phase. The holding pressure is the responsible of pack additional melt plastic into the cavity in order to avoid the shrinkage caused by the cooling phase when plastic is in contact with the cold mold walls. Packing pressure, holding pressure, packing time and holding time are the parameters which controls this second phase. In this work, packing and holding has not been differentiated mentioned as holding phase.

The ideal holding pressure is determined by evaluation the process window of the mold. Two process variables were varied to establish the process window: holding pressure and melt temperature. This windows process is referred to the molding area diagram which is the area where the molded parts are aesthetically accepted. The bigger the window, the more robust process will be the process. It means that the parts which are located outside the illustrated process window will not be acceptable due to defects such as sinks, flash, or internal stresses.

In order to determine the values which will form the process window, an experiment was carried out as follows in Figure 17:

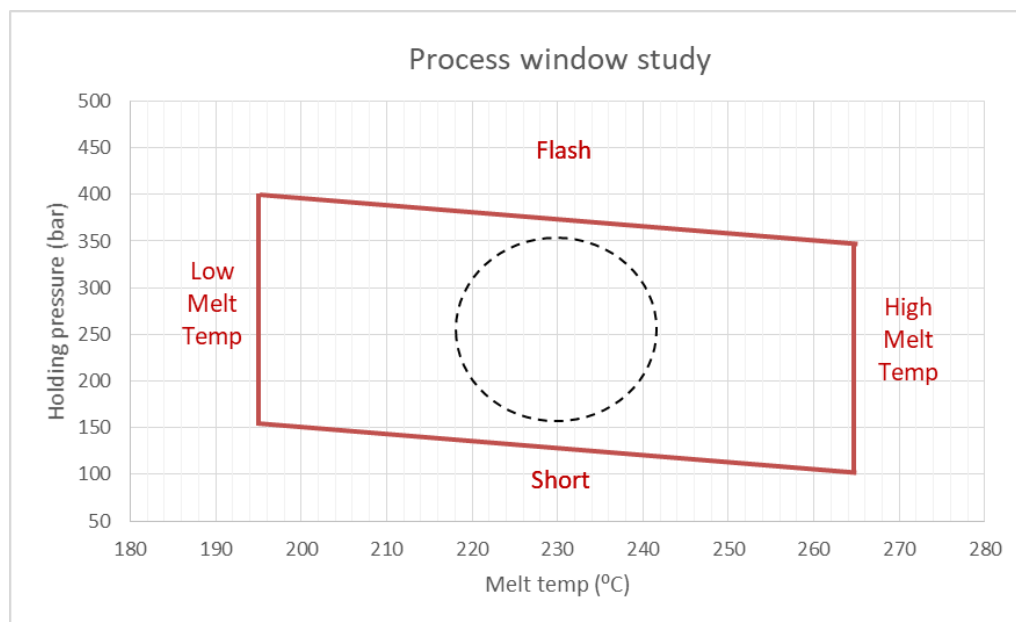


Figure 16. Process window study graph

Following table (Table 7) was constructed using the data of the graph. The size of the process window is an indicator of how much variation the process will tolerate while still producing aesthetically acceptable parts. Regarding to the temperature, both values were applied taking into account the manufacturer recommendation. On the other hand, steps of 50 bar were used during the experiment. Due to the low complexity of the injected part, this values was considered enough. More complex parts could require smaller steps in order to ensure proper performance of the mold used.

Melt temperature (°C)	Low Holding Pressure (bar)	High Holding Pressure (bar)
195	150	100
265	400	350

Table 7. Process Window Worksheet

Step 4: Determining the Gate Seal Time – Gate Seal Study

The molten plastic enters the cavity through the gate. The mold filling phase is dynamic, during which melt temperature, pressure, and flow velocity are all changing with time. For the mold fill phase, time begins with injection, which is the start of the forward movement of the screw. As the cavity begins to fill and is nearly full, the pack and hold pressure phase starts. The melt flow velocity is reduced and the melt temperature simultaneously drops. This causes an increase of viscosity of the melt. The gate has a fixed cross sectional area. When the viscosity of the plastic in this and the surrounding area it drops to a value at which the plastic cannot flow anymore, the gate is considered frozen. The plastic molecules in the gate are now immobile and cannot flow into the cavity anymore. The time it takes to reach this stage is called the gate freeze time.

Within the injection molding process, the pressure must be applied to the melted plastic until such time that the gate is frozen. If the pressure is not applied enough time, either the part will appear with internal voids or plastic pressure inside the cavity is high enough to flow back out of the cavity and then will also result in an under-packed part.

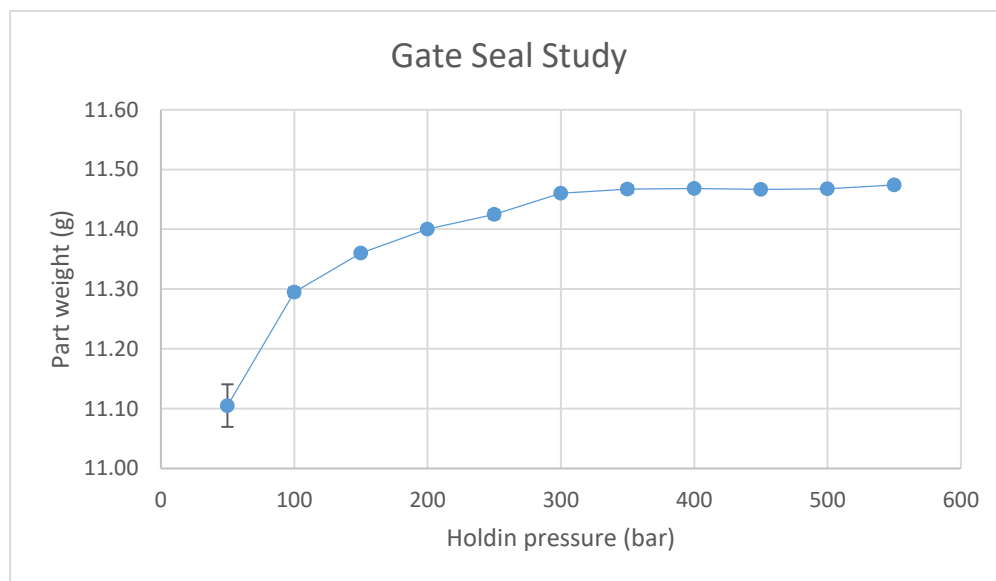


Figure 17. Gate seal graph

Gate freeze time is a function of the type of plastic, gate geometry and the processing parameters of the machine. A gate freeze study is a graph of part weight versus holding time. Once the gate is froze, the part

weight will remain constant due the plastic can no longer get into or out of the cavity. A constant part weight is an indication of gate freeze. Figure 18 shows the study for part studied in this work.

In this procedure, the injection speed was set to the value obtained from viscosity curve experiment. HP time was set high enough to no influence in the experiment. The value 300 bar of HP was considered the value in which part weight start to remain constant. Table 8 shows the values plotted in the gate seal graph.

HP time (s)	HP (bar)	Average part weight (g)	SD
30	50	11.11	± 0.035
30	100	11.30	± 0.007
30	150	11.36	± 0.000
30	200	11.40	± 0.000
30	250	11.43	± 0.007
30	300	11.46	± 0.000
30	350	11.47	± 0.006
30	400	11.47	± 0.002
30	450	11.47	± 0.001
30	500	11.47	± 0.001
30	550	11.47	± 0.006

Table 8. Gate Seal Study Worksheet

Once the optimal HP value was obtained, a study of optimal HP time was carried out. It consists on, using the optimal HP value, decrease the HP time until the weight part starts to also decrease. Table 9 shows the experiment.

HP time (s)	HP (bar)	Average part weight (g)	SD
30	300	11.46	± 0.000
27	300	11.45	± 0.000
24	300	11.43	± 0.000
21	300	11.40	± 0.000
18	300	11.30	± 0.006
15	300	11.17	± 0.061
12	300	10.54	± 0.055

Table 9. Gate Seal Time Worksheet

From this study, the optimal HP time was set to 18s. Figure 19 shows how the part weight varies when HP time decreases.

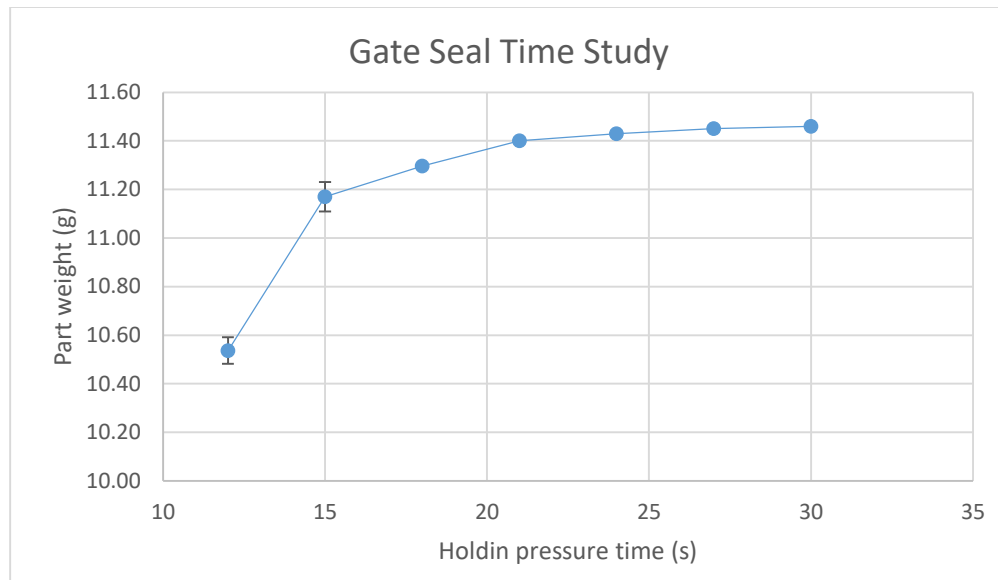


Figure 18. Gate Seal Time Graph

Step 5. Determining the Cooling Time – Cooling Time Study

Once the Holding Pressure Time is finished, the set cooling time starts. The plastic starts to cool down as soon as it hits the walls of the mold. The mold will remain closed until the end of the cooling time. After that, the part is ejected.

Before the part is ejected, it needs to be reach the ejection temperature. If the part is ejected with not enough cooling time, it will be too soft and will get deformed during the injection. Otherwise, excessive cooling time is related to a waste of machine time and therefor profits. Cooling time should also be set so that the part dimensions remain consistent and the process is capable of molding acceptable parts over the time. The process used to determine to optimal cooling time is based on the final dimension part which depends directly on the time that the part remains inside the mold after to be injected.

The standard process was not followed due to the dimensions of the part were not considered a critical point for the work. Different cooling times were tested and 18s was considered as good in order to obtain good parts ensuring that the part was solid enough to be ejected.

Step 6. Determining the Screw Speed and Back Pressure – Dosing Phase Study

There are no scientific experiments that can be easily performed to optimize screw speed or back pressure. The screw speed should be set such that the screw always recovers before the end of the cooling time and not degrades the material due shear stresses. Unlike amorphous plastics, in crystalline plastics, higher screw speeds are recommended because the melting of the crystallites require high energy that can be supplied by shear of the rotating screw. The heat from the heater bands may not be sufficient to produce a homogeneous and uniform melt.

