



**Separation of ABS and PS plastics from waste of
electrical and electronic equipment with froth flotation
using a physical conditioning technique**

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I declare that this document is an original work of my own authorship and that it fulfils all the requirements of the Code of Conduct and Good Practices of the Universidade de Lisboa.

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Abstract

Recycling is an effective way to manage plastic waste and has been receiving considerable attention. Plastic intrinsic characteristics hinder their separation using traditional recycling methods. Froth flotation is a promising technique to separate plastics with similar densities like PS and ABS.

This work focuses on the separation of ABS and PS plastics from the waste of electrical and electronic equipment using froth flotation combined with a physical conditioning technique. A two-level L16 Orthogonal Array of Experiments using the Taguchi design of experiences approach was developed, with 16 tests plus 3 tests on a centre point, resulting in a set of 19 tests, with 7 manipulated variables: treatment time; treatment temperature and elapsed time between the end of the heating treatment and the flotation test, frother concentration, air flow rate, impeller speed and pH. The tests were performed on PS and ABS with size ranging from 2 to 4 mm.

Using the heating treatment, it was possible to obtain an average ABS recovery in the floated product of 98% and the PS recovery ranged from 3 to 55%, indicating that under the treatment conditions PS was depressed while the overall floatability of ABS was slightly altered. It was possible to achieve a selective separation, both floated and sunken products with high purity in ABS and PS, respectively. After two minutes of flotation, it was possible to achieve 91% ABS in the floated product and 97% of PS in the sunken product.

The Taguchi method presents itself as an adequate experimentation methodology to correctly identify and evaluate the effect of several operating variables and their predicted interactions on the flotation results. A linear model (R^2 coefficient of 0,8852) was found to explain the Selectivity Index response and it was demonstrated that impeller speed and elapsed time between treatment and flotation tests, as well as interactions between frother concentration and elapsed time, and air flow rate and pH have the most influence on the process efficiency. Data variability and results have characterized the experimental work. The experimental plan included three replicates at the centre point and even though operating conditions were the same, different responses were produced. Further tests should be carried out to disclose the source of variability.

Supplementary analysis was carried out to evaluate the adequacy of the proposed separation method for the plastic recycling industry. The contact angle analysis shows that there is a change in the wettability characteristics of both plastics with the treatment, which explains the different floatability results. The image analysis did not provide further information on how the surface was changed. This could be either due to poor camera resolution, bad implementation of the image analysis tool or even the wettability change happening at a lower scale, namely in changes in the polymeric chain, clearly not observable in the acquired images. Thermogravimetry analysis showed that this method is suitable to produce products from plastics with additives proper to deliver to the recycling industry, but more studies are needed.

The results show that the proposed treatment can separate PS from ABS, and their possible application in the recycling industry, as well as to disclose the mechanism of action of the treatment. Furthermore, the experimentation methodology enables the correct evaluation of the effect of several operating

variables and interactions on the flotation results. Feasibility studies and analysis of the wetting mechanisms were defined as future studies

Keywords: Plastics separation, WEEE plastics, froth flotation, Taguchi design of experiments, ABS, PS.

Resumo

A reciclagem apresenta-se como um método adequado e preferencial para a gestão de resíduos plásticos e como tal tem vindo a receber atenção considerável. O plástico possui características intrínsecas que dificultam a sua separação através de métodos tradicionais de reciclagem. A flutuação por espumas surge como técnica promissora para separar resíduos plásticos de densidades semelhantes, tal como o ABS e o PS.

Este trabalho propõe a utilização de uma metodologia experimental que envolve a utilização da flutuação por espumas combinada com um pré-tratamento de condicionamento físico para separar ABS e PS provenientes de resíduos de equipamentos eléctricos e electrónicos. Foi desenvolvido um arranjo de experiências ortogonal L16 de dois níveis usando a abordagem de desenho de experiências de Taguchi, com 16 testes mais 3 testes num ponto central, resultando num conjunto de 19 testes. Foram manipuladas 7 variáveis: tempo e temperatura do tratamento, tempo decorrido entre o final do tratamento e o teste de flutuação, concentração de espumante, caudal de ar, velocidade do rotor e pH da solução. Os testes foram realizados em ABS e PS com o calibre entre 2 e 4 mm.

Usando o tratamento proposto, foi possível obter uma recuperação média de ABS no produto flutuado de 98% e a recuperação do PS variou entre 3 e 55%, indicando que nas condições de tratamento foi possível deprimir o PS, praticamente mantendo a flutuabilidade de ABS. Os produtos flutuados e afundados obtidos tinham alta pureza em ABS e PS, respectivamente. Após dois minutos de flutuação, foi possível obter um produto flutuado com uma pureza de 91% em ABS e 97% PS no produto afundado.

A metodologia de Taguchi apresenta-se uma metodologia de experiências adequada para identificar e avaliar correctamente o efeito das diversas variáveis operacionais e interações nos resultados da flutuação. Foi possível obter um modelo linear ($R^2=0,8852$) para explicar a resposta do Índice de Selectividade e foi demonstrado que a velocidade do rotor e o tempo decorrido entre o final do tratamento e o teste de flutuação, bem como as interações entre concentração de espumante e tempo decorrido, e o caudal de ar e o pH têm maior influência no processo. A grande variabilidade de resultados pautou o trabalho experimental. O plano experimental incluiu as três repetições no ponto central e, embora operando nas mesmas condições, as respostas tinham uma variação considerável.

Foram realizadas análises suplementares para estudar a adequabilidade da metodologia proposta para produzir materiais de qualidade para a indústria de reciclagem de plástico, bem como revelar os mecanismos de actuação do tratamento. A análise do ângulo de contacto mostrou que houve uma mudança nas características de molhabilidade de ambos os plásticos, o que explica as diferentes recuperações no produto flutuado. A análise de imagem não forneceu informações sobre como a superfície foi alterada. Tal pode ser devido a resolução insuficiente das fotografias, má implementação da análise de imagem devido à tridimensionalidade das amostras ou mesmo devido a uma mudança a uma escala menor que não se traduz na rugosidade, ou seja, em mudanças na cadeia polimérica. Análises termogravimétricas mostram que o método pode ser adequado para produzir materiais de qualidade para a indústria mesmo na presença de aditivos nos plásticos, sendo no entanto necessária a realização de mais estudos.

Os resultados obtidos mostram a capacidade do tratamento proposto em separar o ABS do PS e a sua possível aplicação na indústria da reciclagem. Além disso, a metodologia de experiências permite uma avaliação do efeito de diversas variáveis e interações no processo de flutuação. Estudos de viabilidade e análise dos mecanismos de molhabilidade foram definidos como estudos futuros.

Palavras-chave: Separação de plásticos, plásticos de REEE, flutuação por espumas, Método de Taguchi de desenho de experiências; ABS, PS.

Table of contents

Acknowledgements	iii
Abstract	v
Resumo	vii
Table of contents	ix
Table of figures	xi
Table of tables	xiii
Acronyms and abbreviations	xv
1. Introduction	1
1.1. Objectives	3
1.2. Thesis outline	3
2. Waste Electrical and Electronic Equipment	5
2.1. WEEE composition	5
2.2. WEEE management in the European Union	6
2.3. Processing of waste of small electrical and electronic equipment	8
2.4. Management of waste plastics from small electrical and electronic equipment	9
2.1. General characteristics of plastics found in the waste of small EEE	9
2.1. Plastics separation methods for mechanical recycling	11
3. Froth flotation for the separation of polymers from small household appliances	13
3.1. Features of plastics flotation	14
3.2. Main methods of plastics flotation	16
3.3. Current challenges of plastics froth flotation	17
4. Materials and methods	19
4.1. Sampling process	19
4.2. Sample preparation	20
4.3. Experimental method	21
4.3.1. Physical conditioning	21
4.3.2. Flotation tests	22
4.4. Experimental design	23
4.4.1. Preliminary tests	23
4.4.2. Design of Experiments using the Taguchi method	24
4.5. Treatment evaluation methods	27
5. Results and discussion	29
5.1. Preliminary tests	30
5.2. Taguchi design results	33
5.3. ANOVA: Selectivity Index	37
6. Treatment evaluation methods	47

6.1. Contact angle results	47
6.2. Image analysis	49
6.3. Thermogravimetry analysis	52
7. Conclusions and future works.....	55
7.1. Conclusions	55
7.2. Future works.....	56
References.....	57
Annex I – Size distribution after fragmentation	61
Annex II – Results	63
Annex III – Contact Angle measurements	69
Annex IV – Image Analysis Tool code	71

Table of figures

Figure 1: Images of plastic waste pollution (Sources: a- https://www.mnn.com/earth-matters/translating-uncle-sam/stories/what-is-the-great-pacific-ocean-garbage-patch , b- https://blueocean.net/the-good-the-bad-and-the-ugly-of-plastic-pollution/ , c- https://www.britannica.com/science/plastic-pollution , d- https://www.letsrecycle.com/news/latest-news/valpak-takes-on-shropshire-weee-contract/ ..	1
Figure 2: Waste management hierarchy (Adapted from Directive no. 2008/98/CE)	9
Figure 3: Estimated plastic polymers concentration in small electrical and electronic equipment (a - Adapted from Martinho et al., 2012; b - Adapted from Maris et al., 2015)	10
Figure 4: Scheme of a mechanically stirred froth flotation cell (Adapted from Wills, 2016)....	13
Figure 5: Contact angles of water on hydrophilic and hydrophobic particles (Adapted. Source: http://www1.lsbu.ac.uk/water/hydrophobic_hydration.html)	14
Figure 6: Bubble-particle aggregate configuration in mineral and plastic particles (Shen et al., 2001)	15
Figure 7: Retsch SM 2000 schredding mill	20
Figure 8: Granulometric curve of ABS and PS samples.....	20
Figure 9: Fragmented plastics in the 2-4mm size fraction (a- ABS, b-PS).....	21
Figure 10: Treatment apparatus	21
Figure 11: Leeds flotation cell and pH meter	22
Figure 12: ABS and PS recovery in the floated product over time at variable treatment temperatures. Treatment time: 60min; MIBC concentration: 0,2 mL.L-1; air flow rate: 60 L.h-1; impeller speed: 640 rpm; pH: 10.....	31
Figure 13: ABS plastic treated at 80°C (a) and 100°C (b).....	31
Figure 14: ABS and PS recovery in the floated product over time at variable pH. Treatment time: 60min; Treatment temperature: 80°C; MIBC concentration: 0,2 mL.L-1; air flow rate: 60 L.h-1; impeller speed: 640 rpm	32
Figure 15: Control ABS and PS (without heating treatment) recovery in the floated product over time (min)	33
Figure 16: Average product purity over cumulative flotation time	35
Figure 17: Average Selectivity Index over cumulative flotation time.....	35
Figure 18: Interaction effects a- BD interaction; b- KM interaction	39
Figure 19: Interaction effects a- AM interaction; b- BP interaction	39
Figure 20: Model surfaces for MIBC concentration and elapsed time interaction	41
Figure 21: Model surfaces for air flow rate and pH interaction	41
Figure 22: Normal probability plot of residuals	43
Figure 23: Predicted values vs. residuals	43
Figure 24: Residuals vs. run test order	44
Figure 25: Response model with highlighted centre point replicates.....	44
Figure 26: Goniometer.....	47
Figure 27: Plastic pieces used to contact angle measurements (a-ABS;b-PS)	48
Figure 28: Image acquisition apparatus.....	50
Figure 29: Masking original image of ABS plastics, prior to texture analysis.....	50
Figure 30: Sharpened image of ABS plastics and texture filtered using entropyfilt.....	51
Figure 31: a - TG, b - DTG from ABS treated and untreated samples.....	52
Figure 32: a - TG, b - DTG from ABS untreated samples and another ABS samples from WEEE	53
Figure 33: TGA and DTG of virgin ABS (Source: https://www.hitachi-hightech.com/file/global/pdf/products/science/appli/ana/thermal/application_TA_066e.pdf)	53
Figure 34: a - TG, b - DTG from PS treated and untreated samples	54

Figure 35: a - TG, b - DTG from PS untreated samples, another PS samples from WEEE and virgin PS.....54

Table of tables

Table 1: Typical composition of WEEE according to equipment category (Adapted from Buekens & Yang, 2014).....	6
Table 2: Some properties of ABS and PS (Billmeyer, 1984)	10
Table 3: Equipment and the plastic collected.....	19
Table 4: Coded variables.....	25
Table 5: Matrix for the Experimental plan (L16 OA plus three centre point tests with the coded values for variables).....	26
Table 6: Columns with two-variable interaction terms aliasing	26
Table 7: Ranges of manipulated variables in the OVAT tests	31
Table 8: Set of control tests performed on untreated samples	32
Table 9: Range of the manipulated variables used for the Taguchi experimental plan.....	33
Table 10: Results of the Taguchi experimental plan	34
Table 11: Minimum, maximum, mean and standard deviation of the Taguchi experimental plan	34
Table 12: Correlation coefficients between independent variables and responses	36
Table 13: Factor effect, sum of squares and % contribution for the Selectivity Index response	37
Table 14: ANOVA summary for the curvature adjusted model.....	37
Table 15: ANOVA results for the Selectivity Index response	38
Table 16: ANOVA results for Selectivity Index model adequacy	42
Table 17: ABS contact angle pictures.....	48
Table 18: Experimental contact angles for ABS and PS plastics without treatment and treated at 80°C for 80 minutes; contact angles for reference (Shent et al. 1999)	48
Table 19: Entropy results for PS and ABS plastics ABS and PS plastics without treatment and treated at 80°C and 100°C for 80 minutes	51

