AINARA AGUIRRE MIQUELARENA

Grafted ABS coagulation effect on surface quality material

Chemistry Degree Thesis

Supervised by Dr.**Ramón Malet**, Company's Tutor

Research and Development Department at Elix Polymers, S.A.

Supervised by Dr.**Antoni Rodríguez**, University Tutor

Rovira I Virgili University

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Abbreviations & Acronyms

ABS	Acrylonitrile-Butadiene-Styrene Polymer
ACN	Acrylonitrile Monomer
AcOH	Acetic Acid
B1 / B4	Grafted Polybutadiene latexes
Dresinate	Emulsifier
EBS	Synthetic wax
FT-IR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
Irganox	Phenolic Primary Antioxidant Stabilizer
$K_2S_2O_8$	Potassium Persulphate Initiator
M 1000	Silicone oil
$MgSO_4$	Magnesium Sulphate
MVR	Melt Volume-flow Rate
Novotex	Grafted Polybutadiene latex mix (B1 + B4)
OCS	Optical Control System
PB	Polybutadiene Monomer
SAN M60	SAN Copolymer
SAN	Styrene-Acrylonitrile Copolymer
S-SAN	SAN copolymer + Irganox Stabilizer
t-DDM	Chain Transfer Agent
VCH	Vinyl Cyclohexene
λ	Wavelength
Ø	Diameter
%	Percentage
Kg	Kilograms
mm	Millimetres
nm	Nanometres

1. ABSTRACT

Thermoplastics based on acrylonitrile-butadiene-styrene (ABS) are widely used due to their good mechanical and surface quality. In order to determinate these parameters, grafted ABS has been produced through an emulsion polymerization process.

The present investigation reviews the emulsion polymerization of grafted polybutadiene in presence of styrene-acrylonitrile (SAN) copolymer followed by a coagulation method in order to obtain the ABS powder, which later is compounded and injected to final material characterization. Two coagulation methods have been carried out to determinate if some consequences could appear on the results.

Processed ABS characterization was done; mainly mechanical analysis has been carried out such as toughness and tensile test, viscosity, yellowness index, gloss and optical control system analysis, among others. The resulting values have been observed and compared with a previous investigation mentioned in section 2.3.

In conclusion, final surface quality material improvement is very important in ABS final products due to their various applications as for example in plating for automotive.

RESUMEN

Los termoplásticos basados en acrilonitrilo-butadiene-estireno (ABS) son ampliamente utilizados tanto por su buena calidad superficial como por sus buenas propiedades mecánicas. Para determinar los parámetros mencionados anteriormente, se ha producido un ABS injertado a través de un proceso de polimerización en emulsión.

La presente investigación revisa la polimerización en emulsión del polibutadieno injertado en presencia del copolímero de estireno-acrilonitrilo (SAN), seguido de un método de coagulación para obtener el polvo de ABS que más tarde se utilizará para llevar a cabo el proceso de “compounding” e inyección para la caracterización final del material. Se han realizado dos métodos de coagulación para determinar si existen diferencias en los resultados finales.

Se realizó la caracterización del ABS procesado, donde principalmente se han llevado a cabo análisis mecánicos como la prueba de tenacidad y tracción, viscosidad, índex de amarillez del material, brillo y análisis del sistema de control óptico, entre otros. Los valores resultantes han sido observados y comparados con una investigación previa mencionada en la sección 2.3.

En conclusión, la mejora final de la calidad superficial del material es muy importante en los productos finales de ABS debido a sus diversas aplicaciones como por ejemplo en el chapado para automóviles.

2. INTRODUCTION

2.1. Company's introduction

This project has been developed at Elix Polymers, S.L. It is located at the southern petrochemical park of Tarragona. Thermoplastics based on ABS (Acrylonitrile Butadiene Styrene) and SAN (Styrene Acrylonitrile) are produced with a production capacity of 24.014 tones/ year and more than 100.000 tones/year respectively.

40 years ago the plant of Tarragona started with the production. Originally, belonged to Bayer Group but several changes were made until finally becomes an independent company named Elix Polymers. With continuous improvement and innovation, has become one of the leading manufacturers of ABS resins and derivatives in Europe, the third one to be exact.

Nowadays, they are specialists in providing tailor-made solutions for high-quality thermoplastics applications. Before analysing the behaviours and preferences of the clients, they implemented processes as ISO 9001 or ISO 14001. In addition, are involved in a Sustainability Program of energy reduction based on energy management, waste and scrap avoidance ISO 50001.

2.2. ABS Thermoplastic

2.2.1. Historical aspects

The origins of ABS Plastic are found in the mid-1940s. Acrylonitrile-styrene copolymer was used since 1940 and its drawbacks led incorporation of the new tri-polymer ABS due to the high strength and impact resistance that butadiene imparted.

High molecular ABS and respective copolymers were used to produce bulletproof polymer sheets during World War II, because the low thermoplastic flow properties give large impact strength. [1]

ABS was patented in 1948 [2] and injection moulding development and graft polymerization gave way to ABS applications revolution. Emulsion process for making ABS has also been commercially practiced since 1950. Plastic ABS starts to be used in 1950 for application in textiles, toys and domestic appliances and was introduced to commercial market by the Borg-Warner Corporation in 1954 [2] [1]

Last advances were made in 1993 with various 3D printers' post led to the increased use of ABS. open source 3D printers capable of printing the majority of its own replicate parts, were introduced in the market in 2008. [1]

2.2.2. Properties & Characteristics

Acrylonitrile butadiene styrene or "ABS" is composed by those three monomers as shown in Figure 1, where each one provides different properties to the final polymer. Firstly, the acrylonitrile provides heat resistance, chemical and mechanical resistance as for example hardness. Secondly, the butadiene gives toughness in a wide range of temperatures because it is an elastomer. Finally, styrene monomer has acrylonitrile similar mechanical property, such as rigidity, in addition to an easy processability and shiny surface. Thus, ABS can be used in a temperature range between -20ºC and 80ªC, having into account that mechanical properties change with the temperature.

Large variations in term of compositions and process to have differences and to achieve the best balance of properties of ABS from the combined product can be made. For example, flame retardant, high heat resistance, chemical resistance, extrusion, transparent and plating moulding, high or low impact resistance, viscosity, glossy surface, among others. In conclusion, customer is able to choose from a wide range of properties to required application.

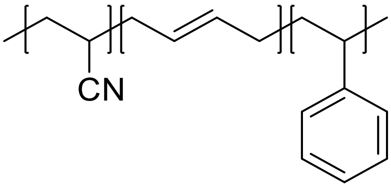


Figure 1.ABS polymer structure

2.2.3. Application & Consumption

The large diversity of end uses makes ABS one of the most successful thermoplastics in terms of properties and price, due to obtaining of the high performance engineering plastics and the lowest price of basic product. It has a wide variety of applications, such as automotive, healthcare, appliances, electrical & electronic, consumer goods, building & construction, toys, sport and leisure, as shown in Figure 2.

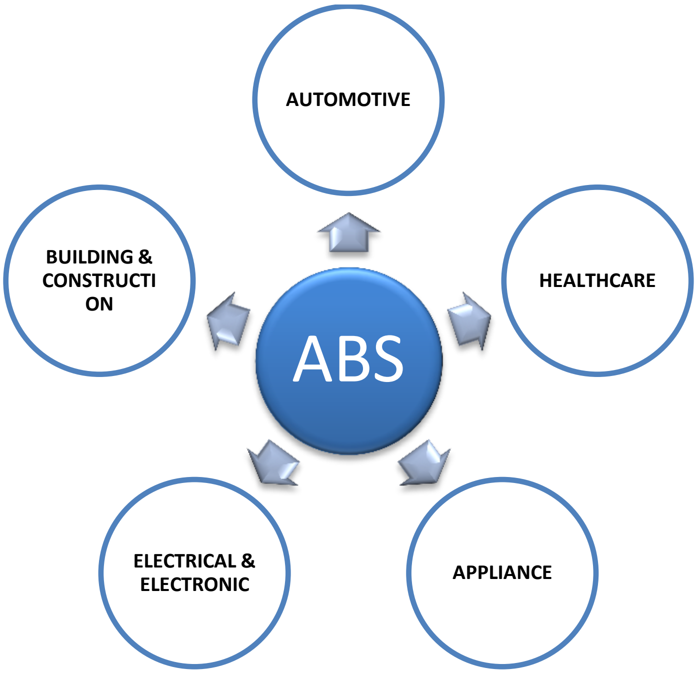


Figure 2.Different ABS applications

The principal applications and relative consumption are listed in Table 1. We can observe that appliance and automotive are predominantly the most used ones. The third most widely used application on different industrial sectors are machines and electronic and electrical products, such as computers, discs, telephones which used properties like the high gloss and impact resistance. Those three are followed by, pipes & fittings market, recreational uses and packaging. [3]

Table 1.Consumption of ABS in different applications

	ABS CONSUMED (%)
Appliance	29.4
Automotive	22.3
Business machine	13.6
Pipes and fitting	7.4
Recreational uses	3.9
Packaging	0.2
Others	23.2

Following pie chart shows global ABS consumption in 2016. China has the first position with more than 50% of consumption, followed by Europe and Southeast Asia with around 9-10%. Next, USA, South Korea and Japan with a little bit lower consumption along with other locations. [3]

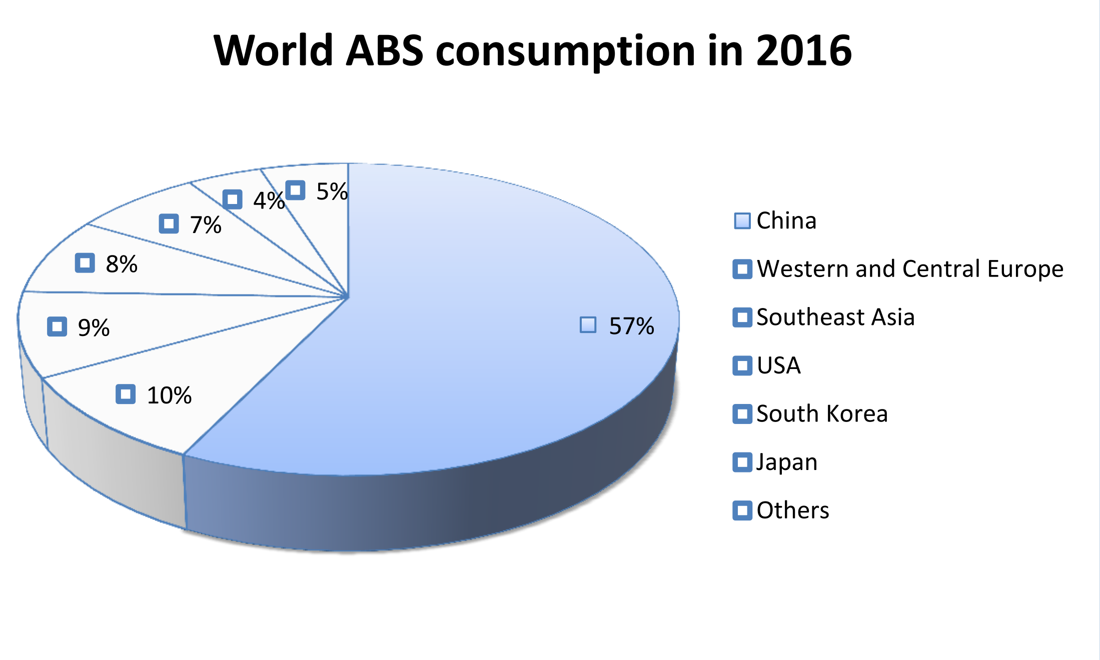


Figure 3.World ABS consumption

ABS is considering an engineering plastic, which has higher performance than standard materials, making it ideal for engineering applications. ABS together with other thermoplastics have been replacing traditional engineering materials such as wood or metal due to its easy manufacture as well as because they equal or exceed them in their weight/strength ratio and in other properties. [4]

2.3. Reason for the Study

Nowadays, almost all companies are using intellectual properties (IP), that is, businesses need the intellectual property system to protect manufacturing secrets or other useful information. Main types of intellectual properties are protected in law for example by patents, copyright and trademarks, which enable people to earn recognition or financial benefit from what they invent or create. This system is the primary key to successful management of business knowledge.