Maximal lineal screw speed recommended by the material manufacturer is 0.7 m/s for this grade. Taking into account the diameter of the screw used in this work, the maximal RPM used in this work was calculated as follows:

$$\omega = \frac{v * 60}{\phi * \pi} = 534.76 \text{ rpm} \quad (\text{eq. 1})$$

Where:

- v is the lineal speed (m/s)
- ϕ is the diameter of the screw used (m)
- 1 revolution is 2π rad

The obtained value is the maximum recommended by the manufacturer in rpm taking into account the screw used in this work. The value obtained above is high due to the small value of the screw diameter. The shear from the rotating screw contributes a significant amount of energy to help melt the plastic. The mold does not open until the screw recovery is completed and the cooling times are reached. If screw recovery takes longer than cooling time, the effective cooling time increases because the mold is still closed.

Then taking into account the cooling time determined previously, the lowest value for the screw speed was set to 50 rpm. Otherwise, highest screw speed was limited by the IMM used to 300 rpm and not by the material manufacturer.

The optimum back pressure is the lowest possible pressure to keep the screw recovery time consistent and avoid any surface and/or internal defects visible on the part. Surface defect would include splay and internal defects would include bubbles and voids. Back pressure was set to 55 bar as optimal value taking into account the recommendation of the manufacturer and finally, fine tuning by the necessity of the process.

At the end of the optimization of the process, most important injection molding parameters were fixed. Table 10 shows all of this parameters:

Parameter	Value	Unit
Injection speed	70	mm/s
Melt temp. Range	195-265	°C
HP	300	bar
HP time	18	s
Screw speed	<300	rpm
Back pressure	55	bar

Table 10. Summary of optimal injection molding parameters

4.6.Design of experiments (DOE)

The goal in this stage was to get the best combination of parameters in which the high dispersion of nano-additive was reached. The experiments were carried out using a formulation made up of the selected PP as matrix and Cloesite20 as nano-additive.

Some investigation's groups have investigated how to optimize the injection moulding process to get best results of nano-additive dispersions. For example: [45], with PP and multiwall carbon nanotubes, [46] with PP and nano-clay nano-composites and [15] with thermoplastics and carbon nanotubes nano-composites studied the nano-additive dispersion with four injection parameters: Injection rate, screw rotational rate, back pressure and melt temperature. Another example is [47] with PC and multi-walled carbon nanotubes [4] using different injection parameters: holding pressure, injection rate, mould temperature and melt temperature.

The suggested DOE consists of **four parameters** with **two levels** as shown in Table 11:

Factors				
Assigned test Level	Barrel temperature[°C]	Injection Rate [mm/s]	Back Pressure (BP) [bar]	Screw rotational Speed [rpm]
Low Level (L)	200	50	30	50
High Level (H)	260	90	80	300
Experiment N°	X ₁	X ₂	X ₃	X ₄
1	240	90	80	300
2	240	90	80	50
3	240	90	30	300
4	240	90	30	50
5	240	50	80	300
6	240	50	80	50
7	240	50	30	300
8	240	50	30	50
9	200	90	80	300
10	200	90	80	50
11	200	90	30	300
12	200	90	30	50
13	200	50	80	300
14	200	50	80	50
15	200	50	30	300
16	200	50	30	50

Table 11. Details of DOE

Injection parameters codification is recommended for two reasons. On the one hand, it is easier to understand the results achieved maintaining the order of magnitude. On the other hand, the loss of decimals during the matrix calculations can be magnified depending on the injection parameter's order of magnitude. The codified table is shown below (Table 12).

Factors				
Assigned test Level	Barrel temperature[°C]	Injection Rate [mm/s]	Back Pressure (BP) [bar]	Screw rotational Speed [rpm]
High Level (H)	200	50	30	50
Low Level (L)	260	90	80	300
Experiment N°	X ₁	X ₂	X ₃	X ₄
1	+1	+1	+1	+1
2	+1	+1	+1	-1
3	+1	+1	-1	+1
4	+1	+1	-1	-1
5	+1	-1	+1	+1
6	+1	-1	+1	-1
7	+1	-1	-1	+1
8	+1	-1	-1	-1
9	-1	+1	+1	+1
10	-1	+1	+1	-1
11	-1	+1	-1	+1
12	-1	+1	-1	-1
13	-1	-1	+1	+1
14	-1	-1	+1	-1
15	-1	-1	-1	+1
16	-1	-1	-1	-1

Table 12. DOE table with codified parameters

From these parameters, the 16 corresponding experiments were carried out and the samples were mechanically tested to obtain an output that was be used to apply linear modelling in order to optimize the process. Table 13 shows two examples of commercial grades of compounded PP with enhanced mechanical properties. A lineal modelling was used in order to maximize the Flexural Modulus

The aim of the work is to maximize the Flexural Modulus thus a linear modelling was run to obtain the highest value of Flexural Modulus as possible

Property	Innopol CS2-9120 (20wt.% talc)	SABIC PP compound 7715
Density (g/cm ³)	1,04	1
MFR (g/10 min)	30	20
Tensile modulus (MPa)	2100	
Tensile stress (MPa), yield	25	26
Tensile strain (%), yield	3	
Tensile strain (%), break		60
Flexural modulus (MPa)	2200	1800

Table 13. Target properties

4.7. Lineal modelling

For the four selected parameters and two levels for each one, a lineal model has been used to determine the effect of each parameter in the dispersion. The output for modelling was the Flexural Modulus and the input was all 16 experiments. Five samples have been tested for each experiment getting a total of 80 flexural tests. General equation to solve for a lineal model was:

$$Y = \hat{\beta}X \rightarrow \hat{\beta} = (X'X)^{-1}X'Y \rightarrow \hat{Y} = \hat{\beta}X \quad (\text{eq. 2})$$

Where:

$$Y = \begin{bmatrix} Y_1 \\ Y_2 \\ Y_3 \\ \vdots \\ Y_n \end{bmatrix}; X = \begin{bmatrix} 1 & X_{11} & X_{21} & X_{11}X_{21} & X_{nk}^m \\ 1 & X_{11} & X_{22} & \dots & \dots \\ 1 & X_{12} & X_{21} & \dots & \dots \\ 1 & X_{12} & X_{22} & \dots & \dots \\ \vdots & \vdots & \vdots & \dots & \dots \\ 1 & X_{1k} & X_{2k} & \dots & \dots \end{bmatrix} \rightarrow \hat{\beta} = \begin{bmatrix} \hat{\beta}_0 \\ \hat{\beta}_1 \\ \hat{\beta}_2 \\ \hat{\beta}_{12} \\ \vdots \\ \hat{\beta}_n \end{bmatrix} \quad (\text{eq. 3})$$

- \hat{Y} is the output or response of the model
- X is the input from all experiments (independent variables)
- $\hat{\beta}$ are the estimated coefficients

In this case, a first model was proposed taking into account all possible interactions between the selected parameters:

$$\hat{Y} = \beta_0 + \beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_4X_4 + \beta_{12}X_1X_2 + \beta_{13}X_1X_3 + \beta_{14}X_1X_4 + \beta_{23}X_2X_3 + \beta_{24}X_2X_4 \quad (\text{eq. 4})$$

Where:

- β_0 is the origin de coordinates
- β_1 coefficient related to barrel temperature
- β_2 coefficient related to injection rate
- β_3 coefficient related to back pressure
- β_4 coefficient related to screw rotational rate
- β_{12} is related to interactions between β_1 and β_2
- β_{13} is related to interactions between β_1 and β_3
- β_{14} is related to interactions between β_1 and β_4
- β_{23} is related to interactions between β_2 and β_3
- β_{24} is related to interactions between β_2 and β_4

Scilab 6.0 was used to solve the matrix operations due the size of the matrix. The size of X was 80x10 and \hat{Y} was 80x1 and the resulting matrix $\hat{\beta}$ was 10x1.

This model will only be valid and repeatable if the process has remained constant and has not changed its conditions for data collection. Therefore, ensure that the configuration of the control parameters will not affect the working conditions of the process, falsifying measured response. This is done via a study of residuals, as well as verification of the significance of the model obtained.

4.8. Residuals

First step corresponds to verify the difference between the estimated response in a defined point and the experimental responses obtained at the same point, known as residuals ($\varepsilon = \hat{Y} - Y$) with 0 of average and a constant variance (for every control factor) (Figure 20).

$$\text{Hypothesis 1: } \varepsilon \sim N(0, \sigma^2 = ct)$$

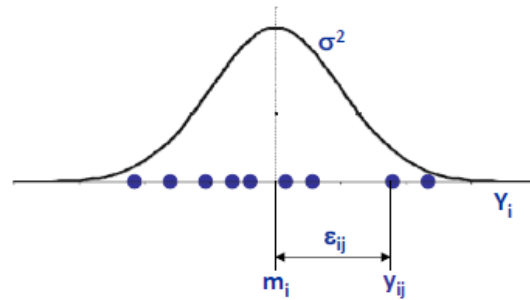


Figure 19. Residuals of a normal experimental sample

To ensure this hypothesis, a test fit normal values of residues obtained has been performed.

The normal setting test is to perform a linear regression between the normal statistical standard (Z) and the concerned values of the sorted residuals (ε). The normal statistical standard classification corresponds to a supposed normal variable (ε) in a normal distribution equivalent on average zero and variance the unit (Z):

$$\varepsilon \sim N(m = 0; \sigma^2 = ct) \rightarrow Z = \frac{\varepsilon - m}{\sigma} \rightarrow Z \sim N(0; 1) \quad (\text{eq. 5})$$

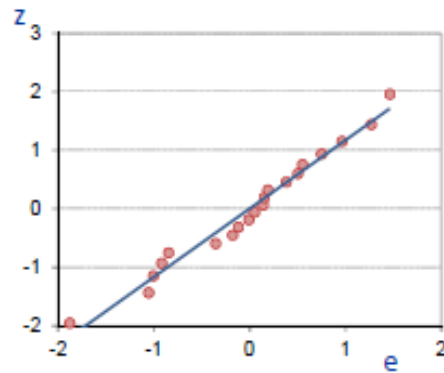


Figure 20. Residuals normal test

In Figure 20 is shown an example of residual normal test and in Figure 21 is shown an example of the model.

Therefore, if the slope of the line obtained approximates the inverse of the standard deviation (σ), estimated from the data, and the average calculated from the origin ordinate (m / σ) corresponds to the value estimated from the data (in this case, should be 0), can be considered part of the first validated hypotheses. Figure 22 shows the residual normal test for studied case.