Acronyms and abbreviations

ABS: Acrylonitrile butadiene styrene

ANOVA: Analysis of variance

d.f.: Degrees of freedom

DTG: Derivate thermogravimetry

EEE: Electrical and electronic equipment

EU: European Union

OA: Ortogonal array

PS: Polystyrene

R²: Coefficient of determination

R_{ABS}: Recovery of ABS in the floated product

R_{PS}: Recovery of PS in the floated product

RoHS: Restriction of certain hazard substances

SI: Selectivity Index

TG: Tthermogravimetry

TGA: Thermogravimetry analysis

WEEE: Waste of electrical and electronic equipment

1. Introduction

The increasing market demand of electrical and electronic equipment (EEE), linked to the fast pace of technological evolution led to an increase in the collected amount of this type of residues in the European Union (Eurostat, 2018a, 2018b). Due to the constant replacement of outdated products by more recent ones, nowadays electronic waste is one of the fastest growing waste streams, growing at 3-5% a year. The high heterogeneity of this waste stream demands an appropriate management that would minimize the impacts resulting from the waste of electric and electronic equipment (WEEE), not only by its prevention, but also on its reutilization, recovery, valorisation and safe disposal. At present, there is no effective strategy for dealing with the increasing plastic waste stream and one of the reasons is that there is a lack of efficient ways to separate different plastics. This results in huge amounts of waste with the nefarious effects seen in Figure 1.



Figure 1: Images of plastic waste pollution (Sources: a-<https://www.mnn.com/earth-matters/translating-uncle-sam/stories/what-is-the-great-pacific-ocean-garbage-patch>, b-<https://blueocean.net/the-good-the-bad-and-the-ugly-of-plastic-pollution/>, c- <https://www.britannica.com/science/plastic-pollution>, d- <https://www.letsrecycle.com/news/latest-news/valpak-takes-on-shropshire-weee-contract/>)

The main plastics group found in WEEE flux are styrenics like acrylonitrile-butadiene-styrene (ABS) and polystyrene (PS), and due to the high plastic content and great diversity of plastic types found, the existence of an adequate management system to treat these materials is imperative. Since EEE represent a potential source of plastic waste, European directives point towards the treatment and recycling of these materials. Some plastics and the presence of some additives make certain mixtures incompatible for their mechanical recycling. Different melting points demand a selective separation of waste plastics, i.e. that some plastic mixtures are separated into the individual plastics.

Several methods have been studied and developed for plastic separation, but due to similar properties between certain plastics, such as close density and electrical properties, make density-based and electrostatic methods highly inefficient. Also, the colour of the plastics is a hindering factor for optical screening, mid and near-infrared, etc., especially for dark coloured plastics, according to Martinho et al., 2012.

The use of froth flotation for the separation of plastic mixtures is referred by several authors as a simple and effective method (Fraunholz, 1997; Shent et al., 1999; Wang et al., 2015). Froth flotation exploits differences in the surface properties of the particles, whether the surface is readily wetted by water or if it repels it instead (Wills, 2016). However, this method is particularly challenging due to the similarity in the surface properties of plastic materials, which have a naturally hydrophobic nature and will easily float with the aid of air bubbles. Thus, it is necessary to manipulate the natural wettability of the plastics in order to provide a selective separation. In Wang et al. (2015) four methods to render plastics surface hydrophilic are highlighted: gamma flotation, selective depression by chemical conditioning through the adsorption of reagents, selective surface modification and selective depression by physical conditioning.

Nevertheless, froth flotation brings some environmental issues on account of the reagents that are used. Therefore, Wang et al. (2014c) developed a physical conditioning technique, that by boiling the ABS and PS plastics for a certain time made ABS surface hydrophilic selectively while minimizing the reagents used in the flotation process (only a frother agent was used). Although associated with a request of energy, a smaller fraction of flotation reagents was necessary, thus making this technique both cost-effective and environmentally friendly and therefore interesting for industrial application of plastics flotation and further recycling.

The work plan involved a collection of ABS and PS plastic samples from WEEE at the premises of Ambigroup Reciclagem S.A. Ambigroup Reciclagem S.A. belongs to the group AMBIGROUP, among several other companies. AMBIGROUP provides waste related services, namely waste management, treatment, recycling and valorisation through seven different companies, with a presence both in Portugal and Spain. Ambigroup Reciclagem S.A. with premises in Seixal deals with the recycling of metals, waste electrical and electronical treatment and recycling of plastic (Ambigroup, 2019).

This thesis aims to revisit the boiling treatment proposed by Wang et al. (2014c) for the separation of ABS and PS plastics with froth flotation, testing new conditions, proposing new temperature ranges and treatment times, as well as studying all identifiable variables and/or interaction variables. Bearing this in mind, a fractional factorial experimental design is proposed – a Taguchi design of experiments – to analyse the process outcomes. This approach is seldomly used in plastic flotation studies, according to Salerno et al. (2018). Salerno et al. (2018) proposed an experimental factorial design using the kinetic parameters to evaluate the response to the method used, instead of testing one variable at a time.

A factorial experimental design is a method for planning experiences involving several factors (variables), in which all possible combinations of the factors at different levels are studied. Generally, in an experience considering k factors each to be studied at two levels, the factorial design would require 2^k runs (Montgomery; 2013). Although useful, factorial experimentation might become unmanageable when considering many factors. In this thesis work seven operational variables are studied related to

the physical conditioning treatment (treatment time and temperature and time elapsed between the treatment and flotation) and the flotation process (concentration of frother agent, pulp pH, air flow rate and impeller speed) using the Taguchi design of Experiments. Taguchi designs are fractional factorial experiments, in which only a subset of the runs of the full factorial design are used. Taguchi designs use Orthogonal Arrays (OAs) for designing of experiments, providing the desired information with the least possible number of trials with adequate precision (Krishnaiah & Shahabudeen; 2012).

To study the separation process, the Selectivity Index proposed by Gaudin (1957) was used instead of the most commonly used Recoveries of plastics in the floated product. This index is considered a convenient measure of a binary separation by denoting both recovery and rejection of two components with each other.

Furthermore, in order to understand the physical conditioning surface modification mechanisms due to the applied treatment, the plastic samples were analysed using thermogravimetry analysis, contact angle measurements and the development of an image analysis technique to evaluate surface roughness.

1.1. Objectives

This work studies the impact of a heating treatment applied on two different post-consumer plastics (PS and ABS) from waste electrical and electronic equipment (WEEE), prior to their separation by froth flotation. A Taguchi Experimental Design was developed to evaluate the process, variables and possible interactions. Seven operational variables were studied, related to the heating treatment (treatment time and temperature and time elapsed between the treatment and flotation) and the flotation process (concentration of frother agent, pulp pH, air flow rate and impeller speed). The application of this method with a view to the plastic recycling industry was studied, by analysing the possible impact of the treatment on the plastics using contact angle measurements, image analysis techniques and thermogravimetry analysis results.

1.2. Thesis outline

This thesis is divided into seven chapters, briefly described as follows:

The first two chapters present the state of the art concerning WEEE and WEEE management focusing on the European Union WEEE management system. WEEE composition is furtherly explained, particularly its plastic content. Some existent technologies for plastic separation are mentioning, focusing froth flotation on Chapter 3.

Chapter 4 presents the materials and developed methodology. The sampling process and sample preparation for the experimental work are described, followed by the applied methodology. The procedure of the physical conditioning treatment that precedes froth flotation is explained. The developed design of experiments is delineated, where the variables under study and the experiment matrix are presented. The analysis of results is explained.

The following chapter presents the experimental results. On account of the Taguchi design, the model that best describes the selectivity index response is presented as a function of the studied variables.

On chapter 6 some supplementary analysis results are presented.

Chapter 7 is a conclusive chapter on the work done and where a possible line of development is proposed for future works.

2. Waste Electrical and Electronic Equipment

As stated in the Portuguese Decree-Law no. 67/2014, transposed from European Directive no. 2012/19/EU, electrical and electronic equipment (EEE) is every “equipment which is dependent on electric currents or electromagnetic fields in order to work properly and equipment for the generation, transfer and measurement of such currents and fields designed for use with a voltage rating not exceeding 1000 Volt for alternating current and 1500 Volt for direct current”. The waste electrical and electronic equipment (WEEE) is understood by EEE discarded or intended to discard by its holder, including all its components, subassemblies and consumables which are an integral part of the equipment at the time it is discarded (Decree-Law no. 67/2014). In each country, EEE and WEEE can be differently defined via inclusive lists and/or legal definitions, as long as they meet the European Union collection and recycling targets (European Directive no. 2012/19/EU; Buekens & Yang, 2014).

The usage of EEE has been growing for the past years, by considering the number of products put on the market, with an average increase of 1% per year between 2010 and 2015 (Eurostat, 2018b). The increasing production of EEE is mainly related to a rapid populational, economic and technological growth, followed by an increase in the amount of generated waste derived from discarded EEE, an increase of 5% being predicted on the collected waste within a ten-year span (2014-2024) (Buekens & Yang, 2014; Magalini et al., 2016).

WEEE is composed out of several materials and substances, some of which pose potential health and environmental risks when not properly managed moreover, the production of new electronic equipment requires the use of costly and limited resources (European Commission, 2018).

2.1. WEEE composition

WEEE is a wide mixture of a great variety of materials and components, making it difficult to establish or define a global composition. In general, WEEE is composed by ferrous and non-ferrous metals, plastics, glass, wood and others, in which the most abundant materials are metals, followed by plastics and glass, each element proportion differing according to the equipment type, thus making WEEE a potential source of secondary raw materials (Chancerel & Rotter, 2009; Buekens & Yang, 2014; Ilankoon et al., 2018). In Table 1 a typical distribution of the materials present in WEEE by equipment category is shown.

Table 1: Typical composition of WEEE according to equipment category (Adapted from Buekens & Yang, 2014)

Category	Ferrous metals (%)	Non-ferrous metals (%)	Glass (%)	Plastic (%)	Wood, cables, other (%)
Large household appliances	61	7	3	9	21
Small household appliances	19	1	0	48	32
IT equipment	43	0	4	30	20
Telecommunication equipment	13	7	0	74	6
Televisions, radios, etc.	11	2	35	31	22

Equipment differ individually in size, weight and composition, therefore WEEE stream composition should not be considered absolute, with great variability depending on the type of equipment and on the production period due to the elimination or introduction of new materials (Almeida, D., 2011; Buekens & Yang, 2014).

One of the main issues associated to the WEEE stream is the presence of potentially hazardous components that are part of its constitution, namely heavy metals and, considering plastics, additives like stabilizers, flame retardants, pigments, plasticizers and carbon fibres (Dimitrakakis et al., 2009; Stenval et al., 2013; Ilankoon et al., 2015). Stenval et al. (2013) analysed batches of plastics from WEEE, identifying wood as one of the main contaminants, as well as heavy metals, rubber and foam. Due to the presence of electrical current and consequential potential ignition in EEE, these products are particularly vulnerable to flammability, thereby making WEEE accountable for the increased flow of flame-retardant plastics. Flame-retardant additives, namely brominated fire retardants (BFRs), entail some environmental issues, mainly related to their persistence in the environment, bioaccumulation and potential toxicity (Birnbaum & Staskal, 2004).

Proper management of WEEE is crucial from an environmental, economic and health point of view, by not only reducing the amount of waste needing treatment but also in the recovery of potentially valuable materials and the disposal of harmful components (Buekens & Yang, 2014).

Increasing efficiency in processes surrounding WEEE management, namely in the collection, treatment and recycling of end-of-life equipment is essential, both by enhancing resource utilization and contributing to a circular economy through the release of secondary raw materials on the market (European Commission, 2018, Parajuly & Wenzel, 2017).

2.2. WEEE management in the European Union

The joint disposal of WEEE with municipal solid waste in landfill, incineration or recovery of valuable materials without a previous treatment can lead to serious environmental and public health problems due to the dispersion of hazardous substances present in its constitution.

Portuguese legislation referring to end-of-life management of electrical and electronic waste is transposed from European Directives, namely the Directive 2012/19/EU and the Commission Implementing Regulation 2017/699/EU. The Community Programme establishes measures intended to minimize resultant impacts from WEEE life cycle, as well as standardise in the EU State Members certain obligations, implementing principles of prevention, recovery and safe disposal of waste and hazardous substances (European Commission, 2018). The Portuguese Decree-Laws currently in force are (Agência Portuguesa do Ambiente, 2018):

- Decree-Law no. 151-D/2017, from the 11th December of 2017, approving the legal framework for WEEE management, transposed to the national law from the European Directive no. 2012/19/EU;
- Decree-Law no. 61/2017, from the 11th of June of 2017, transposed from the European Directive no. 2011/65/EU – also referred to as RoHS Directive (Restriction of Hazardous Substances), establishing rules on the restriction of the use of certain hazardous substances in EEE.