A patent application has been recently published [5] and this present invention relates to thermoplastic compounds containing at least two graft rubbers, which are processed by co-precipitation of the respective mixture of emulsions. More specifically, this patent protects a step of the polymerization process in ELIX polymers together with the respective products obtained, taking into account all raw materials, reagents, additives and their characteristics.

For a freedom to continue operating is necessary to check whether Elix manufacturing process, including testing or commercialising a product, can be done without infringing valid intellectual property rights of others, so further Elix internal studies are needed.

3. OBJECTIVES

The main aim of this degree final project is to study the influence of Grafted ABS latexes coagulation method on plastic surface quality.

Two coagulation methods will be carried out using different Elix raw materials to determinate if differences are observed in the results. In addition, some chemical analysis and different mechanical parameters will be determined, such as toughness, MVR, hardness, vicat softening temperature and finally material surface quality, all taking into account the processing conditions, repeatability, and deviation of the results.

Design of experiments will be based on a previous investigation [5] in order to be compared and observe the similitude or differences that are found.

4. FUNDAMENTALS

4.1. Polymer ABS

4.1.1. ABS preparation

As it mentioned above, ABS is composed of acrylonitrile, styrene and butadiene, where acrylonitrile is mainly produced from reaction between propylene and ammoniac [6]. Over 95% of butadiene is obtained as a by-product of ethylene production from steam crackers [7] and finally more than 90% of styrene is made by dehydrogenation of ethyl benzene [8].

After that, polymerization of styrene and acrylonitrile in presence of polybutadiene is made. More than one polymerization methods are used for ABS preparation, but the most common polymerization methods are emulsion, mass or bulk and suspension. In the two first processes, the heterogeneous medium where happens the reaction is the main similarity. These processes are usually two-phase system where the resulting polymer appears like a fine dispersion on immiscible liquid. Whereas, bulk polymerization is a simple and homogeneous process [9].

4.1.1.1. Emulsion polymerization

Emulsion polymerization was developed in industrial laboratories around 1920, for the production of synthetic rubber latexes as an alternative to the use of natural rubber latexes. Latexes are often added to commercial products with the aim of obtaining specific characteristics, including durability, chemical resistance and dimensional stability. They are also known as emulsion polymers, dispersion polymer or colloidal polymers [10].

On the one hand, it is a unique chemical process used to produce colloidal waterborne resins. It is a free radical polymerization process that involves relatively hydrophobic monomer emulsification in water using an emulsifier, followed by the initiation, propagation and termination reaction [11].

On the other hand, it is a complex process since it takes place in a heterogeneous system wherein stabilized monomer particles are dispersed in an aqueous medium as shown in the following Figure 4. In the first step, free radical initiator is added for monomer to polymer conversion with the application of heat so is carried out correctly. Free radicals initiate polymerisation by reaction with a proximate monomer, this way a new polymer chain is created. Initiator molecules constantly decomposed to form radicals, thus, new polymer chain are also constantly formed. During propagation, monomers come in contact with each other forming dimers containing active and end groups and dimers react with monomers the same way to become oligomers. In the final step, free radical end group is desactivated becoming a termination event. In addition, it happens by combination or disproportion [10]. A large oil-water interfacial area is generated as the particle nuclei form, to which an effective stabilizer such as ionic or non-ionic surfactants is added to prevent the latex particle coagulation. Is either a complex process, because nucleation, growth and stabilization of polymer particles are controlled by the radical polymerization mechanism.

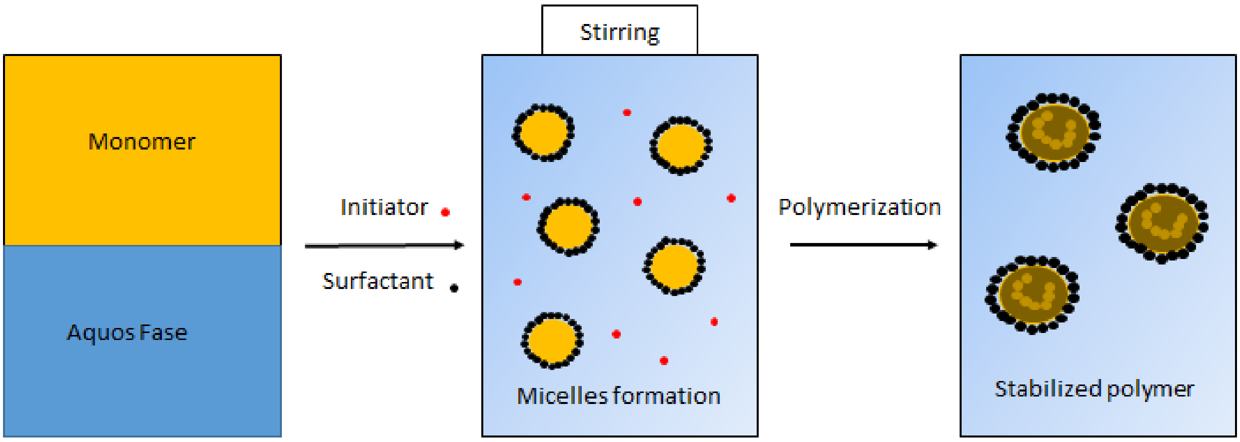


Figure 4.Basic mechanism of Emulsion Polymerization

Although, monomer to polymer conversion is high, the resulting latex has a low viscosity and lattices of high and low molecular weight can be produced. Advantages are the capability of producing higher rubber contents in a faster polymerization rate, comparing with bulk or solution polymerization. Moreover, tailor-made products may be made and probability of having free radicals bimolecular termination can be reduced. However, necessary amount of energy used is higher because of the polymer recovery area.

In the ABS emulsion manufacturing process, firstly, the rubber composed by polybutadiene is made using an emulsion process. Secondly, styrene and acrylonitrile are grafted onto the rubber also by emulsion polymerization. Finally, the grafted ABS polymer can be recovered by precipitation and compounded into a final product.

4.1.1.1.1. Polybutadiene rubber obtaining

Polybutadiene is a synthetic rubber which has a high wear resistance and is used specially on tires manufacturing. It is also used as an additive to improve plastic toughness, such as polystyrene or ABS. So, for ABS emulsion polymerization, the polybutadiene (PB) is prepared first, usually in a batch or semi-batch reactor.

- Batch reactor is a discontinued stirred reactor that corresponds to a closed thermodynamic system as shown in Figure 5; therefore, nothing is put in or taken out until the reaction is done. Advantages are high monomer to polymer conversion, flexibility of operation since one reactor can produce a product one time and a different one next time, in addition to easy cleaning. On the other hand, disadvantages are a high operating cost and final product quality variability. [12] [13]

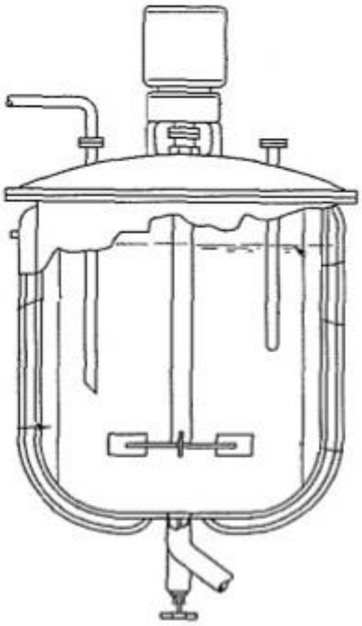


Figure 5.Batch Reactor

- If some of the reactants are added to the reactor while the reaction is occurring as is observed in the following Figure 6, Semi-Batch operation is carrying out. Reactant may be added discontinuously or continuously and the reaction can be single-phase or multi-phase. As in a batch reactor, unstable operation is occurred, although in a more complex way. In comparison with a batch reactor, variable volume reactor use can improve product yield in exothermic processes. Moreover, reactant concentration can be kept relatively low or high, depending on the desired final product, thus product yields may improve. [14]

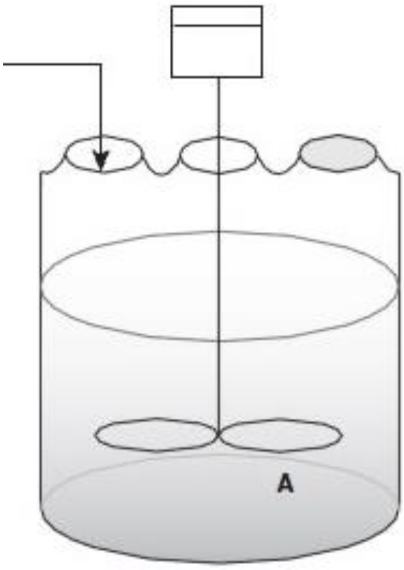


Figure 6.Semi-Batch Reactor

In industry, discontinuous reactors are well suited for the production of valuable products through complex reactions by controlling the temperature, in addition for toxic or hazardous compound processes.

Polybutadiene polymerization results in polymerization 1,4 and 1,2 with double bonds in cis and trans position and with pendant vinyl groups, respectively. Production of these three types depends more upon on the temperature than on concentration of PB. Crosslink density and latex particle size can be controlled by the addition of chain transfer agents and the concentration and type of initiator used. Therefore, the optimum particle size and distribution desired depends on the final application of the ABS.

Tailor-made production is one of the main advantages of emulsion polymerization that's why seed latexes are often used to prepare multiple batches of products with a tightly controlled particle. During seed emulsion polymerization, a batch of seed latex is swollen with monomer, followed by polymerization and finally grown until desired size. Since no new particles are formed during polymerization, the final number will be the original one. The particles produced by seeded polymerization are uniform in distribution. [10]

4.1.1.1.2. SAN Copolymer production

Styrene-acrylonitrile copolymer observed in Figure 7 is a rigid, transparent plastic, result of styrene and acrylonitrile copolymerization. The rigidity of polystyrene together with the hardness, heat and chemical resistance of polyacrylonitrile are combined in order to obtain specific properties to be used in automotive parts, kitchenware, appliances and furniture, among others. [15]

These two compounds are mixed and prepared by radical bulk polymerization process or in a heterogeneous system such as emulsion polymerization. Is good to know that in a radical copolymerization, original styrene-acrylonitrile proportions can differ, therefore, polymer composition is modified. Nevertheless, an azeotropic composition exists in a little range where composition no differs throughout the polymerization, so in that range composition can be controlled. [16]

- Emulsion polymerization process is used to yield well-defined latex particles with controllable high molecular weights, but nowadays is little used due to high wasted material and low efficiency. [17]

- Bulk polymerization is the main used process because of the high efficiency and because no waste is produced throughout reaction. Styrene and acrylonitrile monomers are introduced into reactor, solvent and radical initiator can be added, but reaction can also be initiated thermally. Reaction temperature ranges from 70ºC to 120ºC and with constant stirring. Once high conversion has been obtained, mixture is distilled to carry out monomer and solvent extraction for reuse them.

Styrene-acrylonitrile ratio is approximately 70:30 (%). Resulting material has better heat and chemical resistance than does polystyrene or acrylonitrile alone, but it is important to know that molecular weight and viscosity has to be controlled since their ease manufacturing depends on it. [15]

As said above, SAN Copolymer has a wide range of application and one of them is to improve Graft ABS processability and properties. Therefore, once SAN Copolymer has been produced, it is extruded in order to obtain final SAN product in a pellet form or can also be mixed with Graft ABS and be extruded later.

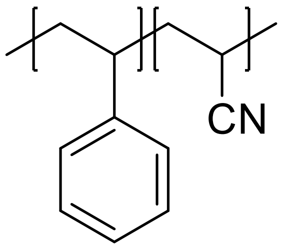


Figure 7.SAN Copolymer structure

4.1.1.1.3. Grafted PB Emulsion Polymerization in presence of SAN Copolymer

Grafting of styrene and acrylonitrile into polybutadiene rubber is the essence of ABS process. Once PB particle size has been achieved, styrene and acrylonitrile monomers (SAN) are polymerised in its presence. It is also an emulsion polymerization process where radical initiator is added followed by styrene and acrylonitrile monomers in order to obtain grafted SAN chains inside the polybutadiene as shown in Figure 8.