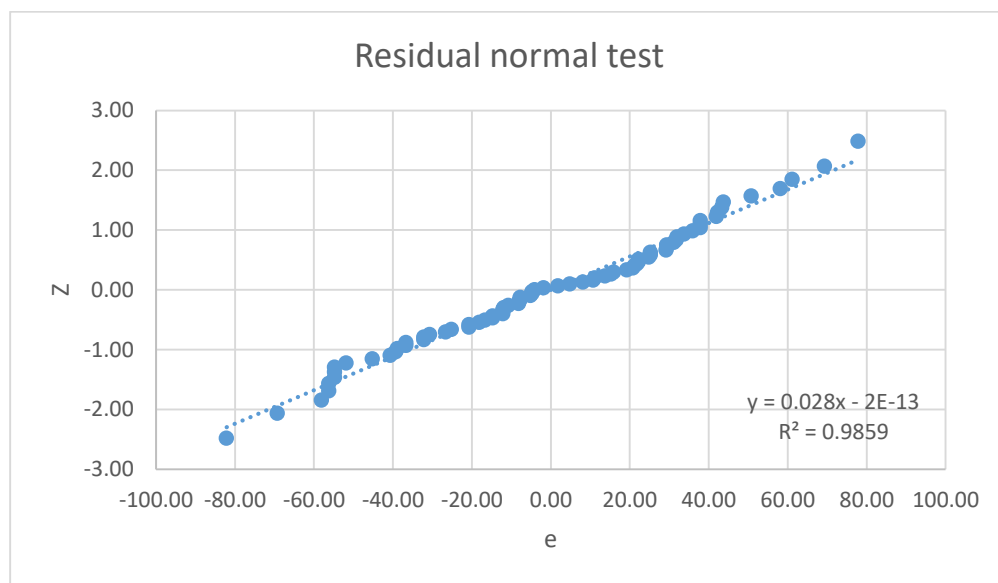


Figure 21. Residual normal test for the third iteration of the model

Figure 22 confirmed that the variance remains constant for all control factors involved in the design of experiments (k).

To confirm this, the residual graphic is obtained for each control factors separately. If there is any trend in terms of the extent of dispersion values or the variation of the average value for each factor level, it can be confirmed that the residual corresponds to a normal random variable probability distribution, with constant variance for all levels of control factors. Two extreme examples are shown in Figure 23.

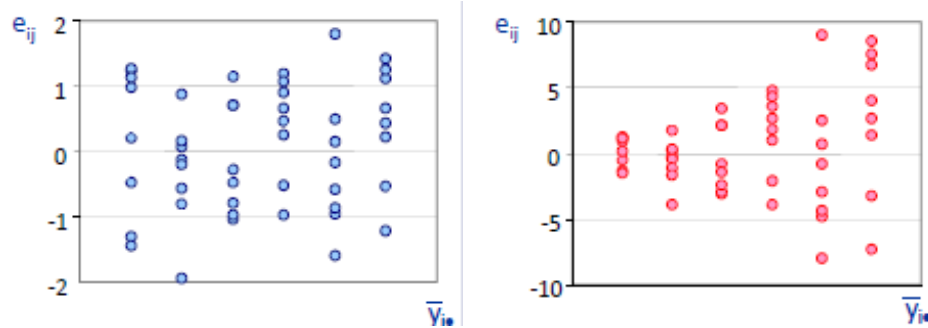


Figure 22. Two examples of probability distribution. Left graph with constant variance and right graph with unstable variance

Figure 24 shows that residuals variance remains constant during all values.

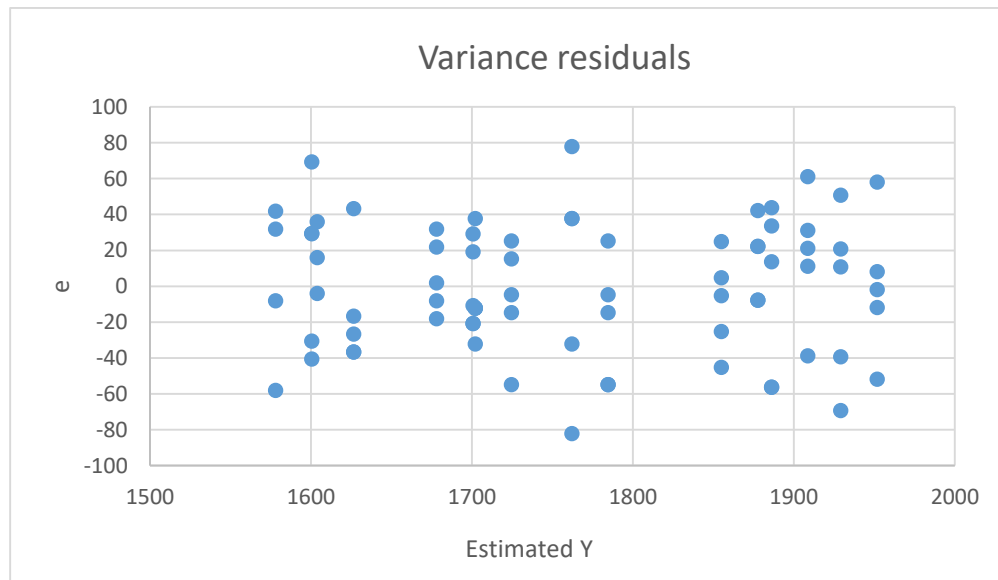


Figure 23. Residual variance for the third iteration of the model

4.9. Model signification study

As for the model obtained by regression ($Y = X \beta$) has been validated in the first place, ensuring that the average experimental responses is equal to the average of the responses estimated.

$$\bar{Y} = \bar{\hat{Y}} \quad (\text{eq. 6})$$

This check serves to confirm that the calculation of the vector of estimated coefficients (β) was successful.

Another factor to consider is the variability of responses measured. Not excessive or constant variability may invalidate the model obtained, inducing erroneous tendencies or averages unreliable.

Therefore, after obtaining the model, it should be checked that it is a model with a probability distribution on the responses of normal and constant variance.

$$\text{Hypothesis 2: } Y \sim N(m, \sigma^2 = ct) \rightarrow \hat{Y} \sim N(m, \sigma^2 = ct)$$

To study the variability of the process, has to realize an ANOVA (analysis of variance) regression using the F-test, which is not normally sensitive to it and will indicate whether the model corresponds to a calculated normal distribution model.

$$F = \frac{\text{explained variance}}{\text{unexplained variance}} = \frac{QMEx}{QMR} = \frac{\frac{SQEx}{v_{Ex}}}{\frac{SQR}{v_R}} \quad (\text{eq. 7})$$

Where:

$$\frac{SQEx}{v_{Ex}} = \frac{\sum(\hat{Y}_i - \bar{Y})^2}{(p - 1)} : p = \text{experimental points}$$

$$\frac{SQR}{v_R} = \frac{\sum(Y_i - \hat{Y}_i)^2}{(n - p)} : n = \text{total of experimental points}$$

The F statistic can check with a probability of false rejection (α) set (typically $\alpha = 5\%$), if the null hypothesis (H_0) that the model is not significant may be rejected. Therefore, to validate the significance of the model, the p-value (or probability of rejecting the null hypothesis is when is true) must be less than the fixed probability of false rejection ($p\text{-value} < \alpha$) (Figure 25).

$$\text{Estimated model: } \hat{Y} = \hat{\beta}_0 + \hat{\beta}_1 X_1 + \hat{\beta}_2 X_2 + \hat{\beta}_{12} X_1 X_2 + \hat{\beta}_{11} X_1^2 + \hat{\beta}_{22} X_2^2 + \dots + \hat{\beta}_n X_n^k$$

$$\text{Null hypothesis: } H_0: \beta_j = 0 \forall j = 1 \dots (p - 1) ; p = \text{different experimental points}$$

$$\text{To calculate } F \rightarrow \text{if } p\text{-value} < \alpha \rightarrow H_0 \text{ reject, therefore the model is validated}$$

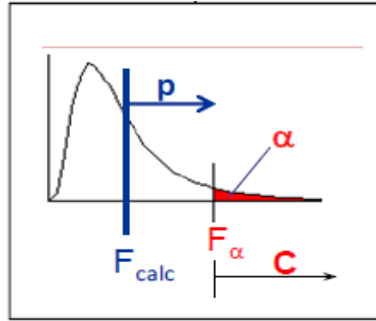


Figure 24. F or Snedecor probabilistic distribution

Once validated the significance of global model, the meaning of each of coefficients separately has been studied because they may have terms that are not valid saturated model, so little impact on the decline, inducing errors estimation and interpretation of the resulting function.

The T-test is a statistical tool that is commonly used for variables that follow normal distributions to determine equality between different populations. In regressions can be used to determine the significance of the various pending induced model of each term.

Therefore, it is defined as the null hypothesis (H_0) that the value of the estimated coefficient ($\hat{\beta}_j$) can be considered zero for each of the coefficients. The statistics associated T corresponds to the estimated coefficient divided by the estimated variance ($S_{\hat{\beta}_j}$). In the same way that the test of hypothesis F must be defined in a probability of false rejection (α , typically 5%). If the p-value (or probability of rejecting the null hypothesis when is true) obtained is less than the probability of false rejection (p-value $< \alpha$), we can reject the null hypothesis a, and therefore accept meaning of the term in particular (**Error! No se encuentra el origen de la referencia.**).

$$\text{Estimated model: } \hat{Y} = \hat{\beta}_0 + \hat{\beta}_1 X_1 + \hat{\beta}_2 X_2 + \hat{\beta}_{12} X_1 X_2 + \hat{\beta}_{11} X_1^2 + \hat{\beta}_{22} X_2^2 + \dots + \hat{\beta}_n X_n^k \quad (\text{eq. 8})$$

$$\text{Null hypothesis: } H_0: \beta_j = 0$$

(for each coefficient separately, excluding the origin ordinate)

$$\text{Static } T = \frac{\hat{\beta}_j}{S_{\hat{\beta}_j}} \quad (\text{eq. 9})$$

$$= \frac{\hat{\beta}_j}{\sqrt{QMR \cdot d_{\hat{\beta}_j}}}; \text{ where } d_{\hat{\beta}_j} \text{ corresponds to the term of the diagonal } (X'X^{-1}) \text{ associated to } \hat{\beta}_j$$

To calculate $T \rightarrow$ if $p\text{-value} < \alpha \rightarrow H_0$ rejected, therefor the model is validated

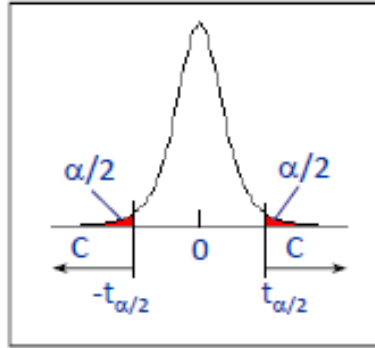


Figure 25. T or Student probabilistic distribution

The t-test was applied to each of the terms is not significant if any should be removed. As deleting a term involves the modification of the model, always will be removed less significant term, and the model must be re-calculated and re-validated, becoming an iterative process to get a model with all significant terms.

4.10. Model validation

Following the steps explained above, several iterations were carried out to validate the proposed model. First model was calculated obtaining a matrix of 10 coefficients. The p column gives the $p\text{-value}$ for each coefficient. To ensure the model is consistent, $p\text{-value}$ must be < 0.025 because α was considered 0.05. Table 14 shows that there are $p\text{-values}$ above the 0.025.