Since 15th of August of 2018, the Decree-Law no. 151-D/2017 groups EEE according to the following six categories:

1. Temperature regulation equipment;
2. Screens, monitors and equipment with screens over 100 cm²;
3. Lamps;
4. Large equipment (any external dimension exceeding 50 cm), excluding equipment falling within categories 1, 2 and 3;
5. Small equipment (no external dimension exceeding 50 cm), excluding equipment falling within categories 1, 2, 3 and 6;
6. Small computer and telecommunication equipment (no external dimension exceeding 50 cm).

The WEEE and RoHS Directives aim to reduce environmental impacts related to EEE life cycle, particularly targeted to promote a separate collection and to increase recycle and material recovery rates, and thereby reducing the amount of WEEE to be disposed of.

The current legislation establishes that WEEE management is the responsibility of all the parties concerning EEE life cycle, referring to the collective responsibility of producers, distributors, municipalities, management operators and consumers. Most European Union Member States, including Portugal, opted for competitive systems, where several collective systems compete for the collection of WEEE (Carvalho, 2008). In Portugal, there are currently three licensed management entities responsible for the WEEE streams management, Amb3E (Associação Portuguesa de Gestão de Resíduos), ERP Portugal (European Recycling Platform) and WEEECYCLE, collecting the six legal equipment categories (Agência Portuguesa do Ambiente, 2018).

2.3. Processing of waste of small electrical and electronic equipment

The small equipment waste stream assembles a diverse equipment typology, sharing the common feature of having small dimensions. This stream can consider vacuum cleaners, irons, toasters, power tools, etc., provided they are classified by Decree-Law no. 151-D/2017. An understanding of this specific WEEE stream is crucial to improve its management system, since WEEE consist of a large diversity of materials and components which in turn may have different sizes and shapes and even contain hazardous substances in its constitution and therefore its components may require a selective and separate treatment.

Despite the great diversity of equipment found in this stream, manual disassembly is usually applied at the beginning of its processing. In this phase, all components liable for recovering and those with hazardous components in their constitution are removed (Almeida, 2011). Through manual disassembly, it is possible to obtain streams with a high plastic content (> 95%) (Buekens & Yang, 2014). Size reduction is usually also carried out to optimize the recovery of ferrous and non-ferrous metals, and consequently resulting in residues of plastic mixtures frequently not suitable for further mechanical recycling (European Commission, 2011).

Almeida (2011) verified that using manual disassembly it was possible to obtain smaller elements without waste and contamination. However, manual disassembly of small EEE is a costly and time-consuming method, due to the high diversity of types of equipment found, each having its own specificities. Thus, some alternative methods were studied and mentioned in the consulted bibliography. Cui & Forssberg (2003) mentioned methods based on differences in physical properties of materials, such as size by screening, shape, magnetic susceptibility, density, through dense media separation and jigging and based on the electrical conductivity of materials.. Gundupalli et al. (2017) further disclosed several indirect separation techniques which utilize sensors, namely optical sorting, laser-induced breakdown spectroscopy (LIBS), mid-infrared spectroscopy (MIR), near-infrared spectroscopy (NIR) and X-ray fluorescence (XRF).

2.4. Management of waste plastics from small electrical and electronic equipment

The end-of-life products management in the European Union is guided by Directive no. 2008/98/CE, according to a waste hierarchy starting by preventing waste production and afterwards in its management, so that State Members enforce measures that would lead to the best environmental results (Figure 2).

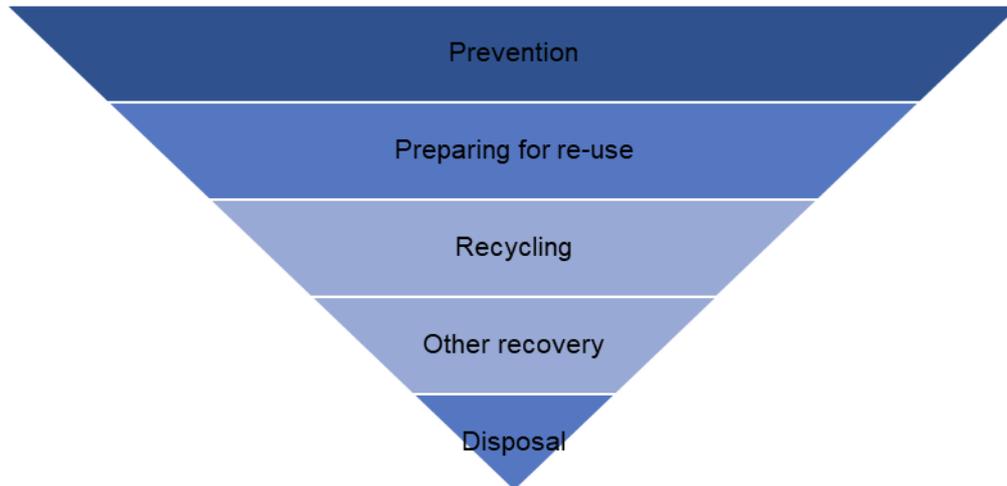


Figure 2: Waste management hierarchy (Adapted from Directive no. 2008/98/CE)

The plastic fraction from WEEE is extremely complex, each equipment may contain more than three different polymers in its constitution. Martinho et al. (2012) analysed the WEEE plastics composition, verifying that the small equipment waste stream can have up to twenty-one different polymers that can correspond to 49.1% of their weight. Likewise, similar results were presented by Maris et al. (2015) for waste of small EEE.

Most of the plastics present in WEEE are not ready for reuse, due to specifications of the design of each product, namely in its conception and the type of raw materials used (Almeida, 2011). Recycling allows the valorisation of some materials through mechanical or chemical recycling.

Mechanical recycling is the most common method of recycling plastic waste, in a process that includes collection, washing, fragmentation and separation, in order to produce a suitable replacement for the virgin material. This type of recycling deals with the reprocessing of plastic waste for the creation of new plastic products with characteristics as close as possible to the original material (Al-Salem *et al.*, 2009).

2.1. General characteristics of plastics found in the waste of small EEE

Plastic is a common term used for a wide range of synthetic or semi-synthetic materials used in a variety of applications. Etymologically, the word originates from the Greek *plastikos*, which means “fit for moulding”, referring to its easy malleability and plasticity during manufacture (PlasticsEurope, 2018). Plastics are macromolecules formed by polymerization, through the repetition of simpler and small-sized chemical units, the monomers, which can be repeated linearly or branched (Billmeyer, 1984).

Plastic materials can be classified as thermoplastic or thermosetting, according to their ability to be repeatedly fused and solidified, with or without loss of their fundamental properties (PlasticsEurope,

2018). Thermoplastics are the most common type, formed by linear or branched chains, unlike thermosetting, which are formed by networked structures, with a high density of interconnection (Billmeyer, 1984). Thus, thermoplastics have softening ability with increasing temperature and solidification with cooling and thermosetting plastics after heated and formed cannot be remelted without chemical degradation.

Due to their characteristics, thermosetting plastics cannot be recycled, whereas thermoplastics have some recycling capacity without total loss of their original properties. Stenval et al. (2013) stated that the main plastics found in the WEEE stream were thermoplastics, consisting mainly of styrene-based plastics and polyolefins, indicating the importance of adapting the recycling processes to these polymers.

The most common types of plastic polymers found in small EEE waste are polystyrene (PS), acrylonitrile-butadiene-styrene (ABS), polycarbonate (PC) and ABS blends, high impact polystyrene (HIPS) and polypropylene (PP) (Figure 3) (Martinho et al., 2012; Maris et al., 2015). This thesis will focus on PS and ABS plastics. Some properties of these polymers are shown in Table 2.

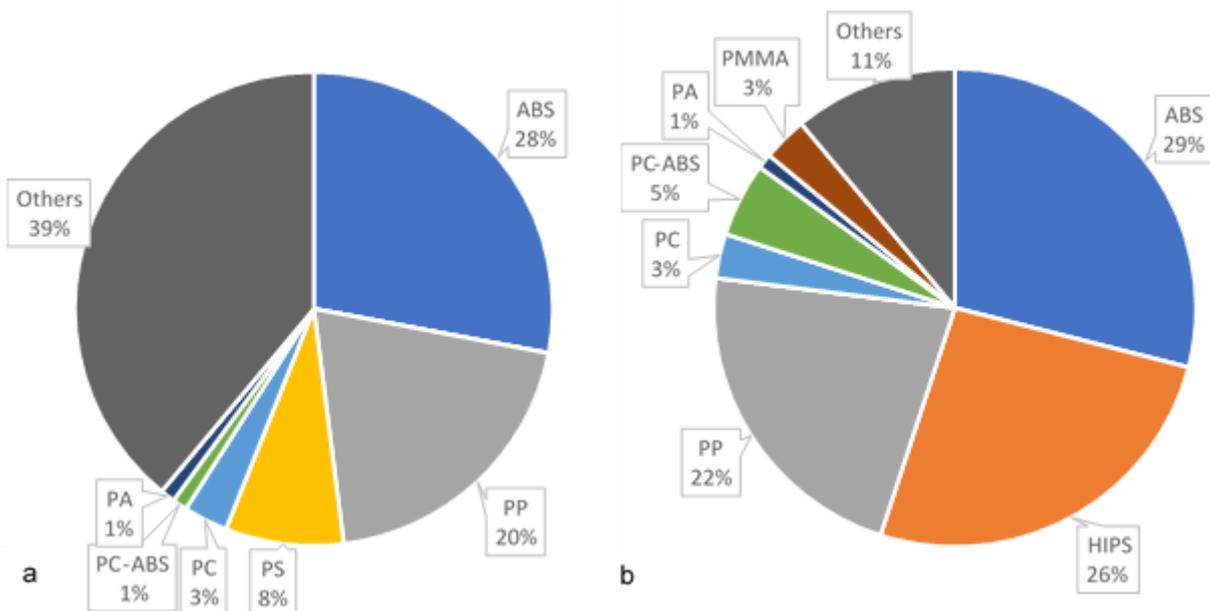


Figure 3: Estimated plastic polymers concentration in small electrical and electronic equipment (a - Adapted from Martinho et al., 2012; b - Adapted from Maris et al., 2015)

Table 2: Some properties of ABS and PS (Billmeyer, 1984)

Polymer	Density (g/cm ³)	Dielectric constant (1000 cycles)
ABS	1,02-1,04	2,4-4,5
PS	1,04-1,09	2,4-2,65

Some polymers and the presence of some additives make certain mixtures of plastics chemically incompatible for recycling. The miscibility or compatibility between plastic polymers is determined by the degree of degradation of the mechanical properties due to the mixture of some species. Peeters et al.

(2014) studied the compatibility between plastics from LCD monitors, with and without the presence of fire-retardant additives, stating that the low recycling efficiency of these materials is connected to the great complexity of blends in WEEE. However, recycling of WEEE plastics is expected to increase in time, as existing equipment containing brominated flame-retardants, as well as other additives are banned and thus out of waste streams in accordance with the RoHS legislation (European Commission, 2011).

Recycling plastic waste from EEE helps reducing solid waste mass and disposal volumes of end-of-life materials, as well as allowing a selective and distinctive treatment for plastics containing toxic chemicals. It is not yet clear whether recovery through recycling for the same original application is possible (European Commission, 2011). Nevertheless, recycling WEEE plastics is an emerging opportunity for not only the management and treatment of these materials but also an opportunity for material recovery, given the large volume of WEEE produced and its content both in valuable and toxic substances (Buekens & Yang, 2014)

2.1. Plastics separation methods for mechanical recycling

The main challenges of plastics mechanical recycling are related to plastic polymers degradation when exposed to heat, light, oxidation, radiation, hydrolysis and tensile stresses. Ragaert et al. (2017) recognized as main causes of polymer degradation thermal and mechanical factors through the lifetime and also incompatibility between polymers.

Singh et al. (2017) addressed some plastics separation methods and their principles. The tribo-electrostatic separation can be used, having an application maximum size of 2-4 mm and low efficiency to separate some polymers due to their similar electrical properties. Identification of different polymers using laser-induced breakdown spectroscopy (LIBS) is done through a spectral analysis of the polymer matrix, with a similar principle to infrared spectroscopic analysis (MIR and NIR, mid and near infrared). The colour of the plastics is, however, a hindering factor for the existing identification and separation processes (optical screening, MIR, NIR, etc.). Martinho et al. (2012) reported that normally only light-coloured plastics are recognized. X-ray fluorescence spectroscopy (XRF), also referred by Singh et al. (2017), was effectively used by Maris et al. (2015) in the identification of polymers with additives like pigments and flame-retardants.