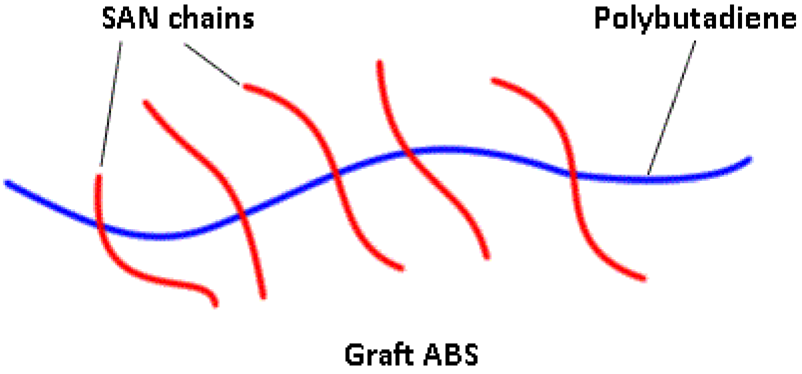


Figure 8.Grafted ABS polymer

The way in which reactants are added to the reactor can have a large influence on the polymer structure and morphology. Rubber contents may range from 5-70% and the amount of SAN, particle morphology and the molecular weight of the SAN depend on many variables such as initiator type and concentration, chain transfer, temperature, etc.

Emulsion process can be carried out in a batch, semi-batch or continuous but in this case, semi-batch process is used. Controlling the amount of initiator, monomer, surfactant and emulsifier provides control over polymerization, temperature, polymer structure and morphology. In conclusion, semi-batch polymerization is useful for addition of functional monomer to graft polymerization.

4.1.1.1.4. Isolated ABS product

In order to obtain grafted ABS powder, the latex must be precipitated usually by the addition of a metal salt or surfactant. Chemical precipitation is always followed by solid separation that may include coagulation/sedimentation, filtration and finally dry process is carried out to obtain the final product.

4.1.1.1.4.1. Precipitation or Coagulation Method

Dried polymers prepared by emulsion polymerization have many uses due to their properties. All of these emulsion polymers must be converted from water stable emulsion to dried polymer before use. [18]

Destabilization of micelles containing polymer inside must be caused in order to obtain latex coagulation. Several techniques such as evaporative coagulation, extruder coagulation or chemical coagulation among others have been developed to destabilize polymeric emulsion and cause desired coagulation.

- Evaporative Coagulation: coagulation by evaporating water using spray drying technique is sometimes used for certain applications. This method eliminates the option of having contaminated water. However, amount of energy used for evaporation is high and all surfactant remains with polymer, in consequence aging is usually accelerated. [18]
- Extruder coagulation: a technique for combining extruder shear field and melt zone high temperature has been developed to coagulate the latex, as well as a process to remove water from already coagulated latex. This operation is carried out along with compounding process which may involve pigments and other additives addition [18].
- Chemical coagulation: ABS particles are recovered from colloidal latex prepared by emulsion polymerization and most common technique for carrying out coagulation is the additions of chemicals. Colloidal particle surface is negatively charged, so adding an emulsifier the latex forms a stable colloidal solution by electrostatic repulsion between particles. Polymer particles begin to coagulate with help of an acid, which will weaken the repulsive forces. In order to obtain final product, coagulated solution is dried and filtered. Usually, this process is so effective that filtrated water is crystal clear avoiding the problem of white water [19]. However, addition of chemicals has the usual problem of producing pollution waste as well as an amount of fine particles may be lost in the recovering process.

4.1.1.1.5. Grafted ABS

The ABS graft obtained has a high impact resistance due to the high rubber content but it may be sold with many different rubber or acrylonitrile levels, in addition to different morphologies and melt viscosity. For this, different material combinations can be used with the aim of obtaining different properties. For example, ABS plus SAN is one of the main combinations used, since, function of grafted SAN chains into polybutadiene nuclei are to improve compatibility with SAN copolymer matrix in order to provide better procesability. Another option could be two different ABS emulsion combination in order to obtain two different rubber particles, among others. All these combinations were processed by the best methods and condition for compounding and moulding.

4.1.2. ABS Processing

Processing of polymers is essential to make them into utility materials, for example incorporation of different additives to ease their processing and to improve properties. Challenge is to design processing optimum methodology, which should be economical and environmentally not toxic. For this reason, additives and additional copolymers selection always requires a complex and careful work due to high diversity of polymers physical and chemical properties [20].

Conversion of raw polymers into end products requires different steps:

- Firstly, after heating polymer, additives and other additional components, all are mixed to achieve the required homogenization and properties improvement. This part of the process is called compounding.

- Secondly, desired form has to be created and there are lot of different methods to achieve it, such as extrusion, injection moulding, compression moulding, among others. Process selection depends on many factors, such as quantity and production rate, dimensional accuracy and surface finish, material nature and final product size, etc.
- Finally, finished material is cooled so that obtains and preserves the desire form.

At Elix polymers, in addition to grafted ABS production, part of processing more specifically the compounding, is also carried out to obtain ABS material as a pellet form, that is, final ABS material with improve properties prepared for final customers processing. In order to this, prepared graft ABS, SAN Copolymer and additional additives were mixed up.

4.1.2.1. Compounding

Term compounding describes various chemicals addition to raw polymer to give product desirables properties, so characteristics are improved. Modern compounding methods and machines for rubber and plastics started to create and be marketed at 1916. They have been many advances in rotor design, drive system and temperature control, as well as on mixer performance. [20]

Mixing should be optimized taking into account parameters like time, temperature, energy. Optimum compound viscosity for easy processing should also be achieved, as well as distribution and dispersion of all materials. [20]

In this experiment, a single extruder will be used to obtain ABS + SAN copolymer compounding.

4.1.2.1.1. Extruder

Extruder is the machines used to carry out extrusion method processing. **Extrusion** is one of the most important continuous methods in polymer processing, therefore, many thermoplastics are converted into useful products by extrusion than by any other methods. Machine can also be used to make compounding, so it is appropriate to distinguish between compounding extrusion and forming extrusion [20]. There are three basic functions that an extruder must perform:

- Melting, pumping and forming
- Devolatilizing and mixing
- Conducting chemical reaction

Therefore, different materials are introduced in extruder through hopper (Figure 9 → 1). They are melted, homogenized or reacted by heaters (Figure 9 → 2) and screw (Figure 9 → 3) respectively, as they advance along the extruder. Finally, are volatilized and transported to the end part called die (Figure 9 → 5), where material is cooled using cooling fans (Figure 9 → 4).

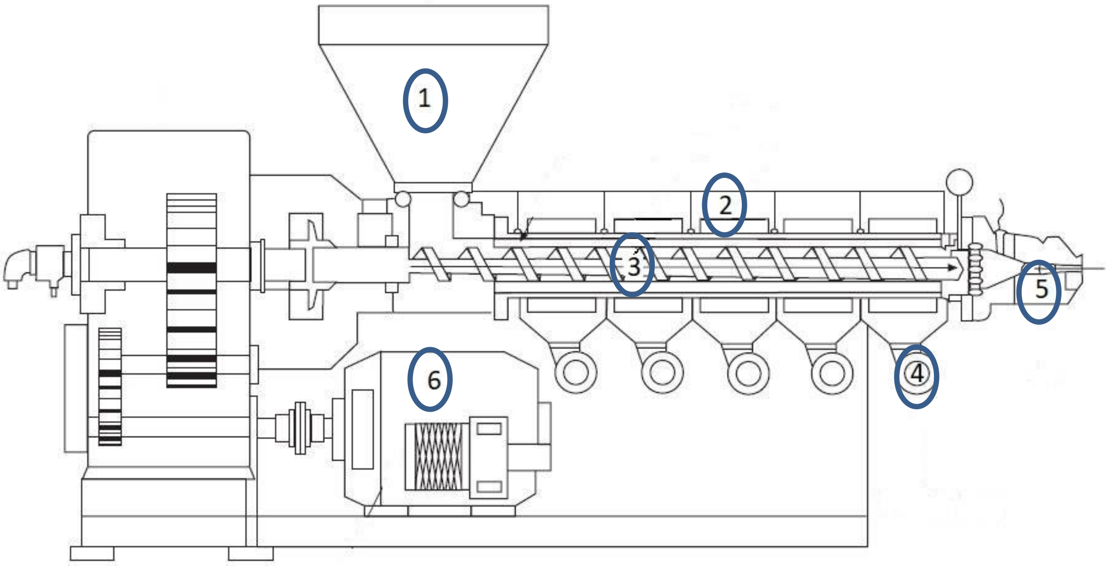


Figure 9.Simple extruder structure & principal components

Screw is rotated at a predetermined speed with electric motor (Figure 9 → 6) and temperature is controlled by connecting heating and cooling elements on the motor to maintain set-point temperature [21]. When aim is to produce pelleted material, screw is conducted at a higher speed than when finished product is manufacturing [20].

Respective mix can be compounded at temperatures between 180-280ºC due to the high flow nature of ABS. Usually heat stabilizers, hydrolysis stabilizers, lubricants and flame retardant additives are being used together with different pigments in order to have amount tailor-made options for customers.

4.1.2.2. Polymer Manufacturing Processes

Different raw polymers are given shape and method selection depends on polymer nature. On the one hand, **thermoplastics** usually starts as regular pellets or granules that can be melted again, therefore, can be recycled. For processing, they have to be above Tg and pressure has to be maintained while shape is cooling below Tg. On the other hand, **thermosetting** materials starts as liquids called resins which need heat for shaping. Usually when working with thermosetting, shaping process involves a chemical reaction, such as crosslinking which may be exothermic and in this case cooling is always required. The main amounts of produced polymers are thermoplastics, more specifically 90% and remaining 10% thermosetting.

Most frequently processing methods are injection moulding, compression moulding, rotational moulding, blow moulding and the one said above, extrusion.

4.1.2.2.1. Injection moulding

Injection moulding is major net shape process for thermoplastic polymers and can be used to make customers end product shapes or also to produce specimens for final product characterization. Is one of the greatly preferred process in industry because it can produce complex-shape products, having good dimensional accuracy in a short cycle time. [22]

It is very similar to extrusion method but it is a discontinuous process composed by an injection system and a clamping system as shown in Figure 10. Firstly, polymer is introduced through the hopper and is heated in a previous camera usually at 250ºC. Once it is melted, using a plunger that works with hydraulic pressure the material is introduced to the mould. Finally, once plastic is cold mould is opened and piece is removed in order to repeat process again. Final piece may be obtained in different forms depending on used mould. [23]

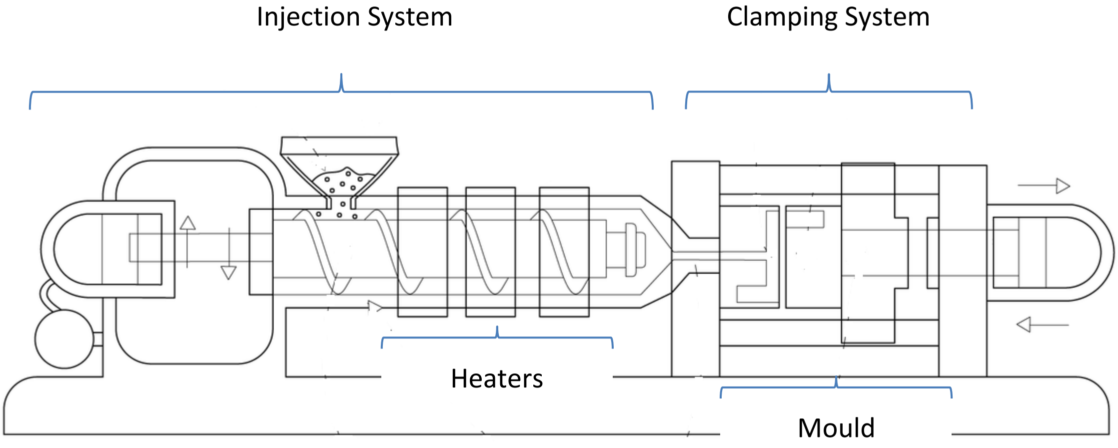


Figure 10.Different Injection moulding parts

4.1.2.3. Plating of ABS plastics

ABS polymer has a wide variety of application such as healthcare appliances, electronics, building, construction and one of the most important, automotive. This industry is looking for raw materials with good mechanical properties, similar appearance to metals and with weight little to produce effective and economical shapes. To carry out this, is needed a thermoplastic with easy processability and good response to plating process which will give the material all these needed conditions. [1]

Plastic substances are usually plated in order to bring metal properties to polymer structure. They enhance parameters such as strength, structural integrity, corrosion and thermal resistance as well as durability. Reason why ABS is described as the most suitable candidate for plating process is that it has uniform distribution of butadiene over acrylonitrile-styrene matrix, qualifying for metal best adhesion to the substrate, that is, it makes possible to deposit an adherent metal coating through chemical pre-treatment process without using mechanical abrasion. [1]

Plating process can be divided in two important parts composed by 5 sub-processes as shown in Figure 11.