	Coefficient β	Diagonal $(X'X)^{-1}$	Error ($S\beta_j$)	T	p
β_0	1756,63	0,0125	5,944		
β_1	-112,88	0,0125	5,944	-18,991	0,000
β_2	-2,13	0,0125	5,944	-0,358	0,722
β_3	-1,38	0,0125	5,944	-0,231	0,818
β_4	15,63	0,0125	5,944	2,629	0,010
β_{12}	-53,63	0,0125	5,944	-9,022	0,000
β_{13}	-15,38	0,0125	5,944	-2,587	0,012
β_{14}	-18,38	0,0125	5,944	-3,092	0,003
β_{23}	-1,63	0,0125	5,944	-0,273	0,785
β_{24}	-13,63	0,0125	5,944	-2,292	0,025

Table 14. First model calculation

First step consisted of deleting the highest value, which was related to β_3 . Next steps consisted of recalculate the model without the rejected coefficient. This two steps will be carried out until all p-values are below 0.025. Iterations are shown in Table 15 to Table 17.

	Coefficient β	Diagonal $(X'X)^{-1}$	Error ($S\beta_j$)	T	p
β_0	1760,92	0,013	4,181		
β_1	-108,58	0,013	4,181	-25,972	0,000
β_2	2,17	0,013	4,181	0,519	0,605
β_4	16,67	0,013	4,170	3,997	0,000
β_{12}	-49,33	0,013	4,181	-11,799	0,000
β_{13}	-1108,07	0,013	4,181	-265,041	0,000
β_{14}	-17,33	0,013	4,170	-4,156	0,000
β_{23}	2,67	0,013	4,181	0,638	0,525
β_{24}	-12,58	0,013	4,170	-3,017	0,004

Table 15. Model validation's first iteration

	Coefficient β	Diagonal $(X'X)^{-1}$	Error ($S\beta_j$)	T	p
β_0	1760,82	0,013	4,189		
β_1	-108,68	0,013	4,189	-25,947	0,000
β_4	16,71	0,013	4,178	3,999	0,000
β_{12}	-49,43	0,013	4,189	-11,801	0,000
β_{13}	-11,18	0,013	4,189	-2,670	0,009
β_{14}	-17,29	0,013	4,178	-4,139	0,000
β_{23}	2,57	0,013	4,189	0,613	0,542
β_{24}	-12,54	0,013	4,178	-3,002	0,004

Table 16. Model validation's second iteration

	Coefficient β	Diagonal $(X'X)^{-1}$	Error ($S\beta_j$)	T	p
β_0	1760,70	0,013	4,200		
β_1	-108,80	0,013	4,200	-25,906	0,000
β_4	16,75	0,013	4,189	3,999	0,000
β_{12}	-49,55	0,013	4,200	-11,798	0,000
β_{13}	-11,30	0,013	4,200	-2,690	0,009
β_{14}	-17,25	0,013	4,189	-4,118	0,000
β_{24}	-12,50	0,013	4,189	-2,984	0,004

Table 17. Model validation's third iteration

After all iterations, a consistent model was obtained. Note that some coefficient parameters or coefficient interaction between parameter have been disappeared. The coefficients related to injection rate and back pressure were deleted but remained in the interactions. The final model is shown below:

$$\hat{Y} = 1760,7 - 108,8X_1 + 16,76X_4 - 49,55X_1X_2 - 11,3X_1X_3 - 17,25X_1X_4 - 12,5X_2X_4 \quad (\text{eq.10})$$

4.11. Results

Once the model was solved, four response surfaces had been plotted. Each surface can represent 2 inputs (i.e. injection rate and back pressure) and the behaviour of the two remaining related to the output can be observed. An example is shown in Figure 26:

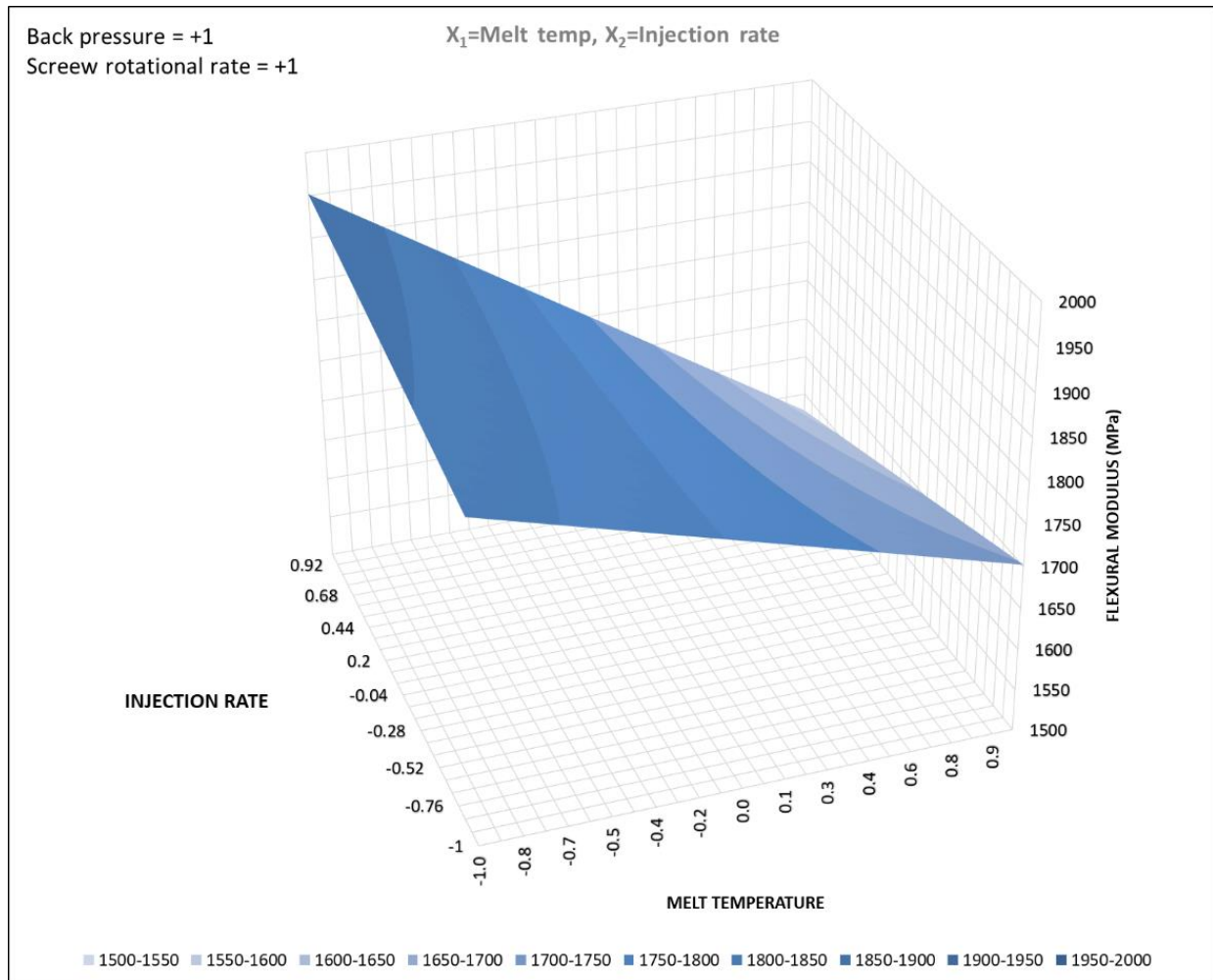


Figure 26. Example of a surface response

Note that the plot above has two variable parameters (melt temperature and injection rate) which varies from -1 to +1 due to the codification. The other two parameters (back pressure and screw rotational rate) have been fixed which in this case, are represented +1 for back pressure and +1 for screw rotational rate (maximum level). All 16 response surfaces are shown in **¡Error! No se encuentra el origen de la referencia..**

In one hand, if two parameters are fixed and two are variable, four combinations of them are possible. On the other hand, 4 combinations between fixed and variable parameters are possible which results in 16 surfaces.

A summary of all combinations is shown in Table 18:

SURFACE 1				SURFACE 2				SURFACE 3				SURFACE 4			
FIXEDED		VARIABLE		FIXED		VARIABLE		FIXED		VARIABLE		FIXED		VARIABLE	
X ₃ +	X ₄ +	X ₁ -	X ₂ +	X ₂ +	X ₃ +	X ₁ -	X ₄ +	X ₁ +	X ₂ +	X ₃ -	X ₄ -	X ₁ +	X ₄ +	X ₂ +	X ₃ -
X ₃ +	X ₄ -	X ₁ -	X ₂ +	X ₂ +	X ₃ -	X ₁ -	X ₄ +	X ₁ +	X ₂ -	X ₃ -	X ₄ +	X ₁ +	X ₄ -	X ₂ -	X ₃ -
X ₃ -	X ₄ -	X ₁ -	X ₂ +	X ₂ -	X ₃ -	X ₁ -	X ₄ +	X ₁ -	X ₂ -	X ₃ +	X ₄ +	X ₁ -	X ₄ -	X ₂ +	X ₃ +
X ₃ -	X ₄ +	X ₁ -	X ₂ +	X ₂ -	X ₃ +	X ₁ -	X ₄ +	X ₁ -	X ₂ +	X ₃ +	X ₄ +	X ₁ -	X ₄ +	X ₂ +	X ₃ +

Table 18. Summary of the 16 surfaces response

All possible combinations between parameters were plotted. Columns called *FIXED* are the immovable parameters (only was used one value: maximum level or minimum level). Otherwise, columns called *VARIABLE* are represented the variable parameter behaviour in order to obtain the high output value (Flexural Modulus).

In Figure 27, X₃ and X₄ are fixed for the high level. In order to obtain the best output value, low level of melt temperature (X₁ = -1) and high level of injection rate (X₂ = +1) were required.

Table 19 was created following the steps mentioned above.

SURFACE 1				SURFACE 2				SURFACE 3				SURFACE 4			
FIXEDED		VARIABLE		FIXED		VARIABLE		FIXED		VARIABLE		FIXED		VARIABLE	
X ₃ +	X ₄ +	X ₁ -	X ₂ +	X ₂ +	X ₃ +	X ₁ -	X ₄ +	X ₁ +	X ₂ +	X ₃ -	X ₄ -	X ₁ +	X ₄ +	X ₂ +	X ₃ -
X ₃ +	X ₄ -	X ₁ -	X ₂ +	X ₂ +	X ₃ -	X ₁ -	X ₄ +	X ₁ +	X ₂ -	X ₃ -	X ₄ +	X ₁ +	X ₄ -	X ₂ -	X ₃ -
X ₃ -	X ₄ -	X ₁ -	X ₂ +	X ₂ -	X ₃ -	X ₁ -	X ₄ +	X ₁ -	X ₂ -	X ₃ +	X ₄ +	X ₁ -	X ₄ -	X ₂ +	X ₃ +
X ₃ -	X ₄ +	X ₁ -	X ₂ +	X ₂ -	X ₃ +	X ₁ -	X ₄ +	X ₁ -	X ₂ +	X ₃ +	X ₄ +	X ₁ -	X ₄ +	X ₂ +	X ₃ +

Table 19. Relations between surfaces response



From Surface 1 and 2, two important facts were concluded: whatever combination of fixed parameters gave the same behaviour of variable parameter meaning that low level of melt temperature (X₁ -), high level of injection rate (X₂ +), and high level of screw rotational rate (X₄ +), boosts the output value that is the flexural modulus obtained is higher.