Due to the approximate characteristics, namely the low density and similar electrical conducting properties, density-based and tribo-electrostatic separation methods have limited efficiency and effectiveness and hinder the separation of some plastic mixtures for recycling.

The use of froth flotation for the separation of plastic mixtures is referred by several authors as a simple and effective method to separate plastics with approximate density (Fraunholz, 1997; Shent et al., 1999; Wang et al., 2015; Singh et al., 2017). This method was initially developed in the mining industry for the separation of minerals, yet its applicability for the selective separation of plastics with approximate density has also been studied.

3. Froth flotation for the separation of polymers from small household appliances

Developed in the early twentieth century, froth flotation is an important and versatile technique of treatment or separation of ore minerals allowing the exploitation of low grade and size ores that would otherwise be discarded. It is a complex process, involving three phases of matter (solids, water and air), besides exploiting different particle's surface physicochemical properties, based on their behaviour at the air-water interface (Durão et al., 2002; Wills, 2016)

Figure 4 schematically depicts the froth flotation system in a mechanically stirred flotation cell.

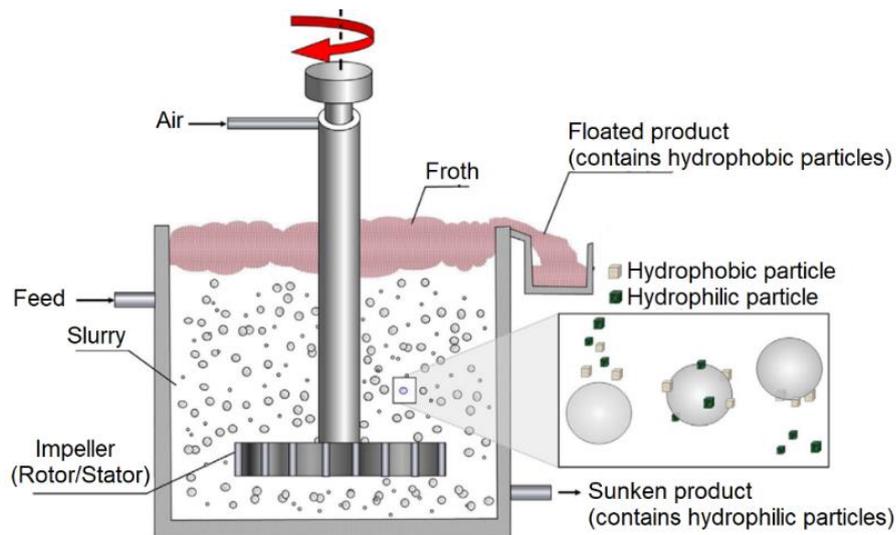


Figure 4: Scheme of a mechanically stirred froth flotation cell (Adapted from Wills, 2016)

The feed is introduced into the flotation cell in the form of a slurry, which is then mechanically stirred and traversed by a stream of air bubbles. The agitation promotes the collision of the particles present in the slurry with the air bubbles, thus resulting in the adhesion of hydrophobic particles to the bubbles, which are then transported to the froth zone where the floated product is recovered. The hydrophilic particles remain in the liquid phase, constituting the sunken product (Wills, 2016).

Froth flotation exploits the differences in surface properties of particles, whether the surface is readily wetted by water or if repels it instead. Therefore, it is necessary that the surface of the materials to be separated exhibit different contact angles with water, defining if the particles are hydrophilic (easily wettable) or hydrophobic (repels water) (Figure 5). Besides the natural wettability a material can have, this characteristic can be manipulated either by the use of reagents or treatments to provide a selective separation (Wills, 2016).

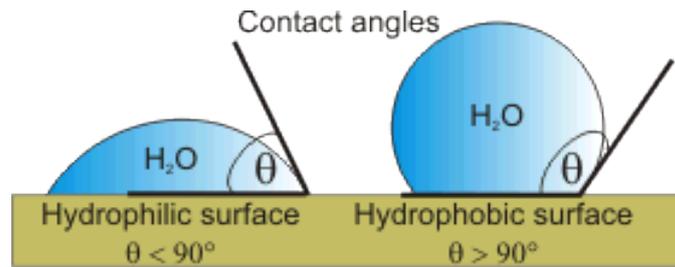


Figure 5: Contact angles of water on hydrophilic and hydrophobic particles (Adapted. Source: http://www1.lsbu.ac.uk/water/hydrophobic_hydration.html)

3.1. Features of plastics flotation

The study of the applicability of the froth flotation method to separate plastic mixtures dates to the late seventies. The method has been studied for virgin plastics separation, having good results, but its applicability to the separation of plastic waste lack some studies (Wang et al., 2015).

Plastics separation using froth flotation exhibits several particularities in view of the same method for the separation of ore minerals, namely related to specific plastic properties like low density and surface charge which confers to these materials a hydrophobic nature (Fraunholz, 1997). However, some plastics present enough difference in floatability allowing an almost complete separation, however, there are certain mixtures where, due to slight floatability differences, the separation happens to be only partial.

According to Wang et al. (2015), the main specific features of plastics froth flotation are related to:

- Properties of plastics;
- Methods for size reduction of plastics;
- Particle size of plastics for separation;
- Source of plastic wastes.

The properties of plastics affect the hydrophobicity, which depends on the chemical structure, degree of polymerization, crystallinity, surface structure, among other features (Wang et al., 2015). Wang et al. (2014a) also referred that the presence of additives in plastics affect its surface and consequently reflecting on floatability. Buekens & Yang (2014) reported that one of the difficulties of using froth flotation in plastic waste separation is due to the plastic surfaces being modified, either for a specific purpose or throughout its lifetime.

As previously mentioned, size reduction is frequently carried out for WEEE separation and recycling. Size reduction involves the creation of a new surface, leading to a new surface alteration through oxidization processes, ergo the environment also has a significant effect on the properties of the plastics. Characterization of surface properties, like the contact angle, should be carried out on plastic waste, to study the effects of crushing (Wang et al., 2015).

Due to plastics low density, the maximum particle size required for flotation is superior when compared to ores. In ores flotation, the particle size ranges between approximately 30-1000 μm , in contrast to plastics that can take up to several millimetres, thus resulting in different bubble-particle aggregate configurations (Figure 6) (Wang et al., 2015). In plastics flotation, numerous bubbles will attach to the plastics surface whilst in ores flotation, a single bubble will carry several solid mineral particles. The bubble-particle aggregate is floated if its specific mass is lower than that of the liquid, therefore depending on the density of the aggregate, particle and bubble size and the specific surface area of the particles where the bubbles will attach (Fraunholz, 1997).

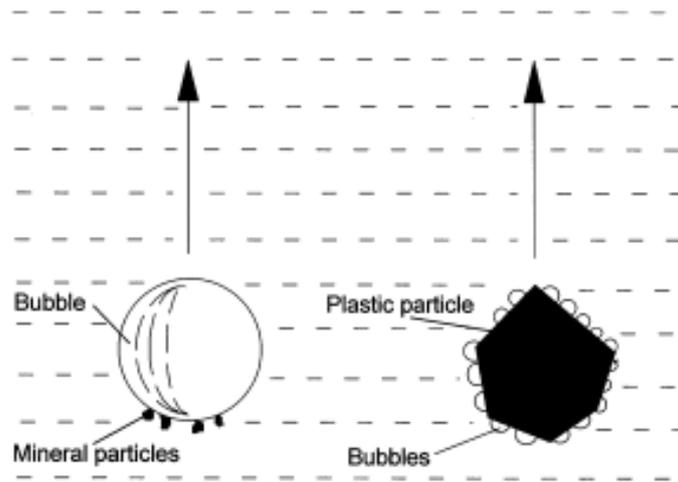


Figure 6: Bubble-particle aggregate configuration in mineral and plastic particles (Shen et al., 2001)

Since specific surface area also depends on the particle shape, it can be concluded that the floatability of plastic particles is related to this property. Pita & Castilho (2017) tested the influence of density, shape and size on plastic separation using froth flotation. Amongst particles of the same size and hydrophobicity with different shapes and density, it was found that lower density particles would float better due to lower weight and consequently form a bubble-particle aggregate with a lower weight too. Besides, lamellar particles float better than spherical ones, needing fewer bubbles to form aggregates with a density lower than water. So, Pita & Castilho (2017) verified that froth flotation in plastics is not only influenced by the surface chemical structure, but also by the size, shape and density of the particles, also stated by Shen (2001). The latter concludes that flotation of plastics as a combination of froth flotation and gravity separation methods, dominated by both surface chemical-related and gravity factors.

The suitable size for the flotation of plastic particles in order to improve selectivity and floatability is between 2 and 6 mm. Flotation of particles with size smaller than 1 mm tends to decrease selectivity of the separation process as all the particles will tend to float, in case of larger particles the floatability is decreased (Fraunholz, 1997). Shent et al. (1999), Marques & Tenório (2000) and Pita & Castilho (2017) presented the same preferable size range for plastic flotation. Wang et al. (2014b) noted that the suitable size range is different depending on the polymer type.

Thanh Truc & Lee (2017), through a modification in the ABS surface by increasing its roughness with a mild heat treatment prior to the froth flotation method obtained a selective separation of this plastic in a binary mixture of ABS and HIPS from WEEE, suggesting that also the surface roughness of a particle affects its wettability.

3.2. Main methods of plastics flotation

In Wang et al (2015) four methods of plastics flotation are highlighted: flotation in a fluid with known surface tension – gamma flotation; selective depression by chemical conditioning, through the adsorption of reagents; selective surface modification and selective depression by physical conditioning.

Gamma flotation enables the separation of two hydrophobic materials providing that they have a significant difference of the critical surface tension (γ_c), allowing a selective wettability by reducing the surface tension of the fluid ($\gamma_{L/G}$). The critical surface tension is defined as the surface tension of a liquid at which the solid surface exhibits a hydrophobic to hydrophilic transition. At adequate values of surface tension of the fluid, the bubbles will adhere to particles with lower critical surface tension, that is, to the more hydrophobic particles and thus promote its flotation, the particles with higher critical surface tension suppress the adhesion of the bubbles to its surface (Shent et al., 1999). However, in Wang et al. (2015) some studies are reported showing that decreasing the surface tension of the liquid results in a gradual wettability of all plastic components and not a selective wetting as desired.

In plastics flotation, reagents of three types are typically used: depressants, frothers and pH regulators. Many reagents have been studied and reported in the literature for plastic flotation. In Wang et al. (2015) the most suitable reagents for certain plastic mixtures are highlighted.

Selective wettability by chemical conditioning occurs by adsorption of hydrophilic reagents, reducing the surface hydrophobicity of plastics (Shent et al., 1999). Depressants are reagents used to increase or induce a hydrophilic nature to particles by adsorbing them to the surface. The action of the depressants on the surface of the plastics is still the subject of many studies and there is still little knowledge about the adsorption mechanisms on the surfaces of the different plastics (Fraunholz, 1997, Wang et al., 2013). The importance of the depressants concentration and conditioning time is, however, recognized and reported in several works, as in Marques & Tenório (2000), Wang et al. (2014b) and Pita & Castilho (2017).

Wang et al. (2015) report the main depressors studied for plastic separation based on the behaviour during and after the flotation process. The authors state that the results obtained in the various studies may be good indicators of the action of these reagents in the different plastics.

Frothers are heteropolar compounds adsorbed at the air-water interface, producing froth under certain conditions. They are composed of one or more hydrophobic groups and at least one hydrophilic group of ionic or non-ionic nature, such as -OH, -O, -COOH, etc. These compounds should promote the formation of stable bubble-particle aggregates, stabilize the froth at the surface until the removal of the floated material, exhibit little sensitivity to pH changes, be soluble in water and do not present collector

effects, i.e. it should not promote hydrophobicity. Frothers are generally organic, like alcohols such as methyl-isobutyl-carbinol (MIBC) and some oils, namely pine oil (Durão et al., 2002).

Wang et al. (2013) studied the flotability of polymers modulated by frother agents in several post-consumer plastics, which include PS and ABS, reporting a relationship between the presence of frothers such as MIBC and the plastics flotability. Floatation rates of the mentioned plastics increase with frother concentration.

The separation selectivity depends not only on the concentration of the froth flotation reagents but also on the pH of the solution which must be regulated since the H⁺ and OH⁻ ions resulting from water dissociation can be adsorbed on the surface of the particles affecting the action of the reagents. Common acids, such as sulfuric and hydrochloric acid, and inorganic bases, such as lime and sodium hydroxide are used for pH regulation. Regulators that may adversely interfere with the flotation process should be avoided and when possible, flotation should be executed in neutral or alkaline medium to prevent equipment corrosion (Durão et al., 2002).

Selective surface modification is a method for increasing the wettability of a plastic surface, in which a hydrophilic feature (e.g.: =O, -OH, -COOH, etc.) is added through oxidation in the superficial polymer chain. This can be achieved with plasma treatments, alkaline solutions and corona discharges (Shent et al., 1999). Thanh Truc & Lee (2017) performed a coating treatment with zinc oxide combined with microwave heating in ABS and HIPS from WEEE. The treatment induced oxidation on the surface of both ABS and HIPS, leading to a surface rearrangement through the creation of a hydrophilic group. However, it is more effective in ABS, resulting in a greater recovery of this plastic in the sunken product.