- Surface preparation involves four chemical processes. Firstly, etching is done with oxidant solution composed by chromium trioxide (CrO_3) and sulphuric acid (H_2SO_4) at high temperatures, around 65-75ºC. ABS thermoplastics surface area is composed by PB matrix and it has to be etched to create micro-pores from which substrate and metal will linked. Secondly, outcome of etchant excess is carried out by a redox reaction. Material is put in a sodium bisulphate ($NaHSO_4$) solution to neutralize and remove oxidant excess. Next step is activation, where precious metal such as palladium (Pd), platinum (Pt) or gold (Au) plus stannous chloride/hydrochloric ($SnCl_2$ / HCl) solution is used to produce catalytic surface required for effective plating. Finally, accelerator step is done to eliminate excess of stannous hydroxide [$Sn(OH)_2$] maintaining palladium sites intact for electroless plating [1].

- Metal plating involves three processes. On the one hand, electroless plating composition is carried out and it includes a metal salt complexion agent, which acts as a reducer, a stabilizer and a buffer system. Activated part is put in the solution and acceleration process is done in order to prepare the material for electroless plating.
  On the other hand, after electroless plating, electrolytic plating of copper acid is done to give a bright conductive surface and to act as a buffer layer between base material and final metal plate, as well as provide final plate stability. Next, electrolytic nickel plating is done for avoid corrosion and abrasion. In order to do this, it sets up a barrier between copper deposit and exterior corrosion. Final coated part may be done using chrome, gold, silver, etc [1].

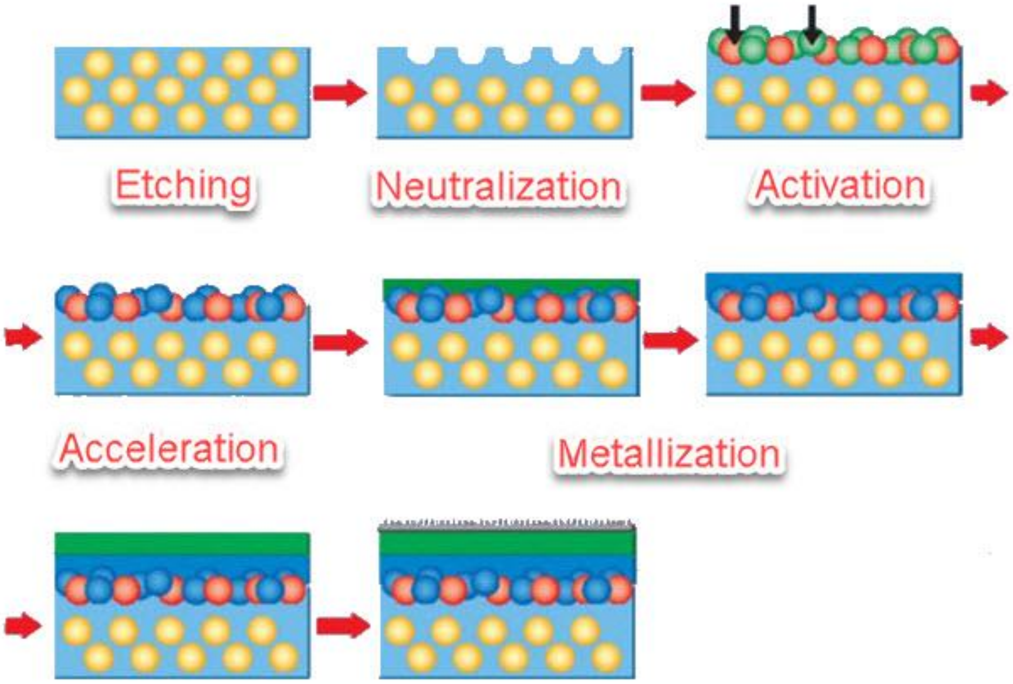


Figure 11.Plating process steps

In conclusion, final surface quality material improvement is very important in ABS metal process due to is necessary to perform the plating process correctly. Cleaning mechanism is also applied as well as acid dip and pickling steps since parts to be plated cannot be introduced into an electroplating solution without pretreatment [24].

5. RESULTS AND DISCUSSION

As mentioned above, the main objective of this project was to determinate different mechanical properties and surface quality of precipitated ABS materials in order to compare them with previous investigations results and be able to confirm if Elix Polymers Company could claim similar results and conclusions.

Five different tests have been carried out, as described in Table 17 of section 7.2. First, Test 1 was performed with a co-precipitated mixture of B1+B4 containing 29,3 % of ABS and 68,3% of SAN copolymer. Second, Test 2 was performed with B1 and B4 separately precipitated which also contains 29,3 % of ABS and 68,3 % of SAN copolymer. Third, Test 3 was again done with a co-precipitated mixture of B1+B4, but containing 39 % of ABS and 58,6 % of SAN copolymer. Next, Test 4 was performed with B1 and B4 separately precipitated containing 39% of ABS and 58,6 % of SAN copolymer. Finally, Test 5 was performed with the same proportions as Test 3 and 4 being sample blank to compare the differences between precipitated powder in the laboratory and precipitated powder in the chemical plant.

5.1. Patent results

The mechanical properties results of previous investigation are shown in the following Table 2.

Table 2.Mechanical properties results of the patent

MECHANICAL PROPERTIES	UNITS	TEST 1	TEST 2	TEST 3	TEST 4
Toughness (Notched)	KJ / m^2	13.8	12.5	22.3	19.8
Toughness (Unnotched)	KJ / m^2	43.9	37.0	97.1	45.0
MVR (220ºC/10 Kg)	mL / 10 min	40.2	38.4	25.8	26.9
Young Modulus (E)	MPa	2478	2481	2138	2148
Tensile Strength (σ_M)	MPa	46.7	46.7	41.5	41.8
Tensile Strength at break (σ_B)	MPa	44.2	42.6	32.9	35.6
Gloss 20°		96.2	96.9	95.7	95.6
Yellowness Index		33.1	33.4	32.2	34.2
OCS < 250 µm	[1 / m^2]	112	154	94	120
OCS 250 – 400 µm	[1 / m^2]	67	105	71	113
OCS < 400 µm	[1 / m^2]	34	42	43	70

5.2. Summary of ABS Compounding Results

The mechanical properties results of realized investigation are shown in the following Table 3. Before comparing the new results with those of the patent, a sample blank (Test 5) has been made to determinate if there may be differences when precipitation process is carried out in the laboratory or in chemical plant. The sample blank is going to be compare with Test 3 and 4 since they have same precipitated latex concentration. In general aspects, there are not significant differences between the two processes in almost all the properties, except in OCS values that are commented in section 5.3.6. Moreover, in properties such as Notched Toughness, Breakdown Tensile, VICAT and Yellowness Index the values are very similar.

However, viscosity varies a little to the powder precipitated at the chemical plant as well as the gloss and Hardness.

Table 3.Mechanical properties results of the New Research referenced in section 7.2 in the Table 17.

MECHANICAL PROPERTIES	UNITS	TEST 1	TEST 2	TEST 3	TEST 4	TEST 5
Toughness (Notched)	KJ / m^2	15.2 ± 0.1	16.6 ± 1.0	21.3 ± 0.2	23.9 ± 0.4	22.8 ± 0.3
Toughness (Unnotched)	KJ / m^2	74.9 ± 11.1	73.2 ± 15.7	111.5 ± 30.8	121.2 ± 18.7	123.2 ± 20.1
MVR (220ºC/10 Kg)	mL/10 min	37.6 ± 0.2	36.3 ± 0.0	27.9 ± 0.1	26.3 ± 0.1	30.73 ± 0.9
Young Modulus (E)	MPa	2293.6 ± 33.5	2266.9 ± 17.1	1989.0 ± 53.4	1846.1 ± 12.4	1833.7 ± 67.7
Tensile Strength (σ_M)	MPa	44.5 ± 0.4	43.6 ± 0.5	39.9 ± 0.6	38.4 ± 0.2	40.1 ± 0.2
Tensile Strength at break (σ_B)	MPa	33.9 ± 0.7	34.9 ± 1.3	30.7 ± 0.5	28.9 ± 0.4	30.0 ± 0.6
Gloss 20°		88.0	88.0	85.3	86.2	89.3
Yellowness Index		23.2	25.4	22.7	24.3	23.0
OCS < 250 µm	[1/m^2]	503	994.41	625.54	919.91	2872.10
OCS 250 – 400 µm	[1/ m^2]	102	212.13	114.37	157.13	593.71
OCS < 400 µm	[1/m^2]	79	118.97	75.58	70.61	309.29
VICAT	ºC	99.4	99.2	97	96.8	95.3
Hardness	N/mm^2	110.77	113.78	93.29	87.17	91.94

5.3. Discussion

5.3.1. Toughness

Toughness is one of the most important mechanical properties since it provides resistance to fracture when the material is stressed. This resistance is provided by butadiene, so the more amount of ABS it contains, the higher toughness values will be obtained. According to this type of ABS, which is mainly used in automotive industry, values around 23 kJ/m^2 to materials that have 41% of ABS content are recommended.

Two different assays have been done with notched and unnotched specimens applying 5.5 J of nominal work with an impact velocity of 3.458 m/s. For each assay, 10 repetitions have been made as seen in Annex 1.

On the one hand, observing the patent average results and new researches results in Figure 12 and 13, it can be said that Test 3 and 4 give higher toughness values than Test 1 and 2 due to higher ABS % that they contain. On the other hand, Test 1 and 2 and Test 3 and 4 are observed separately. The patent results indicate that carrying out B1 and B4 precipitation separately affects the toughness by decreasing it. However, after carrying out the new investigation it can be observed that Test 2 and Test 4 are very similar or even higher than those of Test 1 and Test 4 respectively.