FIXING							
X ₁ -		X ₂ +		X ₃ +		X ₄ +	
X ₁ -		X ₄ +		X ₂ +		X ₃ +	

Table 20. Summing-up from all the surfaces response

5. Conclusions

Scientific Injection Molding is a tool that should be used for every mold set-up in order to ensure the best performance during the injection molding process. It allows to study the most significant parameters taking into account the IMM, the tool features and the rheology of the material used for each specific case. Minimal variation on the system i.e. material batch variation, gate tool, etc. will require a new iteration of the SIM steps. Therefore, this project is focused on a specific system but may be useful as a guideline for another system.

1. Four parameters have been studied to see the significance of them into the mechanical properties of the final part. In this case, the target properties was Flexural Modulus of a standard specimen and depends on the application of the injected part, different property could be studied.
2. After the model was calculated and validated some trends were obtained. High values of back pressure, screw rotational speed and injection speed boosted the output of the model (Flexural Modulus) while low values of melt temperature also boosted the Flexural Modulus.
3. On one hand, high values of back pressure and screw rotational speed may maintain or improve the dispersion achieved during the extrusion compounding. High injection rate may aid the additives orientation and then keep them homogenous.
4. On the other hand, at first sight, high melt temperature should improve the nano-additives mobility but in this case, high temperature and then high viscosity may ease the nano-additive re-aggregation and then reduce the mechanical.
5. To sum up, low values of melt temperature and high values of injection rate, back pressure and screw rotational speed will be required to achieve high values of Flexural Modulus.

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7. Annex

7.1. Annex 1. Surface responses

All surfaces response are shown as a result of the mathematical model in this annex.

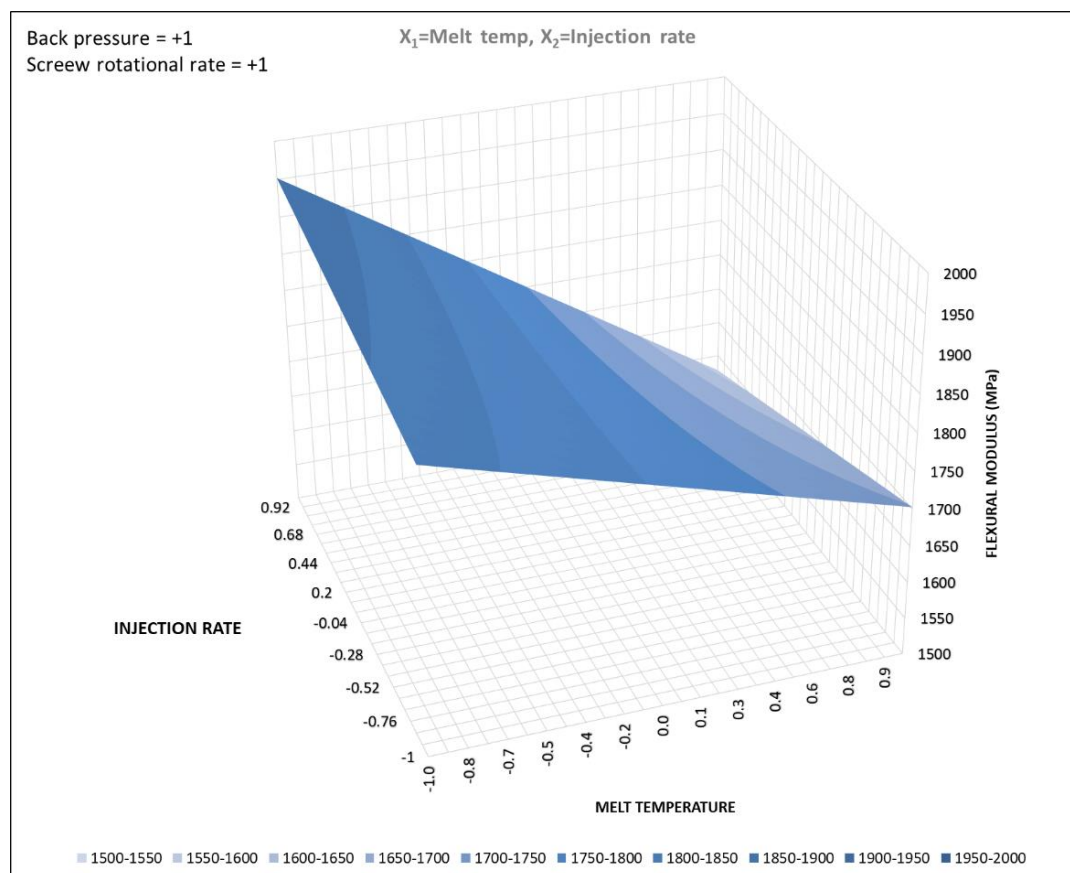


Figure 27. Surface response 1. Fixed parameters: Back pressure and Screw rotational rate. Variable parameters: Melt temperature and Injection rate.

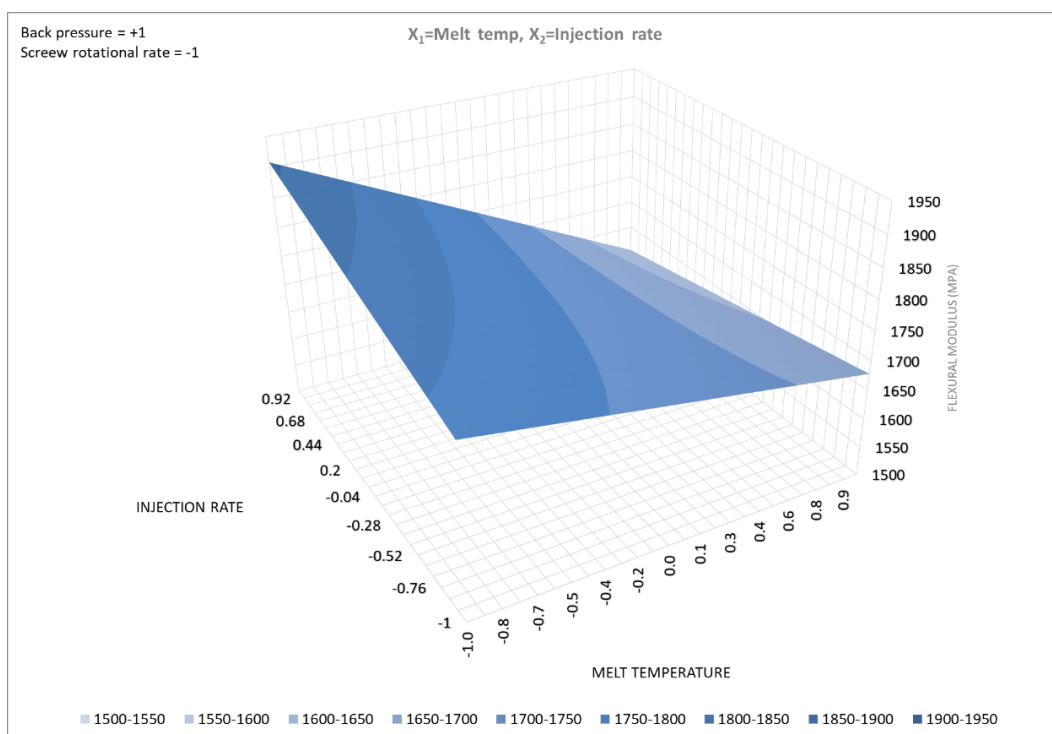


Figure 28. Surface response 2. Fixed parameters: Back pressure and Screw rotational rate. Variable parameters: Melt temperature and Injection rate.

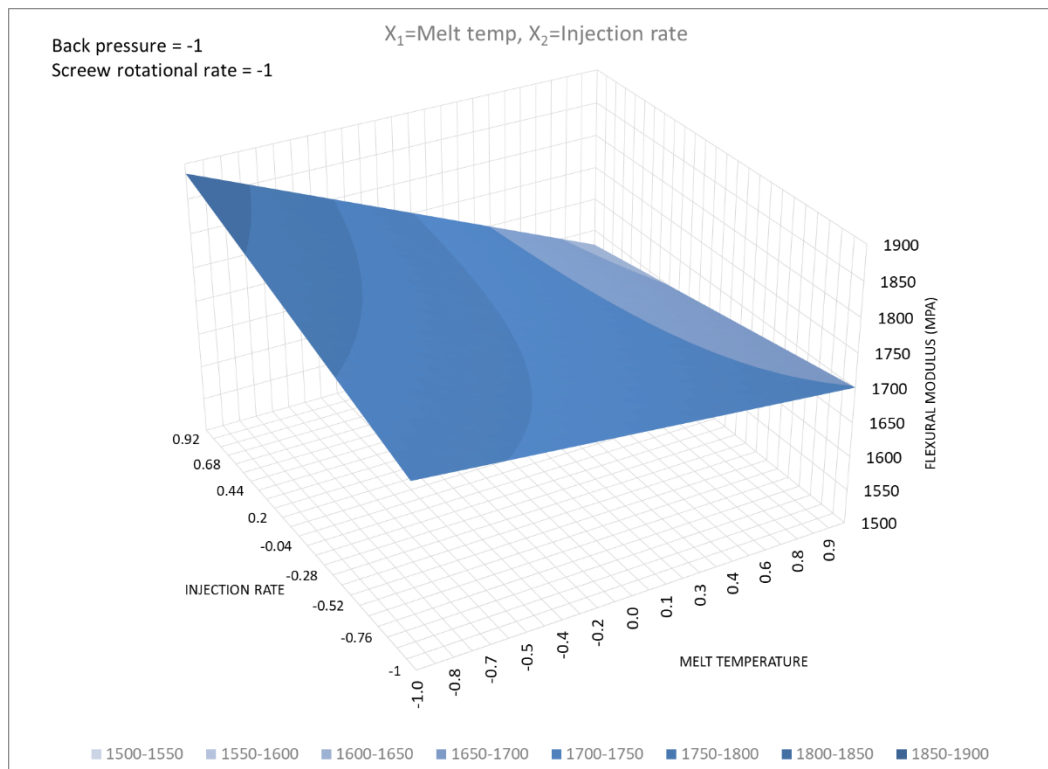


Figure 29. Surface response 3. Fixed parameters: Back pressure and Screw rotational rate. Variable parameters: Melt temperature and Injection rate.