Physical conditioned treatments are based only on the physical characteristics inherent to plastics and on the mobility of the polymeric chains; chemical reactions not occurring in the process and thus differing from surface modification treatments. Wang et al. (2014c), with a boiling treatment in ABS and PS from plastic waste, reported a selective and effective influence on the creation of a hydrophilic surface in ABS. Thanh Truc et al. (2017) through a mild heat treatment of a WEEE plastics mixture of PS, PC, ABS with BFR's and polymethyl-methacrylate (PMMA) increased the surface roughness of the ABS with BFR's and therefore increased its wettability, the surface of other plastics remaining practically unchanged and thus allowing a selective separation with flotation.

3.3. Current challenges of plastics froth flotation

Although a great number of efforts has been made to develop the flotation of plastics from solid waste for their separation, recovery and recycling, there are still several challenges regarding this technique. Buekens & Yang (2014) reported the difficulty of using froth flotation particularly in waste plastics from EEE, since its surface may be altered on purpose or due to degradation during its lifetime. Thermal and mechanical degradation, as well as the presence of certain additives, expose the surface of plastic waste to a long history of physical and mechanical treatments.

According to Martinho et al. (2012), the sorting equipment used does not have the capacity to reach the level of selectivity required, therefore recycling units produce lower quality products for the recycled

polymer industry and for the energy recovery industry. Also, the great variety of types of equipment and the heterogeneity of polymer composition in the EEE waste stream require a differentiated treatment, focused on the recovery of the most common elements of each stream, which in the case of small equipment should be reflected in the main recovery of polymers like PS and ABS.

Surface modification through physical conditioning methods reduces the use of reagents commonly used in froth flotation method, making them environmentally less harmful and industrially more interesting methods due to their lower cost (Wang et al., 2014c; Wang et al., 2015). These are also simple, effective and reliable methods (Thanh Truc et al., 2017).

Froth flotation is a multivariable and complex method. Salerno et al. (2018) addresses this issue and proposes using experimental factorial designs, seldomly used in plastics flotation, where published works normally use the “one-variable-at-a-time” approach. Using a factorial design, the flotation results undergo a statistical analysis to evaluate not only the effect of the independent variables of the flotation process, but also the effect of interactions that may also occur between variables. The comparison between different studies on plastic flotation is thereby possible and simplified.

4. Materials and methods

The experimental work consisted in the study of the separation of ABS and PS plastics from WEEE using froth flotation, after performing a physical conditioning technique to depress one of the plastics.

The chapter at hand begins with a description of the sampling process, followed by processing and preparation methods of the samples. The physical conditioning technique and the flotation tests are described.

This chapter also addresses the design of experiences developed for the experimental work.

4.1. Sampling process

The experimental work started with the collection of small equipment at the facilities of Ambigroup Reciclagem S.A. The materials under study consisted of small equipment with whole pieces of PS and ABS identified with the constituent polymer (Table 3). Samples were selected according to their provenance and colour. The ABS sample was obtained from an electric blender. Since it was not possible to obtain a significant amount of PS sample for the laboratory work from the equipment found in the small equipment stream, the PS sample came from a television. The appliances presented different colours to ease the analysis of the flotation products by manual sorting and image analysis.

Table 3: Equipment and the plastic collected

Equipment	Plastic	Colour
	ABS	Red
	PS	Black

4.2. Sample preparation

The samples were processed at *Geolab* in Instituto Superior Técnico. The equipment was firstly manually dismantled, then a primary manual fragmentation with a guillotine was conducted in order to reduce the size of the pieces to the feeding size of the Retsch SM 2000 shredding mill (Figure 7). The shredding mill was equipped with an 8 mm sieve. A lower mesh size increased the residence time in the mill thus producing a larger amount of fine fraction that could not be used



Figure 7: Retsch SM 2000 shredding mill

After shredding, the items were classified by dry sieving with a Fritsch Analysette, using sieves with a mesh size of 8.0, 5.6, 4.0 and 2.0 mm for 15 minutes. The analysis of the granulometric distribution is presented in Annex I (Figure 8).

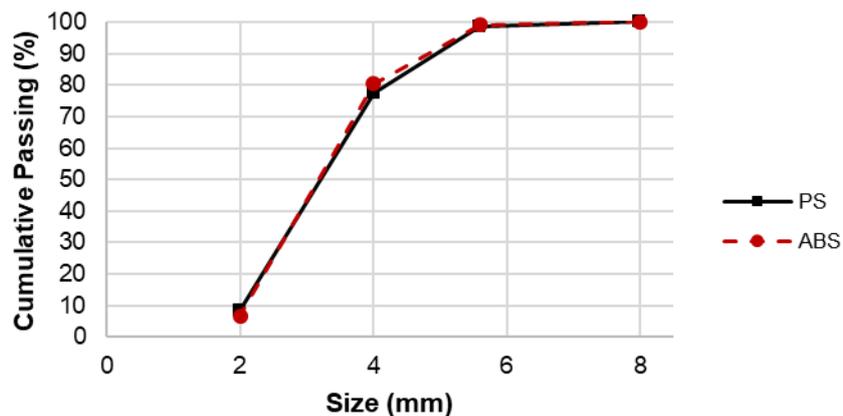


Figure 8: Granulometric curve of ABS and PS samples

Several studies show that the size range most suited to plastic flotation is 2-6 mm (Shent et al., 1999; Marques & Tenório, 2000; Pita & Castilho, 2017). As can be seen from the granulometric curve, both plastic samples show approximately 70% of particles in the 2.0-4.0 mm particle size range after fragmentation. Like in Censori et al. (2016) and Salerno et al. (2018) studies, a narrow particle size of

2,0 to 4,0 mm was selected to the flotation tests so that any unwanted effects of particle size in flotation responses were minimized.

The granulometric fraction to be used in the flotation tests was homogenized with the aid of a Jones splitter. In each flotation test a binary mixture composed of 10 g of each plastic was used (Figure 9).

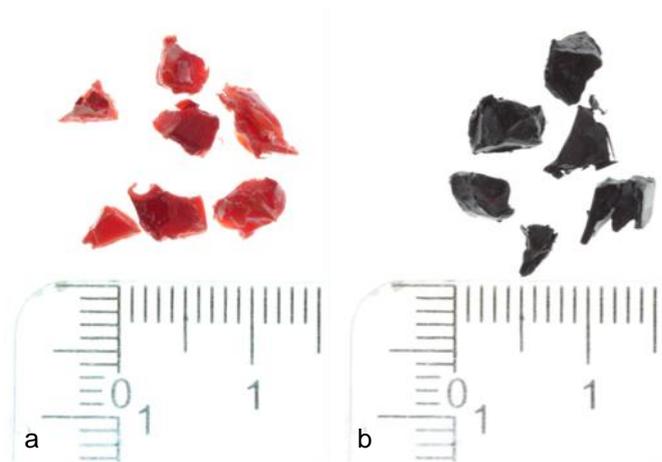


Figure 9: Fragmented plastics in the 2-4mm size fraction (a- ABS, b-PS)

4.3. Experimental method

4.3.1. Physical conditioning

The plastic samples were heated in tap water using a heating plate with magnetic stirring (Figure 10). The treatment followed Wang et al. (2014c) boiling treatment procedure. The samples were soaked and stirred in tap water for 30 min, then the heating plate was switched on to reach a certain temperature and the plastics heated. After that time, the samples were cooled by water directly and left (or not) to rest and later used on the flotation tests.



Figure 10: Treatment apparatus

4.3.2. Flotation tests

The flotation tests were carried out in a single separation stage in a mechanically agitated Leeds Flotation Cell fitted with an extra module and a mid-height placed grid to prevent excessive turbulence, with 5L capacity (Figure 11).. The cell is mechanically agitated by a rotating impeller at the bottom with controllable speed and the compressed air introduced at the bottom, directed to the centre of the impeller blades.



Figure 11: Leeds flotation cell and pH meter

According to Fraunholz (1997), plastics depression in froth flotation must be made in the presence of cations, therefore tap water was used. The reagents used were Methyl Isobutyl Carbinol (MIBC) as frother agent and for the pH modification solutions of 25% of sodium hydroxide (NaOH) and 20% of sulfuric acid (H_2SO_4). Both air temperature during treatment and flotation tests; and flotation water temperature were measured but not controlled.

The flotation process is divided in the following phases:

1. Introduction of the treated samples in the flotation cell;
2. Mechanical stirring of the water-sample system in the cell;
3. Addition of the frother agent (MIBC);
4. Conditioning of the system by the frother agent for 2 minutes;
5. Opening the air valve;
6. Flotation of the samples, with collection of the floated product of 1, 2, 4 and 8 minutes of flotation;
7. Collection of the sunken product;
8. Drying phase of the floated and sunken products;
9. Manual sorting.

4.4. Experimental design

As previously mentioned, the most commonly referred way to evaluate the separation of plastics is the one variable-at-a-time experimentation (OVAT). However, froth flotation is a complex and multivariable process, where interaction between variables affect the process outcome and thus must be studied. Salerno et al. (2018) proposed the use of factorial experimental designs to evaluate the separation of plastics by froth flotation. Factorial experimental designs are methods for planning experiences involving several factors (variables), in which all possible combinations of the factors at different levels are studied. Generally, in an experience considering k factors each to be studied at two levels, the factorial design would require 2^k runs. (Montgomery, 2013). Although useful, factorial experimentation might become unmanageable when considering many factors.

This work studies the impact of a physical conditioning treatment applied to plastics prior to their separation by froth flotation, and used a Taguchi Experimental Design to study the effect of the variables and interaction between variables effects. The Taguchi design is a fractional factorial design of experiments in which only a subset of the factorial design runs is used. Taguchi designs use Orthogonal Arrays (OAs) for designing of experiments, providing the desired information with the least possible number of trials with adequate precision (Krishnaiah & Shahabudeen, 2012). A more in-depth description of the Taguchi design of experiments can be found in Roy (2010) and Krishnaiah & Shahabudeen (2013).

Seven operational variables were studied:

- Treatment time;
- Treatment temperature;
- Elapsed time between the end of the treatment and the beginning of the flotation test;
- Concentration of frother (MIBC);
- Flotation pulp pH;
- Air flow rate;
- Impeller speed.

4.4.1. Preliminary tests

A set of tests was carried out in order to evaluate the effectiveness of the heating treatment in selectively depressing one of the plastics, as well as comparing some preliminary results to the Wang et al. (2014c) boiling treatment results. The frother agent used by the latter was terpeneol. With the boiling treatment applied prior to froth flotation, Wang et al. (2014c) hindered ABS flotation by selectively making the surface hydrophilic. Therefore, it was expected that PS would float, while ABS was expected to remain in the cell.

OVAT tests

A set of OVAT tests was performed to establish the levels for the experimental design, consisting of selecting a baseline set of levels for each factor and then successively varying each factor over its range with the other factors held constant at the baseline level (Montgomery, 2013). A series of tests were made by altering the variables of the treatment and of the froth flotation process, until a response close to the desired one was found, corresponding to a separation between both plastics. The manipulated variables in the OVAT tests were:

- Treatment temperature;
- Treatment time;
- pH.

The elapsed time between treatment and flotation test was kept constant in the OVAT tests. This variable was chosen in order to study a possible reversibility of the treatment.

The air flow rate and impeller speed did not suffer any alteration from the OVAT tests. The chosen ranges were the only ones possible to allow an adequate air dispersion in the cell without too much turbulence.

The MIBC concentration range was chosen taking as a reference Censori et al. (2016) work.

Control tests

A control set was carried out in the absence of the treatment, to figure out the general behaviour of the two plastics.

4.4.2. Design of Experiments using the Taguchi method

The level (value) of the factors tested in the experimental design was established considering the OVAT preliminary tests results. According to the Taguchi design, two levels were chosen for each parameter, plus one centre point.

Unlike full factorial designs that allow an analysis of the variables and interaction effects without aliasing, in the Taguchi experimental designs the effect of interaction between variables is mixed with the main effect of the variables. Thus, when considering interactions special care must be given to the column assigned to each factor.

The variables were assigned to the design columns in order to calculate the main effects without aliasing (Table 4). An L16 (2^7) orthogonal array (OA) of experiments was chosen to determine the effect of the seven manipulated variables (Table 5). The coded values correspond to the minimum and maximum level of a variable and 0 to the centre point between levels -1 and 1.

Some columns were left unassigned and thus have been allocated to calculate the effect of interactions between variables and to calculate the residuals. The allocation of variables was carried out considering the two-variable interaction tables and linear graphs of an L16 OA (Krishnayah & Shahabudeen, 2012).

Three or more variable interaction effects were not studied nor considered due to time restrictions and tests number.