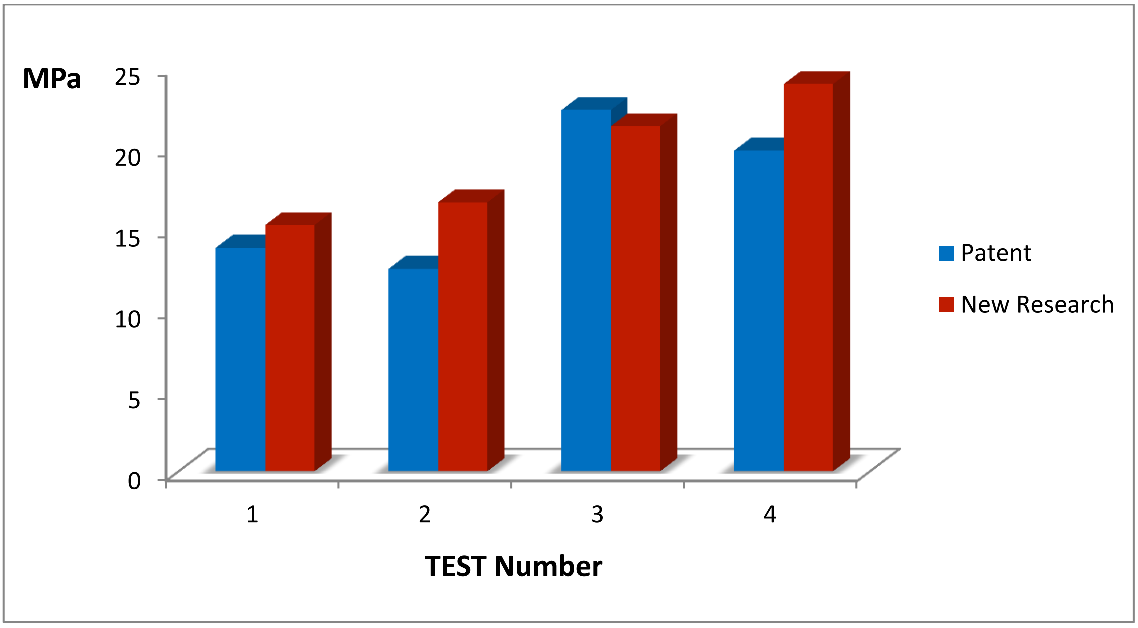


Figure 12.Notched specimens toughness values

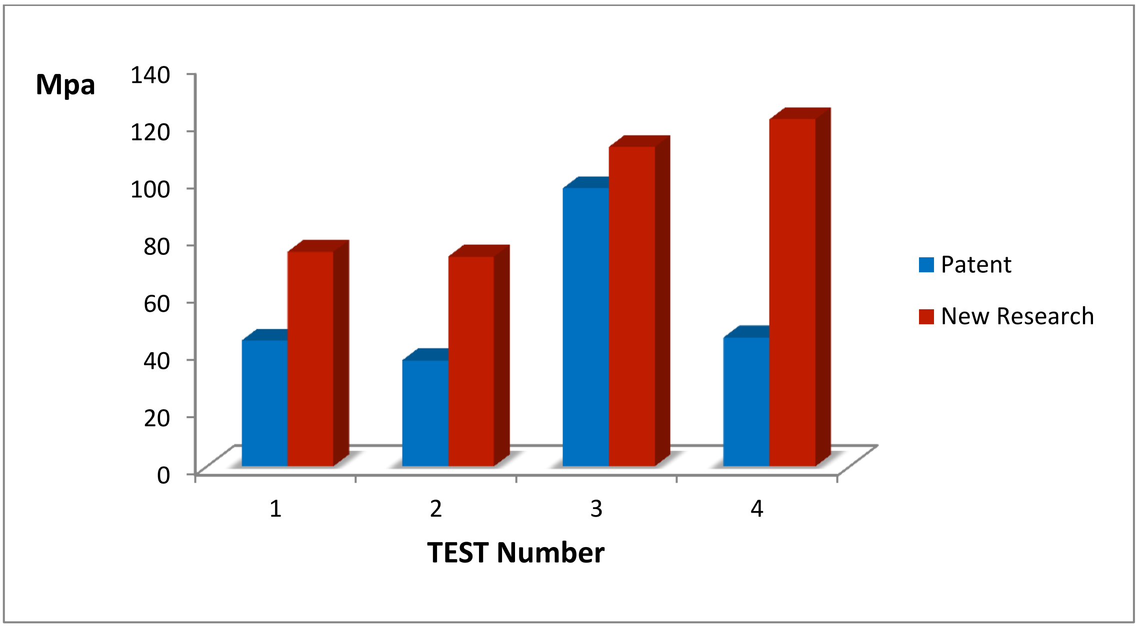


Figure 13.Unnotched specimens toughness values

5.3.2. MVR

The Melt volume flow Rate measures materials fluency. Good processability and fluency is mainly provided by the styrene monomer, therefore, the higher SAN copolymer content the higher material fluency, so that highest values of MRV will be obtained. This value is important since the higher material fluency the shorter injection period and consequently more pieces are obtained per unit of time. Therefore, values around 25 cm^3/ (10 min) for materials with 41% of ABS content are recommended.

As it is determined by ISO 1133, 5.5g of material were used to carry out the test, heating during 5 minutes at 280 ºC and finally applying 10kg force in order to measure material viscosity.

Both in patent and in results of the new research it can be seen that Test 1 and 2 have higher MVR values than Test 3 and 4 due to a higher content of SAN copolymer, as shown in Figure 14. Can also be observed that carrying out B1 and B4 precipitation separately or mixing the two components before precipitation process does not affect, since the values in Test 1 and 2 and Test 3 and 4 are very similar respectively.

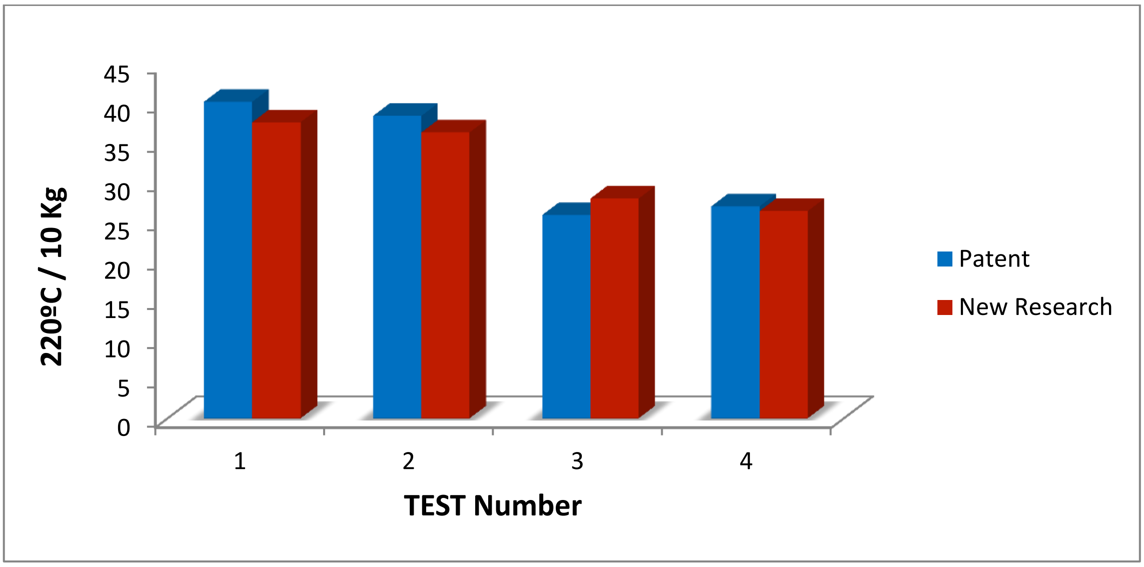


Figure 14.Patent and new research MVR values

5.3.3. Tensile Test

Tensile Test has been carried out to determinate different material parameters, such as Young Modulus, Tensile Strength and Tensile Strength at break. In ABS polymer the Yields Strength value is not significant since is very close to Tensile Strength parameter, they practically have the same value.

As it is determined by ISO 527-1,-2, Alterio specimens must be used and for each Test, five repetitions were carried out as seen in Annex 2.

In Table 4 and 5 can be observed that all values follow a standard where Test 1 and Test 2 as well as Test 3 and Test 4 have very similar values, therefore, using different precipitation methodologies has no consequences on the results. Some differences between both investigations can be observed but there are not significant.

Table 4.Tensile test results of the patent and the new research

		Patent Test 1	N.R Test 1	Patent Test 2	N.R Test 2
Young Modulus (E)	MPa	2478	2293	2481	2266
Tensile Strength (σM)	MPa	46.7	44.5	46.7	43.6
Tensile Strength at break (σB)	MPa	44.2	33.9	42.6	34.9

Table 5.Tensile test results of the patent and the new research

		Patent Test 3	N.R Test 3	Patent Test 4	N.R Test 4
Young Modulus (E)	MPa	2138	1989	2148	1846
Tensile Strength (σM)	MPa	41.5	39.9	41.8	38.4
Tensile Strength at break (σB)	MPa	32.9	30.7	35.6	28.9

5.3.4. Gloss property

The gloss property in end product materials is not essential but some automotive companies demand it in the finishing of their shapes. Different angles measurement can be carried out; in this case, 20˚ angle has been chosen and for each assay 5 repetitions has been made as seen in Annex 3.

The results of the patent and the new research are shown in Figure 15 where between Test 1 and 2 and Test 3 and 4 differences are not observed. On the other hand, patent material gloss is little bit higher than new research material gloss but not significant differences are considered.

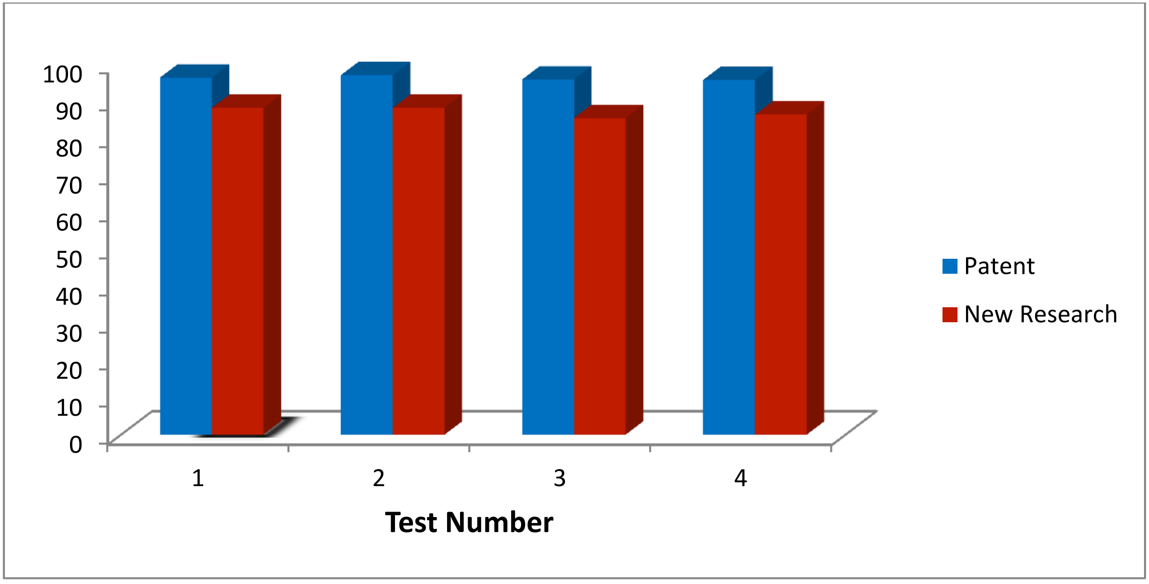


Figure 15.Patent and new research Gloss values

5.3.5. Yellowness Index

Low Yellowness values are preferred for ABS material colour matching and also for aesthetics reasons. For each assay 5 repetitions have been made as seen in Annex 3, using same material standard.

The results of the patent and the new research are shown in Figure 16. Just as in the gloss, there are not differences between Test 1 and 2 neither between Test 3 and 4. On the other hand, new research material yellowness index is lower that patent material index, so it could be concluded that the polybutadiene rubber is less degraded.