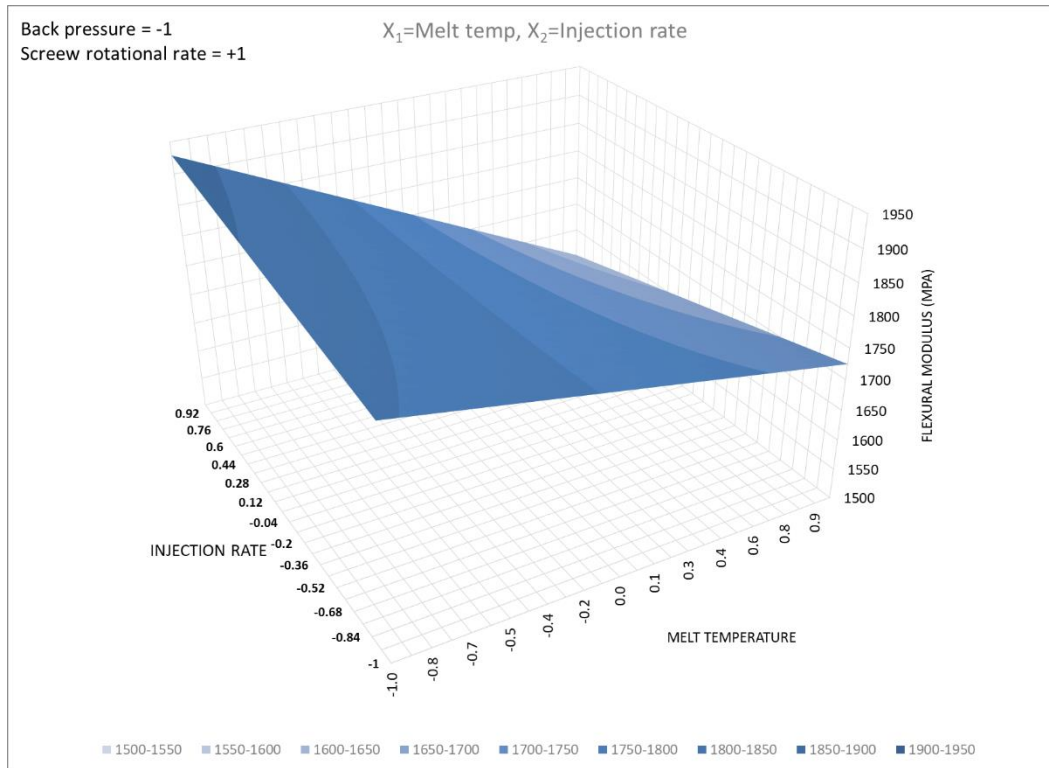


Figure 30. Surface response 4. Fixed parameters: Back pressure and Screw rotational rate. Variable parameters: Melt temperature and Injection rate.

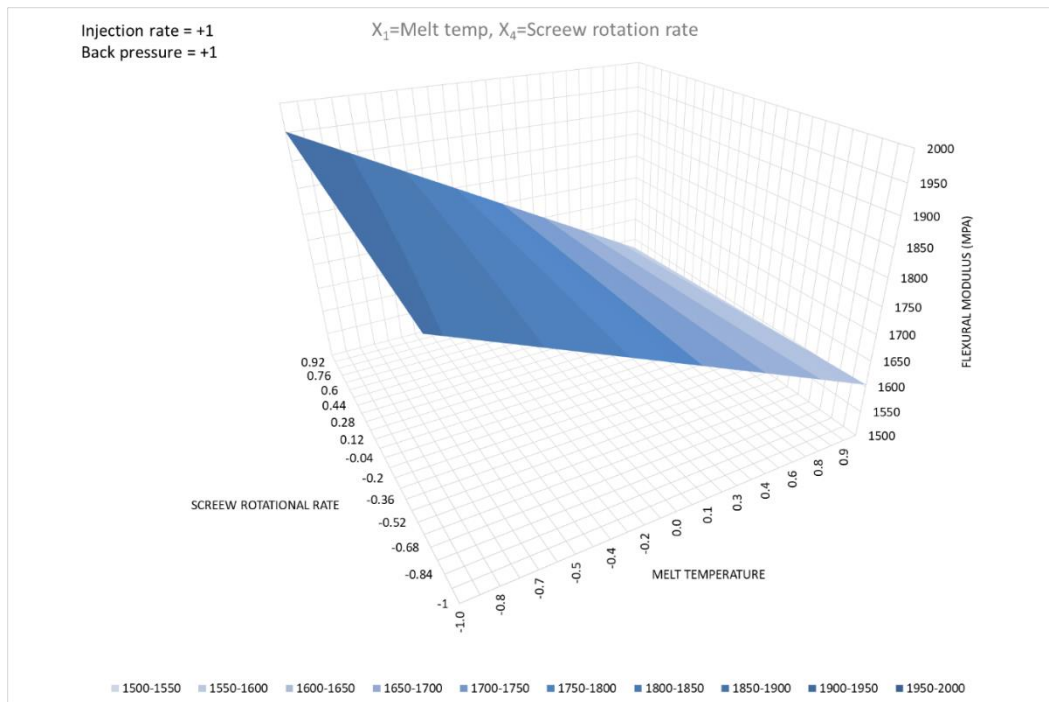


Figure 31. Surface response 5. Fixed parameters: Back pressure and injection rate. Variable parameters: Melt temperature and screw rotational rate.

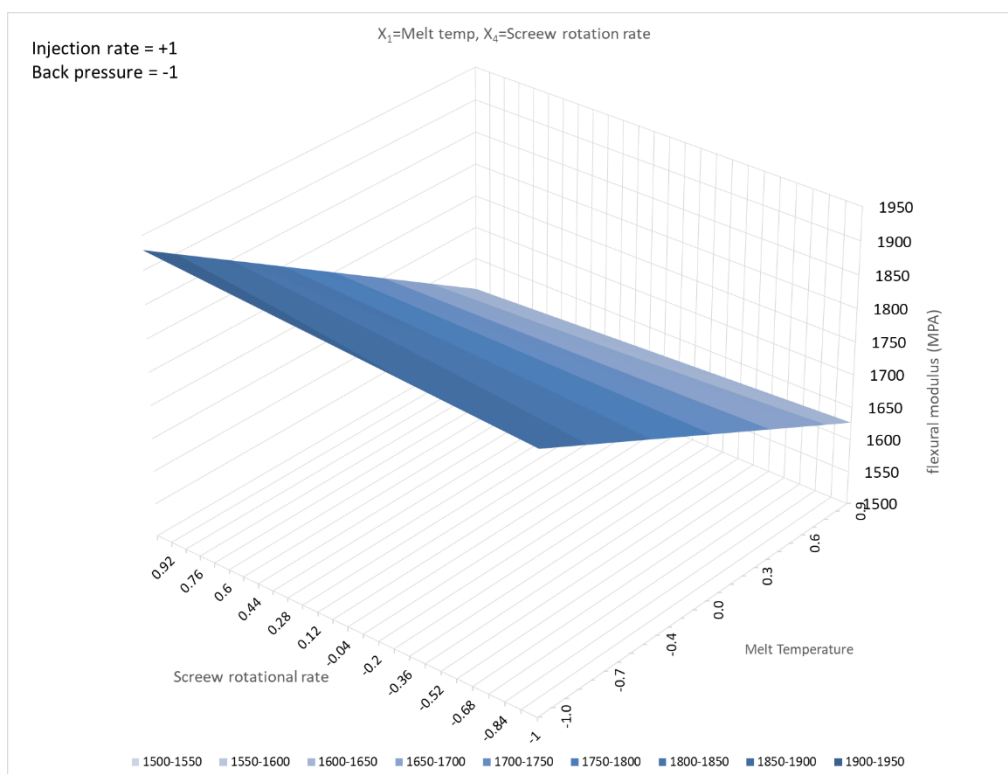


Figure 32. Surface response 6. Fixed parameters: Back pressure and injection rate. Variable parameters: Melt temperature and screw rotational rate.

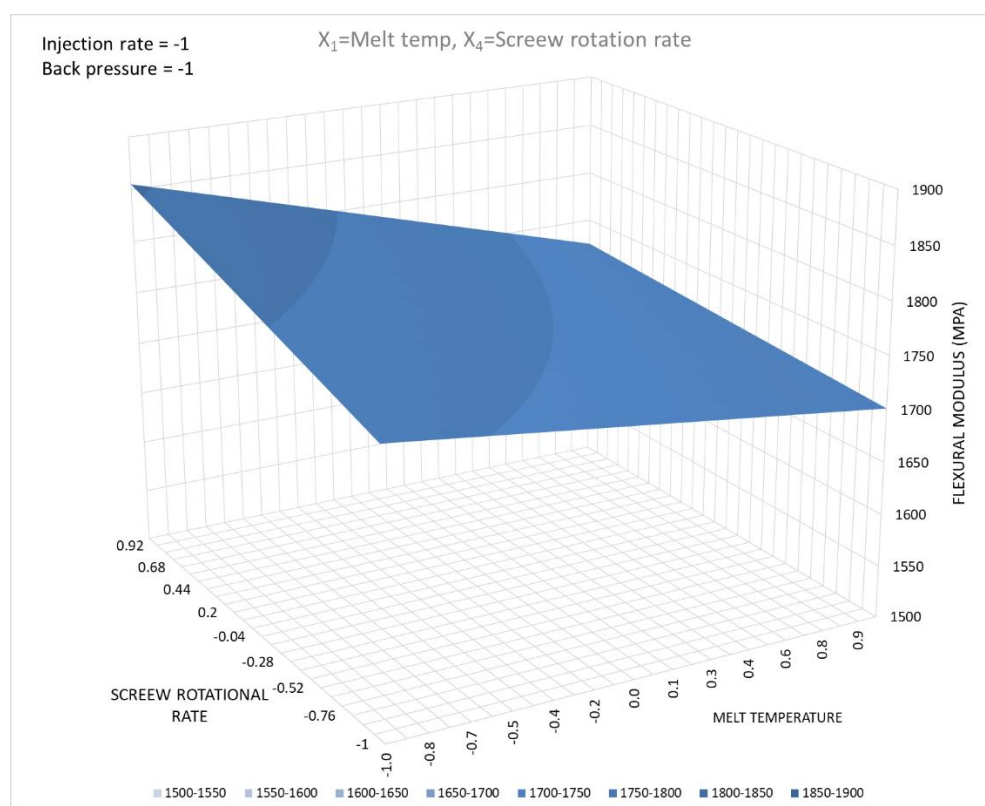


Figure 33. Surface response 7. Fixed parameters: Back pressure and injection rate. Variable parameters: Melt temperature and screw rotational rate.

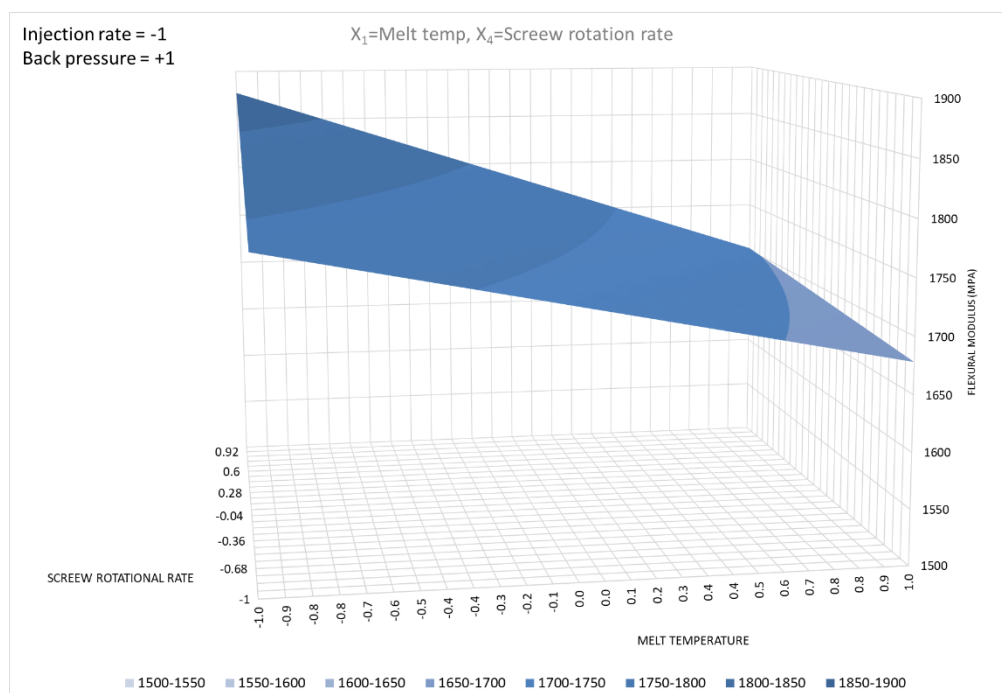


Figure 34. Surface response 8. Fixed parameters: Back pressure and injection rate. Variable parameters: Melt temperature and screw rotational rate.