The experimental matrix includes 3 tests on the centre point. A potential concern of using two-level experimental designs is the assumption of linearity in variables effects. Montgomery (2013) noted that if interaction terms are added to a main effect, it is possible that the response model represents some curvature due to a distortion induced on the response surface model. The replication of the design centre points provides an evaluation of the existence of curvature and should allow an independent estimate of the pure error.

Table 4: Coded variables

Column/coded variable	Variable
A	MIBC concentration
B	Air flow rate
D	pH
H	Treatment temperature
K	Impeller speed
M	Elapsed time
P	Treatment time

Table 5: Matrix for the Experimental plan (L16 OA plus three centre point tests with the coded values for variables)

Test	A	B	C	D	E	F	G	H	J	K	L	M	N	O	P
1	-1	-1	--	-1	--	--	--	-1	--	-1	--	-1	--	--	-1
2	-1	-1	--	-1	--	--	--	1	--	1	--	1	--	--	1
3	-1	-1	--	1	--	--	--	-1	--	-1	--	1	--	--	1
4	-1	-1	--	1	--	--	--	1	--	1	--	-1	--	--	-1
5	-1	1	--	-1	--	--	--	-1	--	1	--	-1	--	--	1
6	-1	1	--	-1	--	--	--	1	--	-1	--	1	--	--	-1
7	-1	1	--	1	--	--	--	-1	--	1	--	1	--	--	-1
8	-1	1	--	1	--	--	--	1	--	-1	--	-1	--	--	1
9	1	-1	--	-1	--	--	--	-1	--	-1	--	-1	--	--	1
10	1	-1	--	-1	--	--	--	1	--	1	--	1	--	--	-1
11	1	-1	--	1	--	--	--	-1	--	-1	--	1	--	--	-1
12	1	-1	--	1	--	--	--	1	--	1	--	-1	--	--	1
13	1	1	--	-1	--	--	--	-1	--	1	--	-1	--	--	-1
14	1	1	--	-1	--	--	--	1	--	-1	--	1	--	--	1
15	1	1	--	1	--	--	--	-1	--	1	--	1	--	--	1
16	1	1	--	1	--	--	--	1	--	-1	--	-1	--	--	-1
17	0	0	--	0	--	--	--	0	--	0	--	0	--	--	0
18	0	0	--	0	--	--	--	0	--	0	--	0	--	--	0
19	0	0	--	0	--	--	--	0	--	0	--	0	--	--	0

Table 6 presents the column aliasing with two-variable interaction terms. The aliasing needs to be considered and only with a posterior analysis the interaction effect can be determined.

Table 6: Columns with two-variable interaction terms aliasing

Column	Aliased two-variable interaction term
C	AB MP
E	AD KP
F	BD KM
G	HP
J	AH
L	AK DP
N	AM BP
O	AP BM DK

The Taguchi design does not specify a guideline for variable interaction prediction. These can be predicted whether by experience or by previous experimental studies (Roy, 2010). Two-variable interaction effects were expected between MIBC concentration and pH (AD interaction), as disclosed by Censori et al. (2016). Therefore, column C can be used to determine its effect, although its effect can be confounded with the interaction between elapsed time between froth flotation and treatment time (MP

interaction). Also were expected interaction effects between MIBC concentration and pH (AD interaction); and between treatment time and treatment temperature (HP interaction).

All the tests were randomly performed to ensure the independence of observations and errors.

4.5. Treatment evaluation methods

To evaluate the treatment action on the plastics, some techniques were applied.

The contact angle of the particles before and after the treatment was studied. Several authors refer that the contact angle value depends on surface roughness, which in turn strongly affects the bubble-particle attachment, hence influencing flotation results (Ahmed, 2009; Prajitno, 2016; Kosior et al., 2018; Szczerkowska et al., 2018).

The relationship between roughness and wettability has already been studied by Wenzel (1936). It stated that adding surface roughness to a particle will enhance its wettability. If the surface is already hydrophobic, it will become more hydrophobic when surface roughness is added. To analyse if the wettability changes observed in the contact angle were due to macroscopic textural changes in the particles surface an image analysis tool was developed in Matlab, using the Image Processing toolbox functions to characterize the texture of the plastic particles.

Thermogravimetry analysis (TGA) is widely used in the chemical industry for identification purposes, usually to determine phase diagrams, heat change measurements and decomposition in various atmospheres. The derivate is plotted against time or temperature and mass loss differences between samples can be detected. The derivate thermogravimetry (DTG) incorporates thermogravimety analysis, in which the mass of a sample is measured over time as temperature changes, thereby providing information about physical or chemical phenomena. The plastic samples went through thermogravimetry analysis to analyse its thermal decomposition process. The effect of the components of the plastics, like additives affect its thermal decomposition behaviour and thus affect their recycling, namely using pyrolysis technology. This type of study has been made to provide useful information for optimal design of recycling operations (Kumar & Singh, 2014).

5. Results and discussion

This chapter presents the obtained results and further discussion from the implementation of the methodology described in the previous chapter. It is divided into the following sub-chapters: 1. preliminary tests results, with the results that conducted to the developed Taguchi design; 2. Taguchi design results, with a brief analysis of the separation method and finally the ANOVA. In the ANOVA, it is performed an overview of the effects associated contributions, curvature evaluation and model presentation and evaluation.

The separation process was evaluated by the Recovery of plastic type i (ABS or PS) in the floated products at the end of the flotation test (Equation 1), i.e., the percentage of a specific plastic present in the flotation feed that appears in the floated product; and using the Selectivity Index (SI) (Equation 2). SI is an index proposed by Gaudin (1957) as a convenient measure of a binary separation by denoting the recovery of the two components in each product (floated or sunken) with each other. The Recovery of one of the plastics in the floated product is denoted with the Recovery of the other in the sunken product, calculated in the same way as the Recovery in the floated product. Product purity in both floated and sunken products was also determined.

$$R_i(\%) = \frac{m_{i,\text{floated product}}}{m_{i,\text{feed}}} \times 100 \quad (\text{Equation 1})$$

$$SI = \sqrt{\frac{R_{ABS,\text{floated product}} \times R_{PS,\text{sunken product}}}{(100 - R_{ABS,\text{floated product}}) \times (100 - R_{PS,\text{sunken product}})}} \quad (\text{Equation 2})$$

Where R_{ABS} and R_{PS} are respectively the recoveries of ABS and PS.

From the experimental results and to have knowledge of which variables or interaction had higher interference in the flotation process, the effect for each one was determined. The effect is defined as a change in a response produced by a change in the level of a factor. Frequently the effect is referred to as main effect, because it refers to the primary factors of interest in an experiment (Montgomery, 2013). The main effect corresponds to a difference between the average response at the high level (+) and the average response at the low level (-) of a factor (Equation 3) Equation 3

$$\text{Main Effect} = \frac{\sum y_+}{n_+} - \frac{\sum y_-}{n_-} \quad (\text{Equation 3})$$

Where y_+ and y_- , correspond to the responses at high and low levels and n_+ and n_- to the number of observations of each level.

The statistical significance of the variables main effects and interactions was confirmed by analysis of variance (ANOVA) with a 95% confidence level. ANOVA is a statistical technique used to analyse the differences among group means in a sample, where the observed variance is partitioned into components attributable to different sources of variation, enabling the quantification of the effect of the variables and/or interactions and identification of which ones significantly affect the responses.

The ANOVA uses the sum of squares, which comprises the amount of information attributed to a certain factor, the degrees of freedom of each factor, which are the number of independent elements in the sum of squares, the mean of squares, that is the quotient between the sum of squares and the degrees of freedom. The F value is obtained by dividing the mean of squares of the parameters by the mean square error and was used to estimate the significant terms within the 95% confidence interval. The probability p-value allows an immediate evaluation for decision making.

Since replications were performed, the residuals can be decomposed into two components: a component that is due to the “lack of fit” of the model to the data and a component that is due to pure error. The pure error is determined using the centre points tests. If the lack of fit is significant component of the residual error, it suggests that the response should not be used for predictions. The lack of fit compares the residual error to the pure error from the replicated design point. By considering the Centre Point tests, in the ANOVA it is possible to determine the contribution of the pure error (experimental error) to the residuals.

To evaluate the model fit and its adequacy, the coefficient of determination (R^2), the adjusted R^2 , predicted R^2 and adequate precision were determined. The R^2 represents the proportion of the variance in a dependant variable that can be explained from the independent variables, providing a measure of how well the observed outcomes are replicated by the model. The adjusted R^2 is a modified version of the R^2 that takes into account the number of parameters present in the model thus its complexity. The predicted R^2 indicates how well a regression model predicts responses for new observations. The adequate precision adequate precision compares the range of the values at the design points to the average prediction error. A good predictive model should have a high adjusted R^2 , a low difference between adjusted R^2 and predicted R^2 and an adequate precision higher than 4 to be a model robust to noise.

The Design-Expert 10.0.0 software (Stat-Ease Inc.) was used for the data analysis and model evaluation.

5.1. Preliminary tests

The results of the OVAT and the control set tests were evaluated by the recovery of each plastic in the floated product and the Selectivity Index.

OVAT tests

The variable ranges are presented in Table 7. In Annex II can be found the experimental plan and results for Recovery on the floated product for both plastics and Selectivity Index.

Table 7: Ranges of manipulated variables in the OVAT tests

Variables	Range
pH	4-10
Treatment temperature (°C)	20-100
Treatment time (min)	40-90

Error! Reference source not found. shows the recovery of both plastics in the floated product obtained in kinetic tests carried out under the same conditions, except for treatment temperature, which varied between 20 and 80°C. The recovery of PS in the floated product was strongly affected by treatment temperature, while the overall floatability of ABS was slightly altered.

At constant operating conditions, the recovery in the floated product for a treatment temperature of 100°C produced the same results as with 80°C, between 98 and 99% for ABS and 27 and 29% for PS.

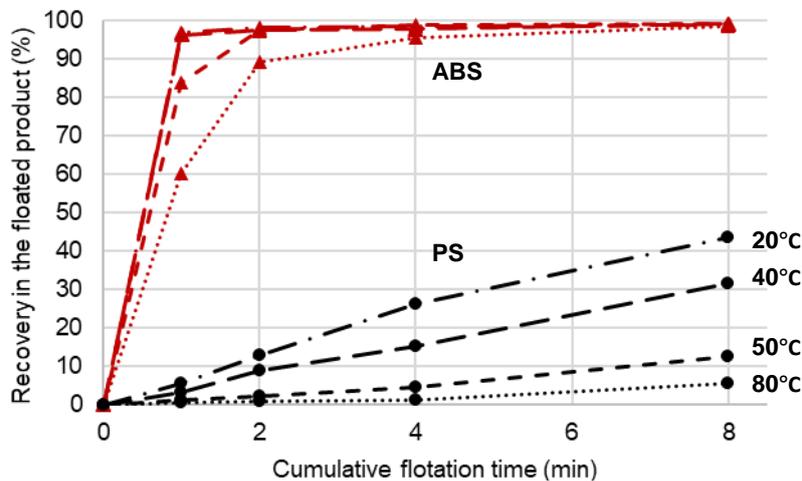


Figure 12: ABS and PS recovery in the floated product over time at variable treatment temperatures. Treatment time: 60min; MIBC concentration: 0,2 mL.L⁻¹; air flow rate: 60 L.h⁻¹; impeller speed: 640 rpm; pH: 10

Furthermore, after being treated at 100°C the plastics presented a change in colour which might indicate a degradation in the plastic properties (**Error! Reference source not found.**).

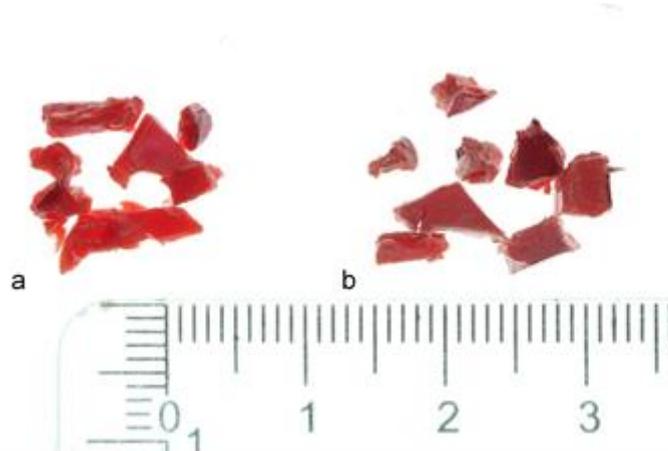


Figure 13: ABS plastic treated at 80°C (a) and 100°C (b)

Therefore, for the previously mentioned and for energy saving reasons, the temperature range chosen to be tested in the Taguchi plan was 40-80°C.

In Figure 14 are presented the pH modification tests results. It can be observed the influence of pH changes, particularly in PS recovery in the floated product. The highest separation efficiency occurred at pH 10, with a SI of 32,17. At pH 4 the SI was 25,96.