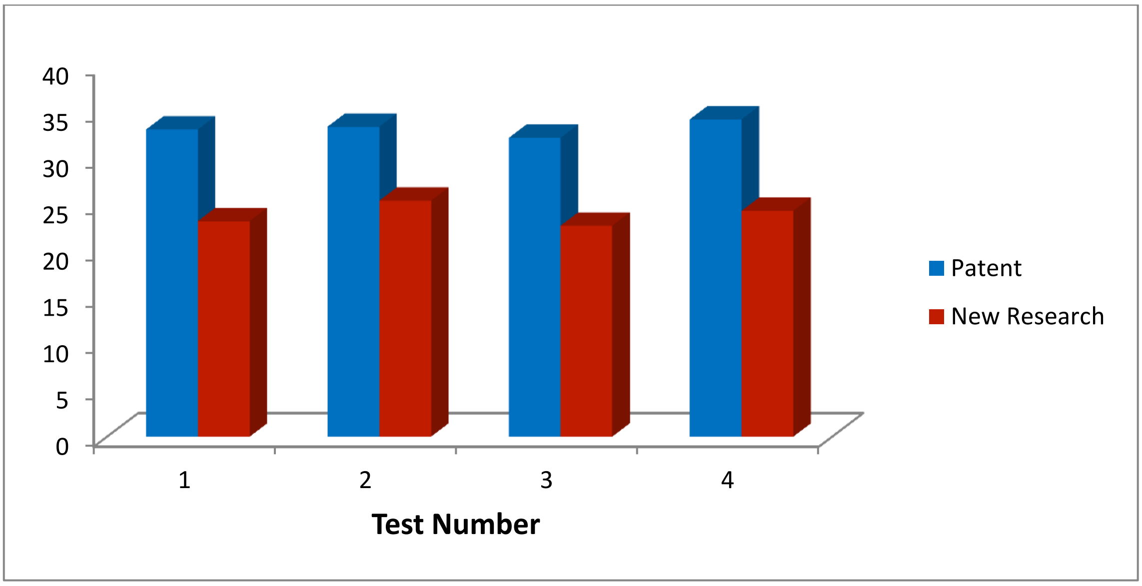


Figure 16.Patent and new research Yellowness values

5.3.6. OCS

In this research, most important property is the optical surface quality due to this type of ABS is mainly used for plating process so it is necessary to have homogenized and smooth surface. With the optical control system different spicks size are identify and quantify in order to determinate material surface quality. In this case, three rang sizes were determined, <250 µm, 250-400 µm and >400 µm and values of <200, <100 and <50 spicks respectively are recommended to be considered high surface quality material.

As shown in Table 6, new research values are much worse in terms of surface quality than those of the patent are. In addition, they are out of normal values since amount of specks is not usual in this type of ABS. Good surface quality material is preferred to be compounded with high quality SAN Copolymer, for this reason, filtered SAN Copolymer with reduced amount of specks is recommended.

Despite of this, due to limit time for the completion of the TFG project, unfiltered SAN was used for the compounding new research work. It could be claimed that SAN raw material selection is very important for OCS values in final ABS material.

Table 6.Optical control system results of the patent and the new research

		Patent Test 1	New Research Test 1	Patent Test 2	New Research Test 2
OCS < 250 µm	[1/m^2]	112	503	154	994
OCS 250 – 400 µm	[1/ m^2]	67	102	105	212
OCS < 400 µm	[1/m^2]	34	79	42	119
		Patent Test 3	**New Research Test 3**	**Patent Test 4**	**New Research Test 4**
OCS < 250 µm	[1/m^2]	94	626	120	920
OCS 250 – 400 µm	[1/ m^2]	71	114	113	157
OCS < 400 µm	[1/m^2]	43	76	70	71

5.4. Chemical Analysis

Before mixing and compounding process, some basics chemical analysis are carried out to determinate that ABS powder is correctly coagulated and dried. This analysis has been applied to B1, B4 and Novotex as shown in the following Table 7.

Table 7.ABS powder different chemical analysis

Material	Compound	B4	B1	Novotex
IR (%)	ACN	11.7	9.3	10.5
	Styrene	33.3	28.2	27.9
	Butadiene	54.2	50.7	45.6
Rest of monomers (ppm)	ACN	1.50	0.57	0.54
	Styrene	423	331	144
	Butadiene	0	0	0
	VCH	4.6	3	2.7
Oligomers (%)	Irganox	0.81	0.9	0.79
Humidity (%)		0.64	0.51	0.54
Yield (%)		96.5	94.2	95.2
pH		4.5	5.2	5.2

First, using Gas Chromatography the amount of monomer no reacted during polymerization reaction and the amount of stabilizer present in ABS powder are quantified, applying rest of monomers method and oligomers method respectively as is explained in section 7.3.1.6, are quantified. On the one hand, as shown in Table 7, B4,B1 and Novotex have low and similar ACN Styrene concentration and there is no butadiene monomer presence, therefore, three latexes polymerization reactions have been correctly carried out is confirmed, since all the amount of butadiene monomer has reacted and very little ACN and Styrene monomers concentration have remained without reacting. On the other hand, VCH presence is due to its formation as a secondary product during polymerization reaction.

Secondly, using Infrared Spectroscopy technique, the presence of monomer in the obtained polymer during reaction is identified and quantified as is explained in section 7.3.1.4. The monomer concentrations are high and similar in the three latexes, this affirming that reaction has been correctly carried out.

Next, ABS powder humidity and pH are determined and lower values than 1% for humidity and between 4-6 for pH are recommended, so the post process can be carried out correctly without danger. In humidity, values above 1% are observed in Table 7, therefore, three latexes materials are well dried and in pH values are also within the accepted rang, so the reaction and precipitation mediums were correctly.

Finally, reaction yield has been calculated and as shown in Table 7 values are around 92-96 %. The amount of ABS powder lost can be due to no reacted amount of latex during the precipitation process and also the lost ABS powder dry process since ABS powder produced in laboratory has high density value so it is very easy to be dispersed and lost during handing.

6. CONCLUSIONS

Coagulation, filtration and drying processes of Grafted PB latexes were carried out.

- In precipitation process, the velocity and the amount of addition of grafted PB latex material and parameters such as stirring and temperature have to be controlled.
- After filtration and drying processes chemical analysis have been carried out obtaining good stability and humidity values, among others.
- ABS powder was obtained achieving good yields (up to 94%).

ABS powder compounding and injection processes were carried out.

- Before compounding process, different ABS powder recipes were designed according to ABS powder density, the quantity that must be produced and machines parameters.
- For injection process, different specimens were made according to the mechanical characterization that was carried out.

ABS specimen's mechanical and surface quality characterization were carried out.

- In general, good and representative values were obtained, despite the fact that in the OCS test greater differences were obtained compared to the reference patent.
- No significant differences were found between the two grafted ABS latexes coagulation methods.
- ABS processing material with 40% ABS polymer and 60% SAN copolymer has better toughness values. However, ABS end material with 30% ABS polymer and 70% SAN copolymer has better fluency, young modulus, tensile strength and tensile strength at break values. Nevertheless, yellowness index and gloss values are similar for both ABS processing material composition.
- Finally, in OCS characterization could be concluded that SAN raw material selection is very important for OCS values in final ABS material, more specifically, filtered SAN Copolymer with reduced amount of specks is recommended.

CONCLUSIONES

Se ha llevado a cabo el proceso de coagulación, filtración y secado de los látex de PB injertados.

- En el proceso de precipitación, se ha controla la velocidad, la cantidad de adición del látex de PB injertado y parámetros como la agitación y la temperatura.
- Después del proceso de filtración y secado, diferentes análisis químicos fueron llevados a cabo para determinar valores como la humedad o estabilidad, entre otros.
- El polvo ABS fue obtenido con altos rendimientos (> 94%).

Se ha llevado a cabo el proceso de compounding e inyección del polvo ABS.

- Antes del proceso de compounding, diferentes recetas fueron diseñadas teniendo en cuenta la densidad del polvo ABS, la cantidad necesaria a producir y los parámetros de la máquina.
- Diferentes tipos de probetas fueran producidas en el proceso de inyección, dependiendo de la caracterización mecánica a realizar.

Se ha llevado cabo los análisis mecánicos de las probetas y la caracterización de la calidad superficial del material acabado.

- En general, los valores obtenidos son correctos y representativos exceptuando por las diferencias mayores obtenidas en el test de OCS a comparación con la referente patente.
- No se encontraron diferencias significativas entre los dos métodos de coagulación del látex de PB injertado.
- El ABS procesado con un 40% de contenido de polímero ABS y un 60% de contenido de copolímero SAN, proporciona mejores resultados en cuanto a la tenacidad. Sin embargo, el ABS procesado con un 30% de contenido de polímero ABS y un 70% de contenido de copolímero SAN proporciona mejores resultados en parámetros como la fluidez, módulo de Young, esfuerzo de tensión y esfuerzo de tensión en el punto de rotura. A pesar de ello, los resultados obtenidos en cuanto al índex de amarillez y brillo han sido similares en los dos procesados de ABS de diferente contenido.
- Finalmente, en cuanto al análisis OCS se ha concluido que la elección del copolímero SAN a utilizar es muy importante para la obtención de buenos resultados de calidad superficial. Por este motivo, se recomienda la utilización de un material filtrado y con cantidad de motas reducidas.

7. EXPERIMENTAL SECTION

7.1. Materials

a) B1, B4, Novotex Emulsion

Intermediate substance for ABS plastic production, provided by Elix Polymers, S.L. ABS compounding has been made with two types of grafted, B1 and B4. Difference between them is polybutadiene particle size, thus B1 having Ø = 0,1 nm and B4 Ø = 0,4 nm. Main toxicity and purity are shown in Table 8.

Table 8.Purity and toxicity of grafted PB latexes

CHEMICAL NAME	PURITY	TOXICITY
Acrylonitrile-Butadiene-Styrene copolymer dispersed in water	Mixture: -ACN-Butadiene-Styrene copolymer (<1000 ppm) -VCH (<0.9 %) -Styrene (<0.5 %)	-Is not considered dangerous. -May contain evaporative monomer residues → assisted extraction. -Harmful gases formation during evaporation process or at high temperatures → assisted extraction

b) SAN copolymer

SAN copolymer production is needed to be used in ABS productions second step, PB and SAN matrix emulsion polymerization. Main toxicity and purity are shown in Table 9.

Table 9.Purity and toxicity of SAN Copolymer

CHEMICAL NAME	PURITY	TOXICITY
Styrene Acrylonitrile Polymer	100 %	Is not considered dangerous.

c) S-SAN stabilizer

PB latex needs a thermal stabilizer S-SAN containing Irganox antioxidant to stabilize it. Main toxicity and purity are shown in Table 10.

Table 10.Purity and toxicity of S-SAN Stabilizer

CHEMICAL NAME	PURITY	TOXICITY
Stabilizer agent FC-S-SAN Latex	Mixture: -SAN Copolymer in water - Schwefel-S-SAN latex - ABS Copolymer + irganox	-Harmful in case of ingestion -Harmful in case of contact with skin -Harmful is case of inhalation -May cause cancer

d) $MgSO_4$ & CH_3COOH

In order to precipitate latexes and Novotex, a sulphate salt and acetic acid is needed. Main toxicity and purity are shown in Table 11.

Table 11.Precipitants purity and toxicity

CHEMICAL NAME	PURITY	TOXICITY
Acetic Acid	100 %	- Flammable - Corrosive - Cause severe skin burns - Cause eye injuries
Heptahydrated Magnesium Sulphate	>99 %	- Not dangerous or toxic substance

e) Additives

Different additives are used to final ABS recipe in order to achieve desired properties.

- EBS
- Mg Stearate
- Silicone oil (M1000)

Main toxicity and purity are shown in Table 12.

Table 12.Different additives purity and toxicity

CHEMICAL NAME	PURITY	TOXICITY
Ethylene bis Stearamide (EBS)	100 %	- Environmentally toxic - Cause skin irritation - Cause eyes irritation
Magnesium Stearate	100 %	- Cause skin irritation - Cause eyes irritation - Hazardous in case of ingestion - Hazardous in case of inhalation
Polydimethylsiloxane	Mixture	- Toxic to aquatic life - Environmentally toxic - Harmful in inhalation - May cause skin and eyes irritation

f) ACN, Styrene monomers.

Main toxicity and purity are shown in Table 13.

Table 13.Different additives purity and toxicity

CHEMICAL NAME	PURITY	TOXICITY
Acrylonitrile	>99 %	- Very irritating in contact with skin and eyes - Very hazardous in case of ingestion and inhalation. - Severe over exposure can result in death - Carcinogenic effects. - Mutagenic effects. - Teratogenic effects. - Environmentally very toxic .
Styrene	100 %	- Very irritating in contact with skin and eyes - Very hazardous in case of ingestion and inhalation. - Toxic substance for the nervous system and the upper respiratory tract. - Prolonged exposure can cause organs damage.

g) t-DDM Chain transfer agent. Main toxicity and purity are shown in Table 14.

Table 14.Purity and toxicity of the chain transfer agent.

CHEMICAL NAME	PURITY	TOXICITY
Mercaptan (tert-dodecantethiol)	90-100 %	- cause skin irritation - case eyes irritation - environmentally toxic

h) Dresinate emulsifier. Main toxicity and purity are shown in Table 15.