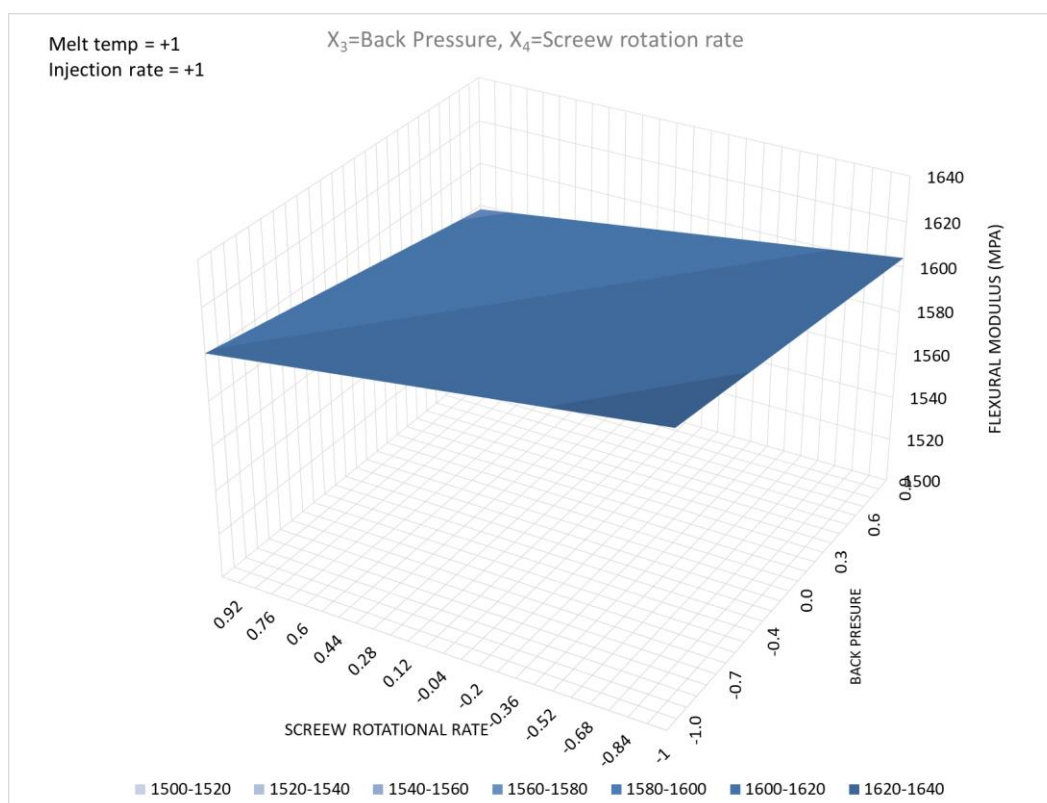


Figure 35. Surface response 9. Fixed parameters: Injection rate and melt temperature. Variable parameters: back pressure and screw rotational rate.

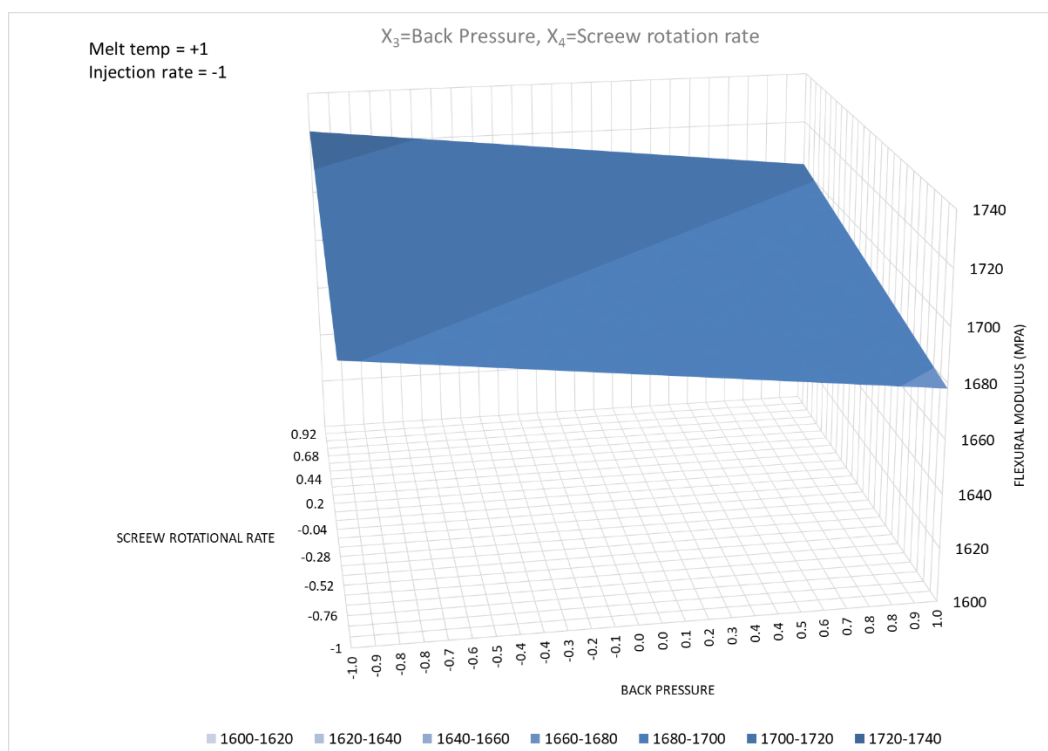


Figure 36. Surface response 10. Fixed parameters: Injection rate and melt temperature. Variable parameters: back pressure and screw rotational rate.

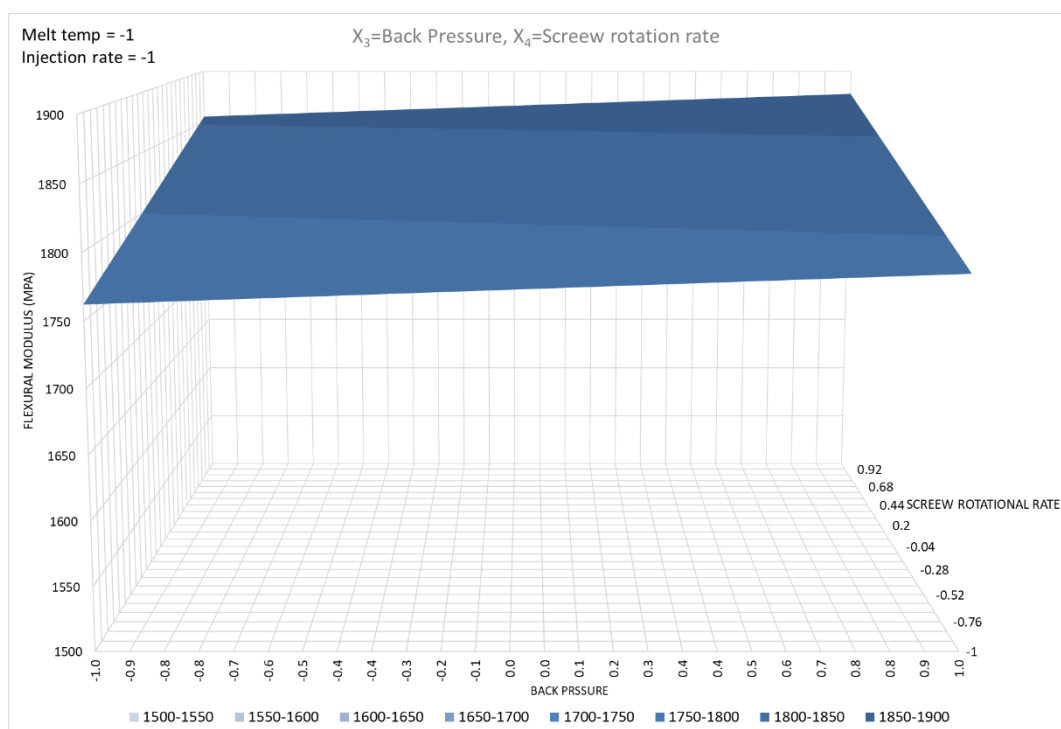


Figure 37. Surface response 11. Fixed parameters: Injection rate and melt temperature. Variable parameters: back pressure and screw rotational rate.

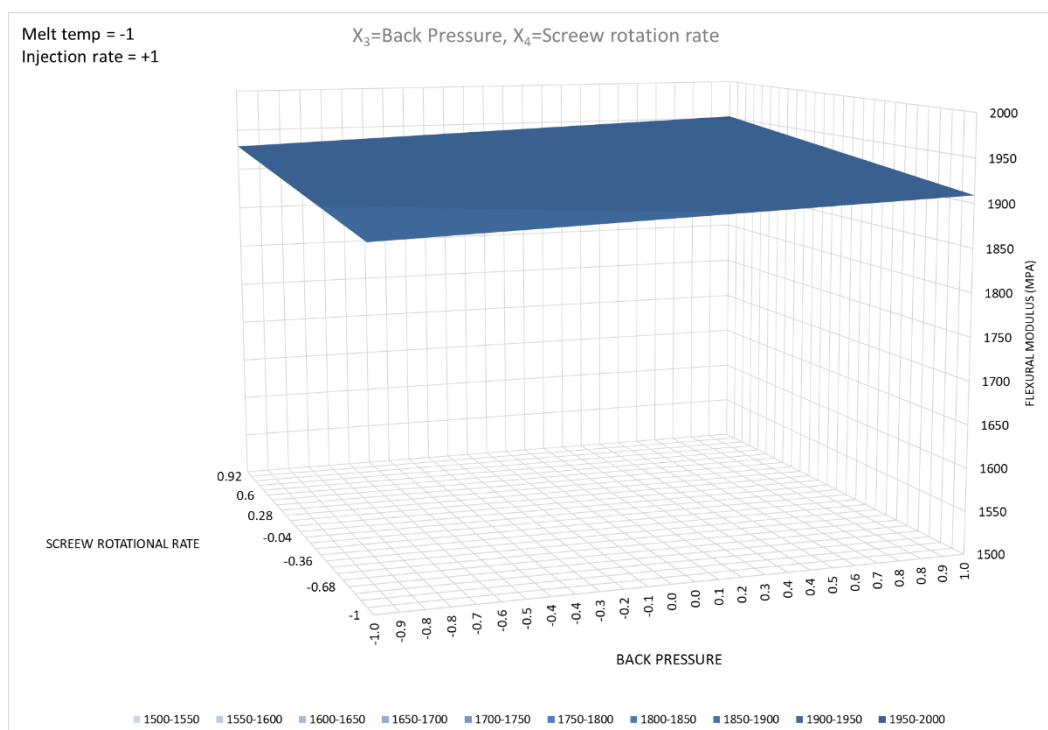


Figure 38. Surface response 12. Fixed parameters: Injection rate and melt temperature. Variable parameters: back pressure and screw rotational rate.