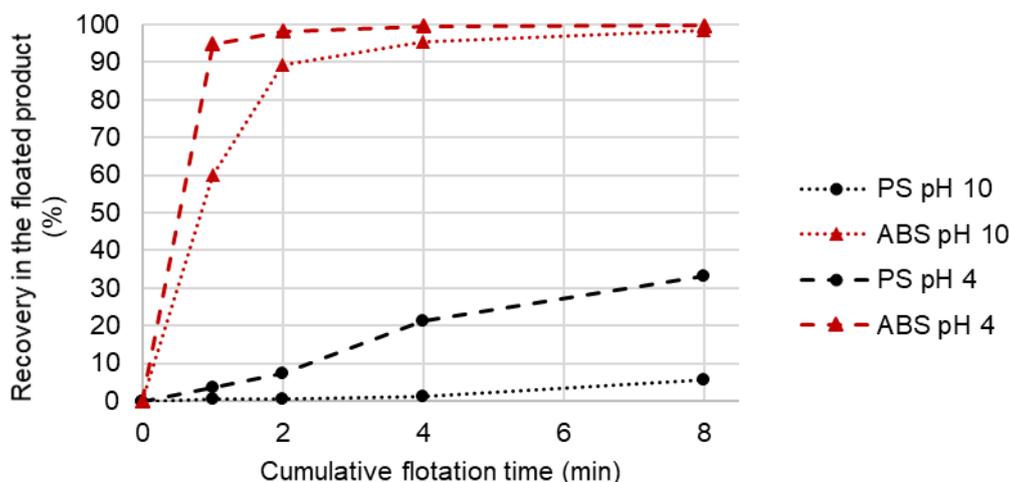


Figure 14: ABS and PS recovery in the floated product over time at variable pH. Treatment time: 60min; Treatment temperature: 80°C; MIBC concentration: 0,2 mL.L⁻¹; air flow rate: 60 L.h⁻¹; impeller speed: 640 rpm

Control tests

The experimental plan of the control tests is shown in Table 8 below.

Table 8: Set of control tests performed on untreated samples

Test	MIBC (mL.L ⁻¹)	Air flow rate (L.h ⁻¹)	pH	Impeller speed (rpm)
1	0,2	40	6	600
2	0,2	40	6	640
3	0,2	60	10	600
4	0,2	60	10	640
5	0,5	40	10	600
6	0,5	40	10	640
7	0,5	60	6	600
8	0,5	60	6	640

Figure 15 shows an overview of the experimental results. As can be seen, the ultimate recovery is higher in the ABS samples than in the PS ones. A selective separation was not achieved with the untreated samples, with an average Selectivity Index of 3,26. In all tests, the ABS maximum recovery in the floated product was between 98 and 99% and PS recovery in the floated product varied between 78 and 92%.

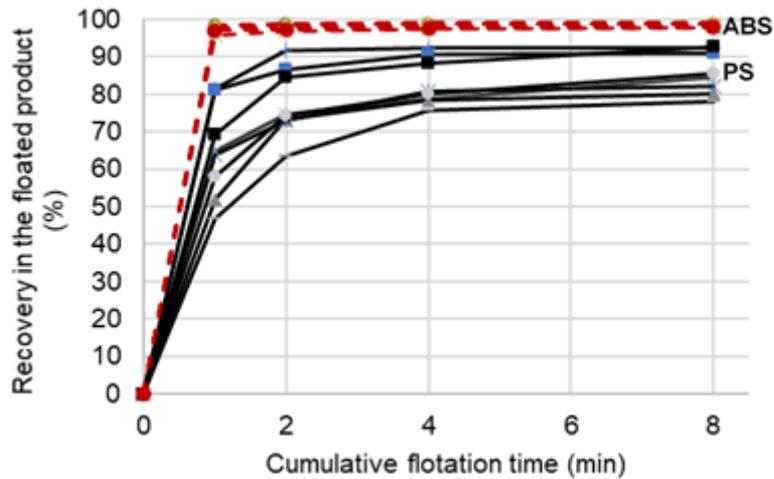


Figure 15: Control ABS and PS (without heating treatment) recovery in the floated product over time (min)

5.2. Taguchi design results

The range of the manipulated variables used for the Taguchi experimental plan are presented in Table 9. The variables were set based on the preliminary test results.

Table 9: Range of the manipulated variables used for the Taguchi experimental plan

Variable	Min -1	Centre 0	Max +1
A MIBC concentration (mL.L ⁻¹)	0,2	0,35	0,5
B Air flow rate (L.h ⁻¹)	40	50	60
D pH	4	7	10
H Treatment temperature (°C)	40	60	80
K Impeller speed (rpm)	600	620	640
M Elapsed time between treatment and flotation (h)	0	12	24
P Treatment time (min)	40	60	80

The experimental results can be found in Table 10. A total of 19 tests were performed, 16 of which were part of the L16 OA. Some statistical results are shown in Table 11.

Table 10: Results of the Taguchi experimental plan

Test	Manipulated variables							Responses		
	A	B	D	H	K	M	P	R _{ABS} (%)	R _{PS} (%)	SI
1	0,2	40	4	40	600	0	40	99,20	30,37	16,90
2	0,2	40	4	80	640	24	80	98,80	29,01	14,22
3	0,2	40	10	40	600	24	80	99,00	9,10	31,38
4	0,2	40	10	80	640	0	40	99,10	30,49	15,88
5	0,2	60	4	40	640	0	80	98,71	38,42	11,06
6	0,2	60	4	80	600	24	40	98,10	7,48	25,28
7	0,2	60	10	40	640	24	40	98,21	55,71	6,61
8	0,2	60	10	80	600	0	80	99,10	23,02	19,19
9	0,5	40	4	40	600	0	80	98,11	29,85	11,05
10	0,5	40	4	80	640	24	40	98,79	25,50	15,43
11	0,5	40	10	40	600	24	40	99,30	5,67	48,67
12	0,5	40	10	80	640	0	80	99,30	14,39	15,76
13	0,5	60	4	40	640	0	40	98,31	28,66	12,02
14	0,5	60	4	80	600	24	80	98,09	3,23	39,17
15	0,5	60	10	40	640	24	80	98,61	15,57	19,60
16	0,5	60	10	80	600	0	40	99,20	28,51	17,58
17	0,35	50	7	60	620	12	60	99,10	17,12	23,04
18	0,35	50	7	60	620	12	60	98,21	10,12	22,05
19	0,35	50	7	60	620	12	60	98,59	41,65	9,90

Table 11: Minimum, maximum, mean and standard deviation of the Taguchi experimental plan

	Response	Unit	Observations	Min.	Max.	Mean	Standard Deviation
R _{ABS}	ABS Recovery in the floated product	%	19	98,09	99,3	98,73	0,44
R _{PS}	PS Recovery in the floated product	%	19	3,23	55,71	23,36	13,68
SI	Selectivity Index		19	6,61	48,67	19,73	10,46

R_{ABS} results show low variability as displayed by the low Standard Deviation (0,44). Conversely, the high Standard Deviation presented by the R_{PS} is evidence that the manipulated variables had an impact in PS floatability and therefore in the process selectivity.

In terms of flotation products, the purity and the selectivity index over flotation time were analysed. The results can be found in Annex II. In Figure 16 can be observed that the purest ABS products are obtained after one minute of flotation with an average of 95,2%, decreasing after that in time. PS purity in the sunken product increases with flotation time. The purest PS product is obtained after 8 minutes of flotation time.

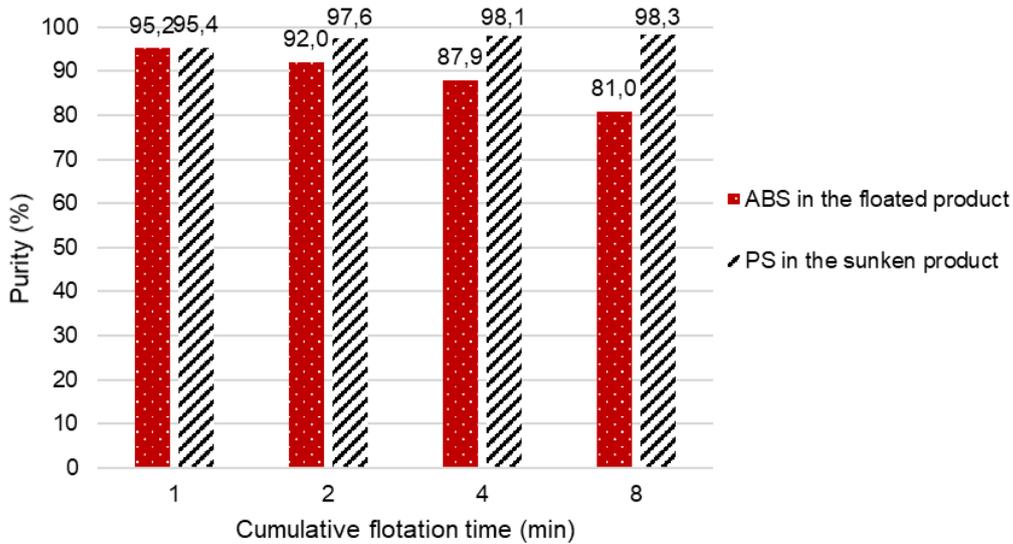


Figure 16: Average product purity over cumulative flotation time

Figure 17 shows an overview of the average Selectivity Index results over flotation time. The selectivity index is higher at one minute of flotation, decreasing with time following the same trend found in the cumulative ABS purity in the floated product.

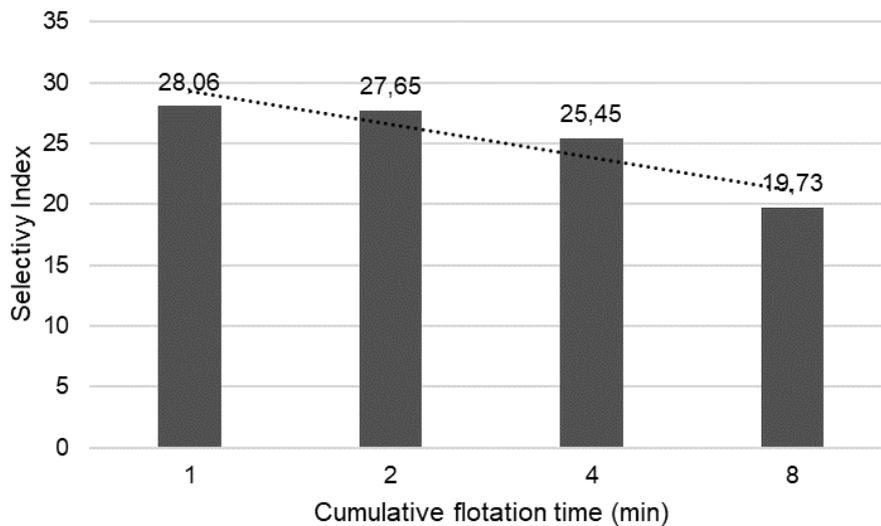


Figure 17: Average Selectivity Index over cumulative flotation time

From the trends in Figure 16 and Figure 17, it can be observed that the selectivity decreases in time, due to an increased PS flotation with time. While ABS purity in the floated product decreases with time, PS increases. This behaviour might be due to uncontrollable factors, namely kinetic factors related to the reagent used.

The correlation coefficient between independent variables and responses is presented in Table 12. The colours identify whether a correlation is positive (red) or negative (blue) and the colour intensity is related to the magnitude of the correlation. After the 19 tests, it appears that relation between independent variables and responses are not very strong.

The most relevant correlations are the following:

- PS recovery: negative correlation with the impeller speed (0,43);
- ABS recovery: negative correlation with air flow rate (-0,44) and positive correlation with pH;
- Selectivity Index: negative correlation with the impeller speed (-0,56) and positive correlation with elapsed time between the end of the treatment and the flotation test (0,46)

Regarding the PS recovery, the negative correlation implies that PS recovery decreases with an increased impeller speed. This indicates that this plastic floatability is more affected by the turbulence inside the cell.

An increase in the air flow rate affects negatively the ABS recovery in the floated product. ABS floatability is affected on how the air is dispersed inside the cell. The positive correlation between pH and ABS recovery indicates that its floatability is promoted at high pH levels.

On account of the Selectivity, this response is more affected by the impeller speed and the elapsed time between treatment and flotation. An increase in the impeller speed decreases the selectivity.

The most relevant correlations between independent variables and responses are related to the flotation process and not to the applied treatment, except for the elapsed time variable.

Table 12: Correlation coefficients between independent variables and responses

	Test	A	B	D	H	K	M	P
R _{PS}	-0,19	-0,31	0,11	-0,04	-0,22	0,43	-0,31	-0,21
R _{ABS}	-0,17	-0,07	-0,44	0,49	0,14	-0,04	-0,28	-0,07
SI	0,09	0,22	-0,11	0,17	0,03	-0,56	0,46	0,02

In order to reach a model that best described the obtained results, an analysis of variance (ANOVA) of the Selectivity Index response was performed. This response combines both PS and ABS response, minimizing PS recovery in the floated product and maximizing ABS recovery in the floated product.

5.3. ANOVA: Selectivity Index

The main variables and interaction effects were firstly determined. The variables with higher effect and consequently higher contribution in the Selectivity Index response can be verified in Table 13. The unassigned columns terms present the possible confounded interaction effects, previously shown in Table 6.