Table 15.Purity and toxicity of the emulsifier

CHEMICAL NAME	PURITY	TOXICITY
Acid colophone resins, sodium salts	70 %	- Cause eyes irritation

i) $K_2S_2O_8$ initiator. Main toxicity and purity are shown in Table 16.

Table 16.Purity and toxicity of the initiator

CHEMICAL NAME	PURITY	TOXICITY
Potassium Persulphate	100 %	- Not combustible - Risk of fire and explosion on contact with other combustible substances

- Harmful to aquatic organisms

7.2. Experimental Test

The main aims are to reproduce four tests with different formulations shown in Table 17, obtained from previous research [5] and to carry out final product characterization, both chemical and mechanical.

Table 17.Different tests formulations including all the compound and additives

	RAW MATERIALS	**TEST 1**	**TEST 2**	**TEST 3**	**TEST 4**	**TEST 5 SAMPLE BLANK**
Polybutadiene latex (%)	**B4**		16,8463		22,4617	
	B1		12,4363		16,5817	
	Co-Precipitated (B1 + B4)	29,2826		39,0434		39,0434
	Total PB	29,2826	29,2826	39,0434	39,0434	39,0434
	SAN M60 ASF	68,3260	68,3260	58,5652	58,5652	58,5652
Additives (%)	**EBS**	1,9522	1,9522	1,9522	1,9522	1,9522
	Mg Stearate	0,2928	0,2928	0,2928	0,2928	0,2928
	Silicone oil (M1000)	0,1464	0,1464	0,1464	0,1464	0,1464
TOTAL (%)		100	100	100	100	100

In order to obtain main components such as B1, B4 and Co-Precipitated (B1+B4) in desired form, that is, in solid form as powder, first stage to carry out is stabilize, followed by precipitation and filtration process.

7.2.1. Stabilization process

The stabilization is a simple process where stabilizer, S-SAN, is added little by little to respective grafted latex material to obtain thermal control in the drying process, since it is carried out at high temperatures, therefore, powder could be burn. The material contains an antioxidant called Irganox, which gives the stabilization function. This process has been carried out with the latexes observed in Table 17 and constant stirring is all that is needed along with an addition funnel.

7.2.2. Precipitation & filtration process

The stabilized product is liquid latex, which needs precipitation or coagulation process to obtain product-desired form, powder, in order to be used in compounding process. It is somewhat complex process since temperature and stirring had to be strictly controlled during whole process. Localized extraction, eye protection glasses and latex gloves are necessary during entire process and the process is carried out in a glass cabinet including material weighing.

Firstly, after assembly mounting as shown in Figure 17, calculated proportional amount of water is introduced and heated into metallic recipient until desired temperature is achieved, 95ºC. Once arrived at the temperature, stirring is turned on with 190 rpm of power. Sulphate salt and acetic acid are added quickly followed by slow addition of material to precipitate. It is important to make this step fast because when sulphate salt and acetic acid are added temperature drops 2ºC, so precipitation ideal condition are achieved. In process course temperature has to be between 92-94ºC, stirring is maintained constant and material addition has to be little by little to carry out precipitation correctly.

Secondly, when all material has precipitated, heat is turn off so that precipitated solution cools. Nevertheless, stirring is maintained due to avoid precipitated coagulations. When temperature is around 60-70ºC filtration process can be started using a big Büchner funnel and a filter. Mainly water quantity has to be removed so drying is faster. Wasted water pH analysis must be done to verify if precipitation basic medium was correctly.

Finally, wet powder will be dry in a stove at 50ºC, between 48-60 hours until humidity is less than 1%, since material with water present can react at high temperatures and cause an explosion.

Figure 17. Precipitation proces assembly

7.2.3. ABS Emulsion Polymerization Reaction

The polymerization reaction is a very important term to understand all the following processes carried out during the entire investigation. Therefore, in spite of not carrying out all the necessary chemical reactions to raw materials obtaining, due to the limited time of the work, it was considered necessary to carry out a polymerization reaction by way of illustration to obtain knowledge about the complete production of ABS.

Localized extraction, eye protection glasses and latex gloves are necessary during entire process and if it is possible, process must be carried out in a glass cabinet including material weighing.

Firstly, latex GB1 dry matter % is determined, since depending the %, latex, water and other compounds quantities can be calculated, as shown in the following table 18.

Table 18.Components quantities to be used for emulsion polymerization reaction

Raw Materials	Quantities (mL)	Recipe (%)
GB1 37.3 %	2816	50.8
Styrene	886	16.0
ACN	368	6.6
H20	796	14.4
Dresinate	288	5.2
Potassium persulphate	388	7.0
t-DDM	4.4	0.1

Once the calculations are made, the amount of water and GB1 latex are mixed and introduced into reactor followed by the completion of remaining assembly, observed in Figure 18. Secondly, 5g of initiator $K_2S_2O_8$ are added in the addition funnel and condenser cooler, resistance to heating the water and agitator (120 rpm) light up. In order to begin initiator addition, temperature of 66ºC must be arrived. The addition estimated lasts about 20 minutes where at the end temperature decreases to 62ºC.
Next, monomer ACN and Styrene are introduced into each correspondent addition funnel, followed by the emulsifier Dresinate, which is introduced in a jacketed addition funnel. The amount of chain transfer agent (t-DDM) used is very small, therefore, it was previously added to the monomer styrene solution. Then, continues additions begin with duration of 5’ hours controlled every hour as shown in the following Table 19.

Table 19.Quantities addition control to 5 hour reaction

Hora	ACN (mL)	Styrene (mL)	Dresinate (mL)	t-DDM (mL)	$K_2S_2O_8$ (mL)
0	61.2	147.6	86.2	0.88	-
1	61.2	147.6	86.2	0.88	-
2	81.8	197	57.6	0.88	-
3	81.8	197	29	0.88	-
4	81.8	197	29	0.88	-
5	-	-	-	0.88	194

Finally, 194 ml of $K_2S_2O_8$ are weighing before ending up the fourth hour, which are added during the fifth hour in order to reduce rest of monomers.

There are some important things to take into account.

- During hour 1-2, a temperature of 59ºC must be arrived.
- In the end of hour 2, a temperature of 59ºC must be maintained.
- In the end of hour 3, temperature parameter must be raised to 69ºC.
- In the beginning of hour 4, temperature is grown up until a maxim of 80ºC just because the exothermic reaction.
- Once addition process is finish, solution must be cooled until 40ºC to ABS latex characterization.

1. ACN addition funnel
2. Styrene + t-DDM addition funnel
3. $K_2S_2O_8$ addition funnel
4. Dresinate addition funnel

Figure 18.Polymerization Reaction assembly

7.2.4. Compounding

As stated above, compounding process has two main steps. On the one hand, additives and material mixture has to be made and for this, material recipe is designed taking into account the amount of compound to be mix, its density and machines parameters.

- For Test 1 & 2, 10 mixtures of 1 kg have been made, designed recipe is in the following Table 20.

Table 20.Test 1 and 2 designed recipe for mixing process

TEST 1			TEST 2		
MATERIAL	%	g	MATERIAL	%	g
SAN M60	68,33	683,26	SAN M60	68,32	683,26
BMG	29,28	292,83	B4	16,85	168,46
EBS	1,95	19,52	B1	12,44	124,36
Mg Stearate	0,29	2,93	EBS	1,95	19,52
M1000	0,15	1,46	Mg Stearate	0,29	2,93
			M1000	0,15	1,47

- For Test 2 & 3, 3 mixtures of 3,33 kg have been made, designed recipe is the following Table 21:

Table 21.Test 3 and 4 designed recipe for mixing process

TEST 3			TEST 4		
MATERIAL	%	g	MATERIAL	%	G
SAN M60	58,57	1932,65	SAN M60	58,57	1932,65
BMG	39,04	1288,43	B4	22,46	741,24
EBS	1,95	64,42	B1	16,583	547,20
Mg Stearate	0,29	9,66	EBS	1,95	64,42
M1000	0,15	4,83	Mg Stearate	0,29	9,66
			M1000	0,15	4,83

- For Test 5, 2 mixtures of 5 Kg have been made, designed recipe is in the following Table 22:

Table 22.Test 5 designed recipe for mixing process

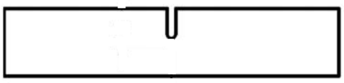
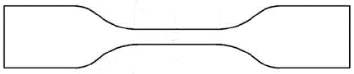
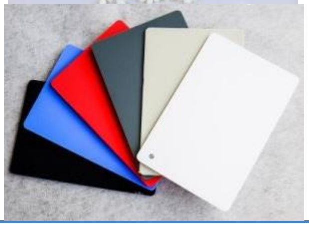
TEST 5		
MATERIAL	%	g
SAN M60	58,565	2928.26
BMG	39,043	1952.17
EBS	1,952	97.61
Mg Stearate	0,293	14.64
M1000	0,146	7.32

Once recipe is designed, the mixture of powder and additives is carried out and introduced into one of the extruder hopper, while in the other SAN copolymer is separately introduced. The optimal parameters to carry out the process correctly are introduced in the system, that is, the amount of each hopper that has to be passed in order to have desired proportions in final compounding. The final product is obtained as pellets which will be introduced in ovens at T=80ºC in order to be dry for injection process.

7.2.5. Injection

Final product characterization such as determining mechanical properties are carried out with specimens, so the pellet must be converted into different specimens types, depending on the property to be determined as shown in the following Table 23 as well as the mount of specimens needed to carried out the analysis.

Table 23.Mechanical properties and specimens type and quantity

Mechanical Property	Used Quantity	Type
Toughness **VICAT** **Hardness**	10 specimens 3 specimens 10 specimens	
Tensile	5 specimens	
MVR **OCS**	5.5 g pellet 2 kg pellet	
Yellowness Index **Gloss 20°**	5 specimens 5 specimens	

7.3. Analysis & Characterization

Different analysis and characterizations has been made in order to determinate different necessary parameters. Some of them were determined to obtain information for subsequent experiments and other ones were made to final product characterization.

Depending on whether it is a raw material, intermediate material or end product material different tests are carried out. The characterization and analysis that correspond to each material are shown in the following Table 24 and 25.

Table 24.Chemical analysis selection for each material

		CHEMICAL ANALYSIS
RAW MATERIALS	**B1**	• Dry matter % • pH
	B4	• Dry matter % • pH
	Novotex	• Dry matter % • pH
	S-SAN	• Dry matter % • pH
	MgSO4	• Index Refraction • pH
	CH3COOH	• pH
INTERMEDIATE MATERIALS	**Coagulated B1** **Coagulated B4** **Coagulated Novotex**	• GC (Rest of monomers) • GC (Stabilizer) • Humidity • IR

Table 25.Mechanical analysis selection for each material

		MECHANICAL ANALYSIS
END PRODUCT MATERIAL	**Compounded ABS**	• Toughness • MVR • Hardness • Softening temperature • Tensile Test • Yellow Index Test • OCS

7.3.1. Chemical Analysis & characterization

7.3.1.1. Dry matter % calculation

In raw materials such as B1, B4, Novotex and S-SAN is necessary to determinate dry matter % because when material is subjected to high temperatures a certain amount of dry matter is loosed, which must be taken into account in following calculations such as the quantity of latex to precipitated. For this analysis, it must be use a vacuum oven at 150ºC during 30 minutes.

7.3.1.2. pH analysis

Croison model GLP 21 is the pH-metre that has been used. It is a basic analysis in order to known compounds stability and medium such as more specifically to control the emulsion solution basic medium in order to

7.3.1.3. Humidity

Once powder is dry, humidity must be controlled to be used in compounding process. The value must be less than 1% to be able to use it at high temperatures and does not modified or cause explosions due to water reaction. Sartorius MA 35 is the instrument used to carry out the assays.

7.3.1.4. FT-IR

Fourier Transform Infrared Spectroscopy used was IR Affinity Shimadzu. Made analysis allow observation of different compounds IR and ATR in order to identify and calculate main components in spectrum range. In this case was used to determinate butadiene, styrene and acrylonitrile ratios with absorbance at 971 cm^{-1}, 1602 cm^{-1} and 2242 cm^{-1} respectively.