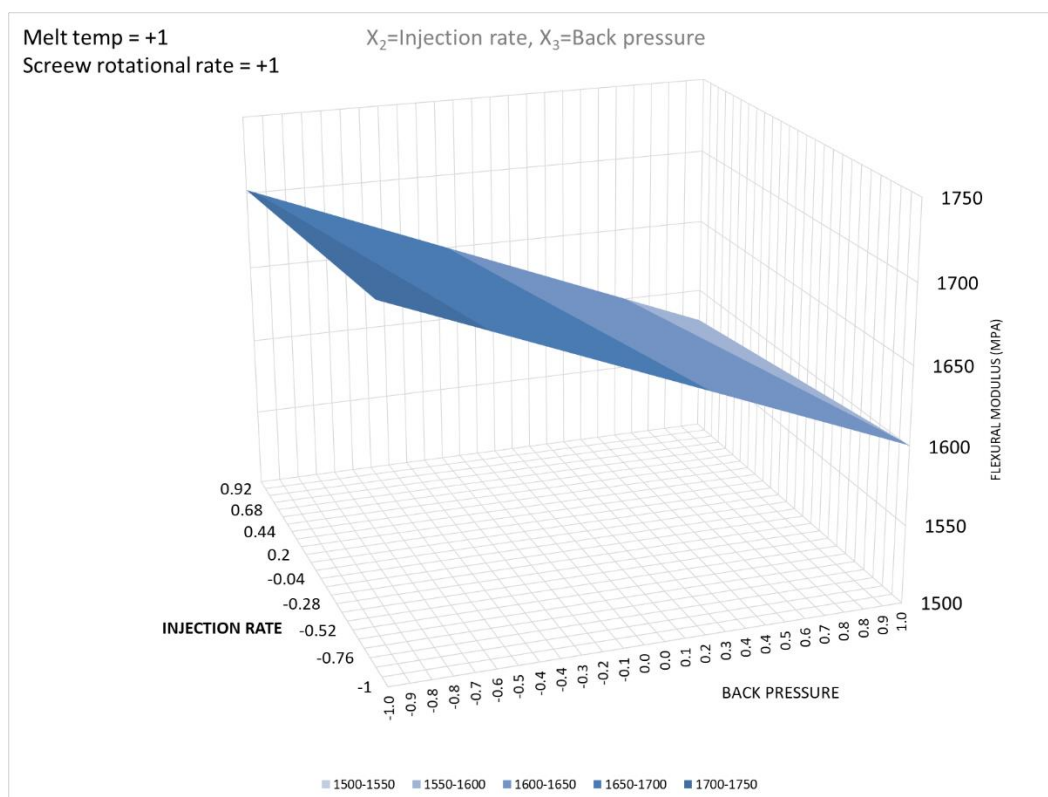


Figure 39. Surface response 13. Fixed parameters: Screw rotational rate and melt temperature. Variable parameters: injection rate and back pressure.

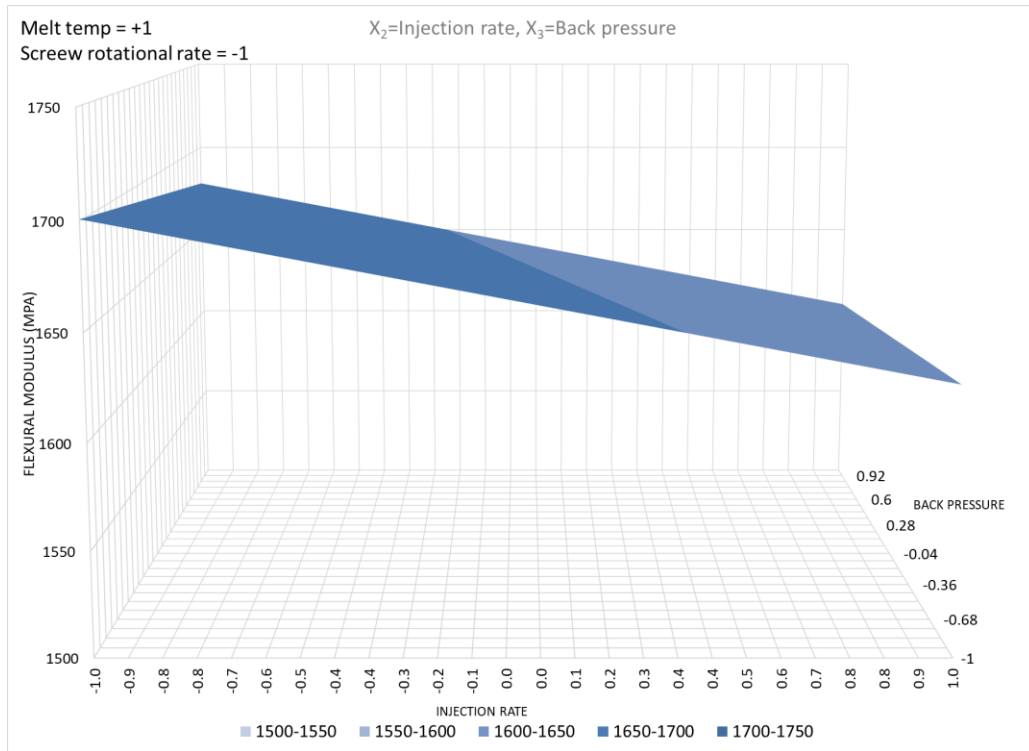


Figure 40. Surface response 14. Fixed parameters: Screw rotational rate and melt temperature. Variable parameters: injection rate and back pressure.

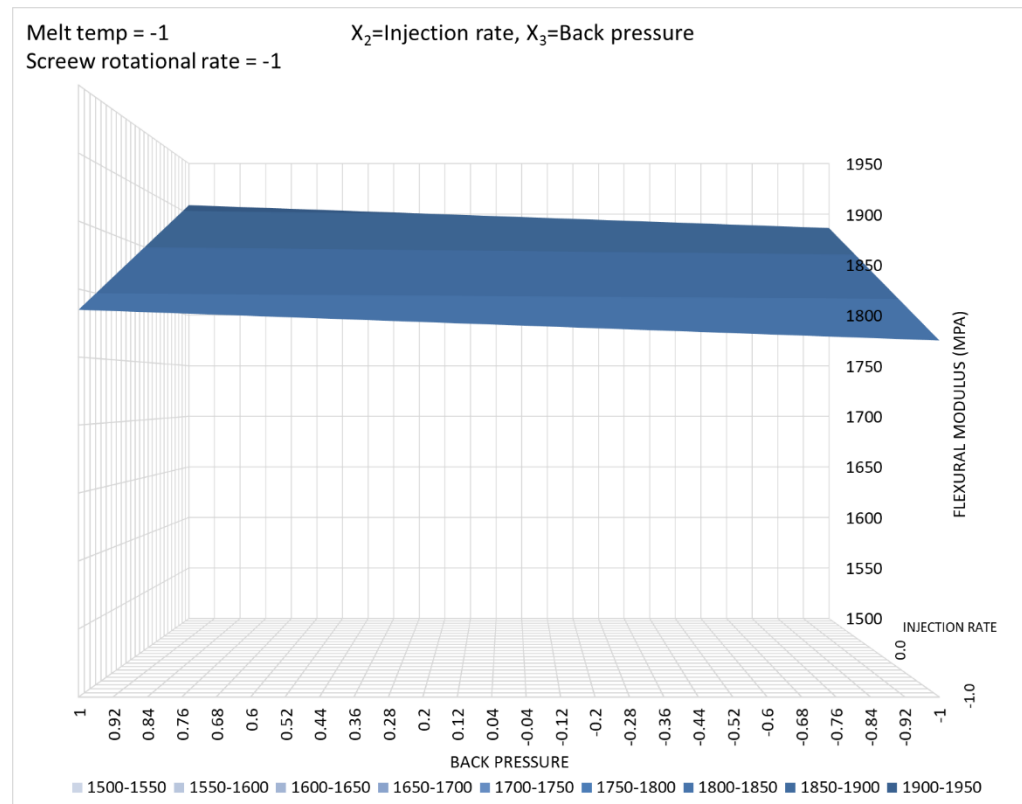


Figure 41. Surface response 15. Fixed parameters: Screw rotational rate and melt temperature. Variable parameters: injection rate and back pressure

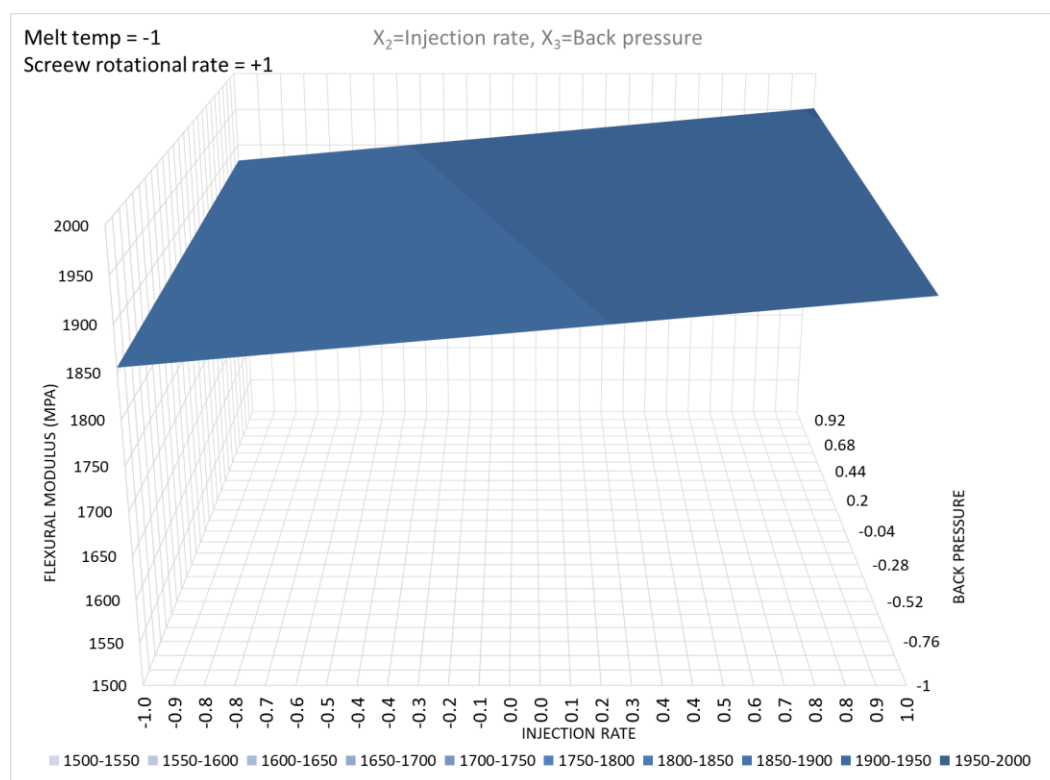


Figure 42. Surface response 16. Fixed parameters: Screw rotational rate and melt temperature. Variable parameters: injection rate and back pressure.