7.3.1.5. Refraction Index

Refractmeter used to determinate refraction index was Atago RX-5000. Through refraction, index analysis a material can be identified, since each substance has specific wavelength (λ). Material can also be quantified to determinate concentration.

7.3.1.6. GC

Two different chromatographs with internal standard method were used to identify main components and each quantity (percentage or ppm). To identified and quantified rest of monomers, Agilent Technologies 7697A Headspace Sample was used because monomers are volatilized and headspace method was need. However, to identified and quantified the amount of oligomers Agilent technologies 7890B GC System with FID detector was used.

7.3.2. Mechanical Characterization

7.3.2.1. Toughness

The technique was used to obtain end product specimens ability to absorb energy and plastically deform without fracturing. Measurements were made at 23ºC with Notched and Unnotched specimens defined by Izod impact strength ISO 180-1A, using Zwick Roell HIT 5-5P and Zwick Roell Notching Machine.

7.3.2.2. MVR

Melt volume-flow rate technique was used to obtain melted thermoplastic flow in order to determinate material fluidity. Measurement was made at 220ºC and applying 10 kg weight, defined by ISO 1134, using Götfeat 011.5 instrument.

7.3.2.3. Hardness

Ball indentation hardness property was defined by standard ISO 2039-1. This technique provides measurement of the strength that must be applied. Used instrument was Zwick Roell H04.3106 E.

7.3.2.4. VICAT or Softening Temperature

Vicat softening temperature technique was used to determinate material softening point. This point can be defined as the temperature at which material further softens after its arbitrary softness point is reached drilling 1mm of profundity. Test was defined by Vicat method ISO 306 and was carried out using Coesfeld Material Test instrument.

7.3.2.5. Tensile Test

This technique was used to determinate different thermoplastic parameters such as Young Modulus, Tensile Stress and Tensile Stress at break. Alterio specimens were used to carry out this test which is subjected to a controlled tension at both ends until it breaks, stretching 50mm/min in the first both two tests and 1mm/min in the final test respectively. This method is defined by standard ISO 527-1,-2 and was carried out using Zwick Roell Z010 instrument.

7.3.2.6. Yellow Index Test

This optical test was used to observe materials Yellow Index DIN67530 using Spectral Flash SF600 Plus instrument. Yellowness is an important property in many industries for several reasons and specifically in this case and generally, for all ABS plastics it is determined by two main reasons. First, some products degrade and turn yellow with exposure to sunlight, temperature and other environmental factors during use due to reactivity and sensitivity to degradation of polybutadiene rubber. Second, addition of pigments to colour the material is practiced in almost all post-processes. Therefore, it is much easier to obtain desired colour on a white base material than on a yellowish material.

7.3.2.7. OCS

Optical control system is done to determinate materials cleaning degree by counting specks or impurities. Technique is used in materials, which will later be applied painted, lacquered or chromed treatment.

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ANNEX

1. Toughness assays

Table 26.Toughness total assays of Test 1, 2 and 3

ASSAY		TEST 1		TEST 2		TEST 3	
		Notched	Unnotched	Notched	Unnotched	Notched	Unnotched
1	KJ/m^2	15.1	83.0	14.8	63.7	20.9	137.0
2	KJ/m^2	15.3	69.4	14.9	77.5	21.1	92.4
3	KJ/m^2	15.3	68.9	16.8	48.4	21.3	87.0
4	KJ/m^2	15.0	62.9	17.3	79.7	21.4	137.0
5	KJ/m^2	15.3	70.9	17.4	95.1	21.3	137.0
6	KJ/m^2	15.0	83.4	17.4	74.6	21.3	128.9
7	KJ/m^2	15.0	85.8	17.4	65.6	21.4	123.5
8	KJ/m^2	15.1	71.9	16.7	53.2	21.5	137.0
9	KJ/m^2	15.3	59.0	16.7	95.2	21.4	85.1
10	KJ/m^2	15.3	93.8	16.6	79.3	21.5	111.5
$\overline{X}$	KJ/m^2	15.2	74.9	16.6	73.2	21.3	117.6

Table 27.Toughness total assays of Test 4 and 5

ASSAY		TEST 4		TEST 5	
		Notched	Unnotched	Notched	Unnotched
1	KJ/m^2	23.4	102.2	22.3	137.0
2	KJ/m^2	24.6	101.9	23.0	137.0
3	KJ/m^2	24.2	128.3	22.5	134.3
4	KJ/m^2	24.0	136.8	22.8	123.2
5	KJ/m^2	23.8	101.0	23.0	136.7
6	KJ/m^2	23.3	137.0	22.7	137.0
7	KJ/m^2	23.9	137.0	22.6	132.9
8	KJ/m^2	24.0	137.0	22.8	122.7
9	KJ/m^2	24.2	94.4	23.0	111.4
10	KJ/m^2	23.6	36.3	22.9	108.1
$\overline{X}$	KJ/m^2	23.9	111.2	22.8	128.0

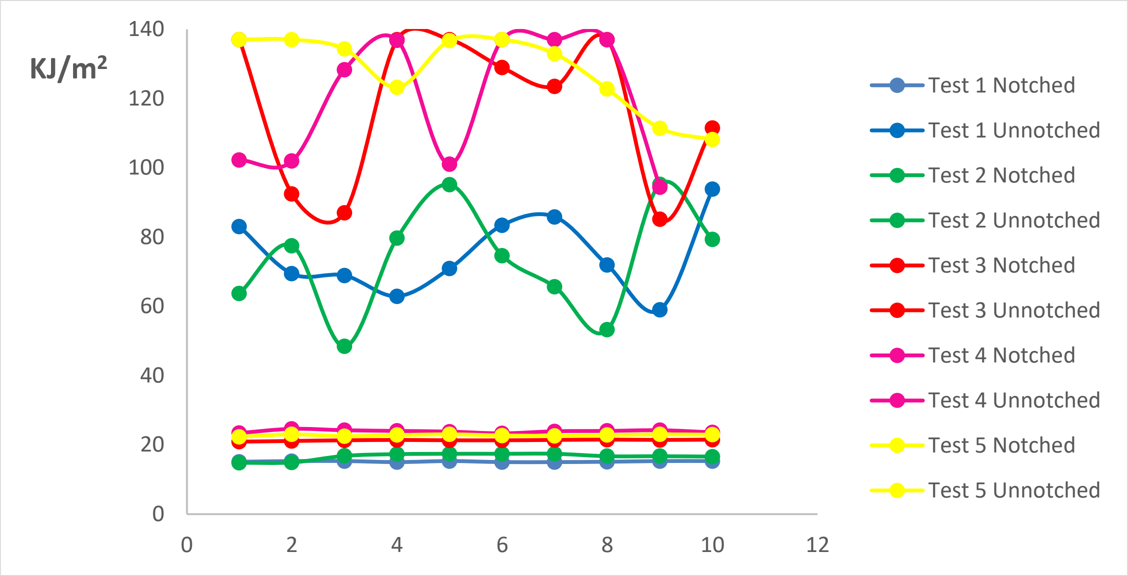

Figure 19.Toughness variation graphic

2. Tensile Test assays

Table 28.Tensile total assays of Test 1, 2 and 3

ASSAY		TEST 1			TEST 2			TEST 3		
		E	σM	σB	E	σM	σB	E	σM	σB
1	MPa	2234.9	44.5	33.6	2256.5	43.9	35.2	2061.0	40.2	30.9
2	MPa	2322.5	44.1	34.7	2267.2	43.2	35.6	1996.9	40.2	29.9
3	MPa	2263.9	44.3	34.3	2281.6	44.2	32.7	1910.6	38.8	31.4
4	MPa	2262.6	45.1	33.8	2284.9	43.4	35.3	1989.4	40.4	30.9
5	MPa	2283.8	44.3	32.9	2244.1	43.2	35.8	1990.1	40.0	30.4
$\overline{X}$	MPa	2293.6	44.5	33.9	2266.9	43.6	34.9	1989.0	39.9	30.7

Table 29.Tensile total assays of Test 4 and 5

ASSAY		TEST 4			TEST 5		
		E	σM	σB	E	σM	σB
1	MPa	1861.3	38.1	22.9	1914.9	40.3	30.7
2	MPa	1838.9	38.5	29.3	1889.0	40.3	30.5
3	MPa	1846.4	38.4	28.8	1973.7	40.1	29.4
4	MPa	1854.1	38.3	29.1	1845.2	39.7	29.8
5	MPa	1829.7	38.7	28.3	1795.8	40.1	29.6
$\overline{X}$	MPa	1846.1	38.4	28.9	1883.7	40.1	30.0

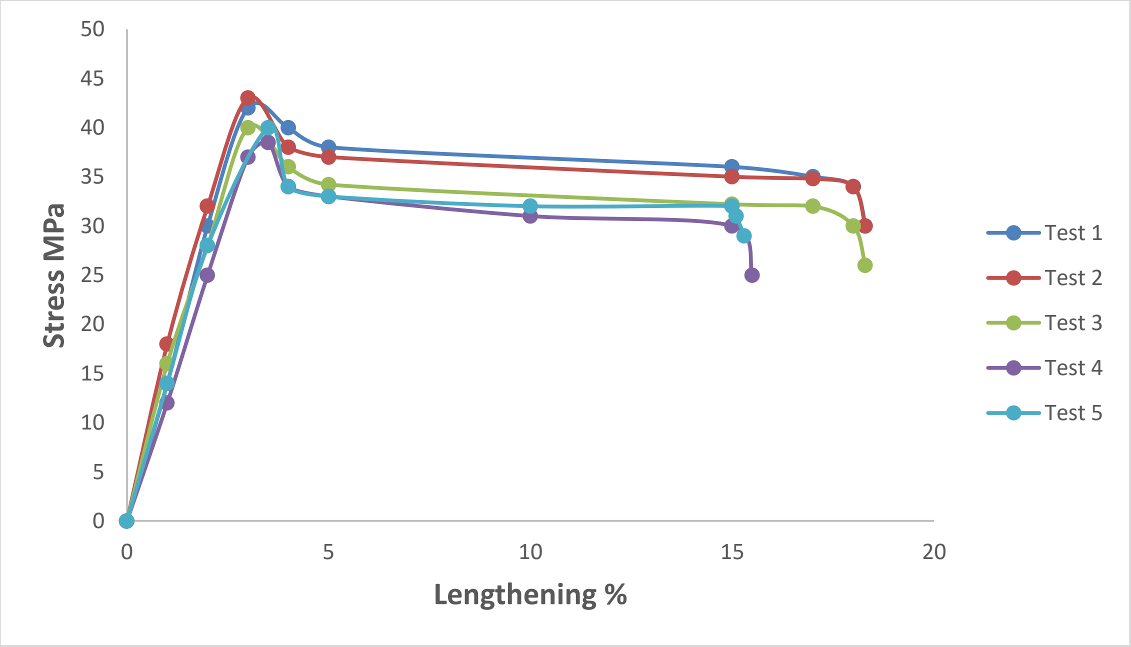

Figure 20.Tensile variation graphic

3. Gloss 20° assays

Table 30.Toughness total assays of Test 1, 2, 3, 4 and 5

ASSAY	TEST 1	TEST 2	TEST 3	TEST 4	TEST 5
1	88.2	87.7	86	86.9	89.7
2	87.9	87.3	85.5	85.6	89.5
3	86.5	87.8	86.4	85.9	90.1
4	88.8	88.8	83.9	87	89.4
5	88.8	88.8	84.8	85.6	87.9
$\overline{X}$	88.0	88.1	85.3	86.2	89.3

4. Yellowness Index assays

Table 31.Yellowness Index total assays of Test 1, 2, 3, 4 and 5

ASSAY	TEST 1	TEST 2	TEST 3	TEST 4	TEST 5
1	23.3	25.2	22.7	24.5	18.7
2	23.4	25.3	22.5	24.2	19.3
3	23.3	25.1	22.9	24.4	19.3
4	22.9	25.6	22.9	24.4	19.3
5	23.2	26.0	22.7	24.2	19.3
$\overline{X}$	23.2	25.4	22.7	24.3	19.2