Table 13: Factor effect, sum of squares and % contribution for the Selectivity Index response

Term	Effect	Sum of Squares	% Contribution
A: MIBC concentration	4,84	93,90	4,77
B: Air flow rate	-2,35	22,04	1,12
C: AB/ MP	-1,71	11,73	0,60
D: pH	3,69	54,54	2,77
E: AD/KP	-2,29	21,02	1,07
F: BD/KM	9,83	386,52	19,63
G: HP	-3,16	39,94	2,03
H: Treatment temperature	0,65	1,70	0,086
J: AH	1,50	9,003	0,46
K: Impeller Speed	-12,33	608,12	30,88
L: AK/DP	1,08	4,71	0,24
M: Elapsed time	10,12	409,25	20,78
N: AM/BP	-6,50	169,00	8,58
O: AP/BM/DK	2,41	23,28	1,18
P: Treatment time	0,38	0,59	0,030

The impeller speed and the elapsed time produce high effects in the Selectivity Index. Also unassigned columns F and N presented high effects.

The curvature of the response model was studied using the centre point replicates (Table 14).

Table 14: ANOVA summary for the curvature adjusted model

	Adjusted F-value	p-value	
Model	11,37	0,0005	significant
Curvature	0,32	0,5859	
Lack of fit	0,26	0,9317	

The p-value show that there is no significant curvature effect in the model. Therefore, a linear model can be fit to the data.

The ANOVA results are in Table 15. The response model results from a selection process through which only factors and interactions between them considered as significant for the model were chosen, integrating the remaining variables and interactions to the lack of fit of the residuals.

Table 15: ANOVA results for the Selectivity Index response

Source	Sum of Squares	d.f.	Mean Square	F Value	p-value	
Model	1743,36	7	249,05	12,12	0,0002	significant
A: MIBC concentration	93,90	1	93,90	4,57	0,0558	
B: Air flow rate	22,04	1	22,04	1,07	0,3226	
D: pH	54,54	1	54,54	2,65	0,1316	
K: Impeller speed	608,12	1	608,12	29,59	0,0002	
M: Elapsed time	409,25	1	409,25	19,92	0,0010	
F: BD or KM	169,00	1	169,00	8,22	0,0153	
N: AM or BP	386,52	1	386,52	18,81	0,0012	
Residual	226,03	11	20,55			
Lack of fit	118,94	9	13,22	0,25	0,9444	not significant
Pure error	107,09	2	53,54			
Total	1969,39	18				

Variables with p-value greater than 0,05 were eliminated from the model because they were not significant. Only the impeller speed, elapsed time, and interactions assigned to source F and N were significant model terms. The MIBC concentration, air flow rate and pH variables integrate the model by participating in significant interactions.

The lack of fit F-value of 0,25 implies that the lack of fit is not significant relative to the pure error. The pure error contribution to the residuals is very high. Indeed, as previously depicted, the design includes three replicates at the centre point and even though operating conditions were the same, the responses had great variability, which reflects on the pure error that is based on these repeated experiments.

In order to disclose which interactions were taking part in F and N, the confounded interactions for both model terms were studied. Figure 18 shows the interaction effects plots for air flow rate and pH (BD interaction) and the impeller speed and elapsed time (KM interaction), confounded in the F term effect.

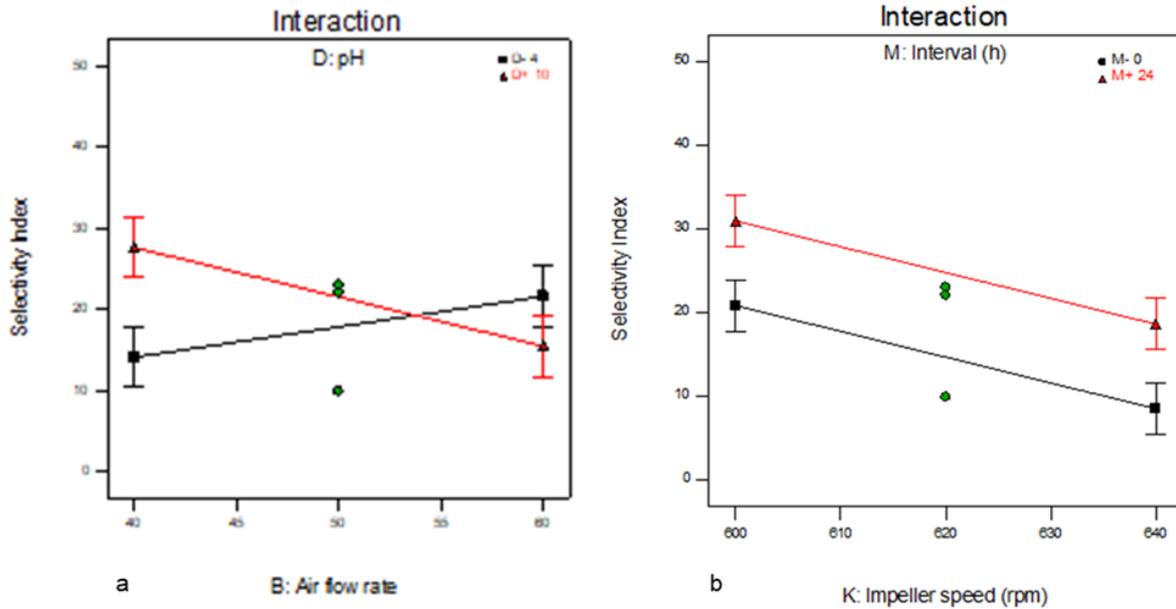


Figure 18: Interaction effects a- BD interaction; b- KM interaction

The effect of the air flow rate is dependent on the pH level (Figure 18a). At lower air flow rates, a higher pH induces a better selectivity. On the other hand, at higher flow rates, the selectivity is not greatly affected by the pH change. In Figure 18b can be observed that the impeller speed and the elapsed time do not present interaction effect. The parallel lines suggest there are no synergies between the two variables. Thus, it can be inferred that the significant effect in model term F corresponds to the interaction between air flow rate and pH (BD).

The same analysis was carried out for the confounded interactions in model term N, the interaction between MIBC concentration and elapsed time (AM) and interaction between air flow rate and treatment time (BP).

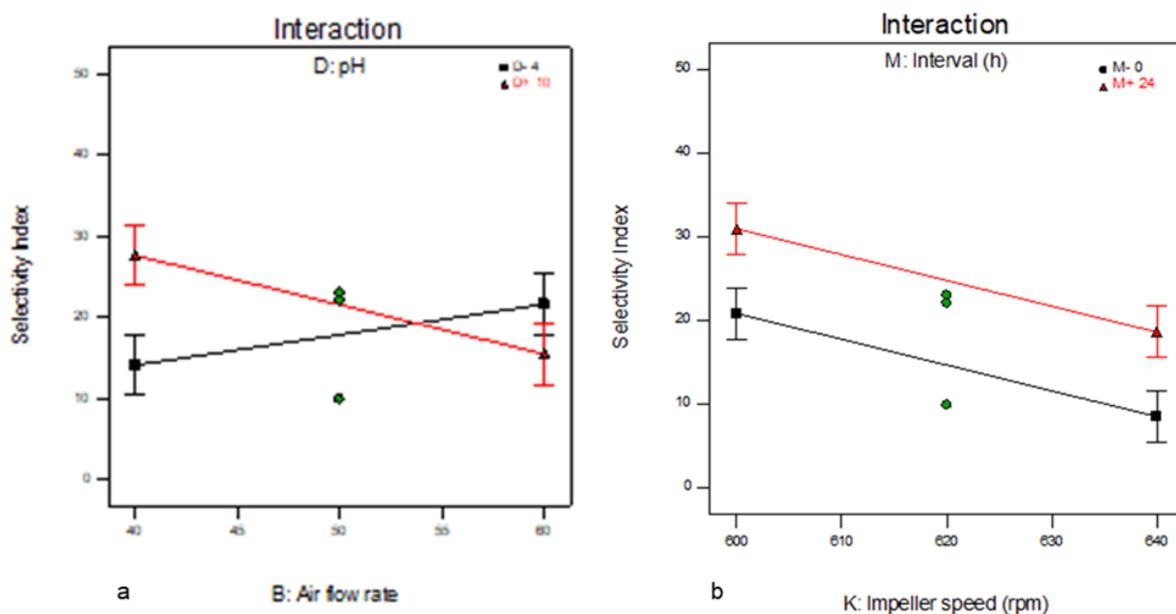


Figure 19: Interaction effects a- AM interaction; b- BP interaction

From Figure 19 can be concluded that the effect of MIBC concentration depends on the elapsed time between the end of the treatment and the flotation test. When MIBC concentration is at the low level, the Selectivity Index is not affected by a change of the elapsed time levels. When increasing MIBC concentration and the elapsed time, Selectivity Index increases. The same type of synergetic relation is not observed in the air flow rate and treatment time interaction (BP) (Figure 19b). The parallel lines indicate the absence of interaction between both variables. Thus, it can be inferred that the significant effect in model term F corresponds to the interaction between MIBC concentration and the elapsed time (AM). Concurrently to what was concluded regarding F, it can be concluded that the effect of N is due to the interaction of air flow rate and elapsed time (AM).

Considering the above, the equation of the linear regression model for the Selectivity Index response is presented in Equation 4, where the low level of variables is coded as -1 and the high level as +1. The coded variables enable the comparison of the relative impact of each variable and interaction by comparing the equation coefficients.

$$SI = 19,73 + 2,42A - 1,17B + 1,85D - 6,17K + 5,06M + 3,25AM - 4,92BD \quad (\text{Equation 4})$$

The equation that models the Selectivity Index response is conditioned by multiple variables and interactions. The coefficients show that the process selectivity is mainly influenced by the impeller speed (K) which is a variable that control particle transport in the cell, namely the impeller speed. The negative value shows that the impeller speed and selectivity are inversely related. When increasing the impeller speed, the selectivity decreases. Increasing impeller speed might cause an increase in cell turbulence thus affecting the bubble-particle aggregate. Selectivity is also influenced by the air flow rate and pH interaction (BD), followed by the interaction between MIBC concentration and the elapsed time between treatment and flotation (AM).

The MIBC concentration (A), air flow rate (B), pH (D) and elapsed time (M) effect should not be considered independently, because their effects are not independent.

For a better understanding of the model, the next figures show the model surfaces for the Selectivity Index response (Figure 20 and Figure 21).

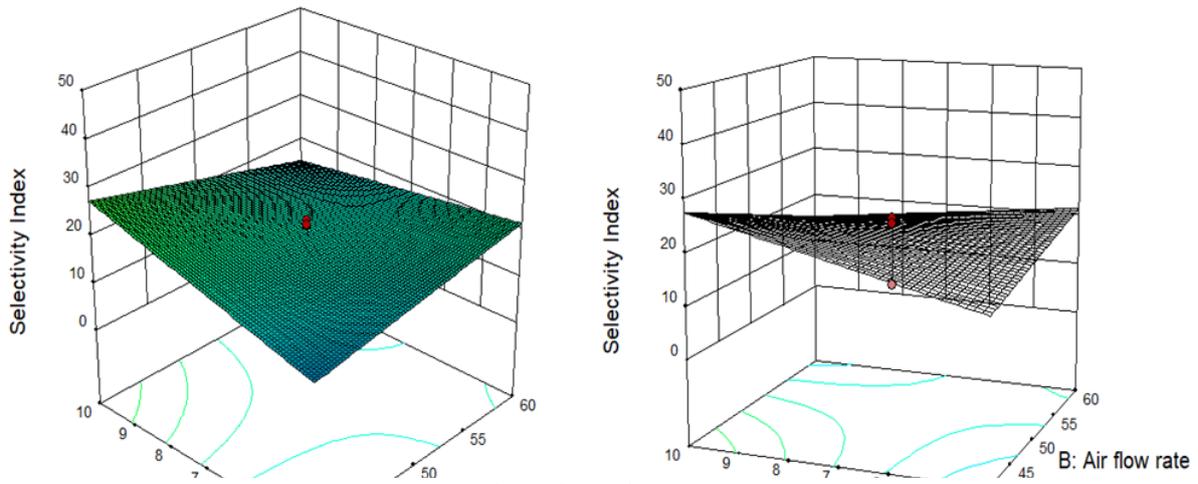


Figure 21: Model surfaces for air flow rate and pH interaction

4 * 40

Both model surfaces present a distortion due to the interaction effect. These models complement the information drawn from the interaction plots previously presented. Regarding Figure 20, when running across the surface model MIBC concentration on itself does not significantly change the selectivity. The same happens with the elapsed time on itself. When MIBC concentration is on the lower level, when changing the elapsed time to a higher level the Selectivity is slightly altered. However, when MIBC concentration is on the higher level and the elapsed time is altered to the high level, selectivity is considerably affected.

Error! Reference source not found. also shows the synergies between the air flow rate and the pH observed in the interaction plot. Both variables present little effect on their own, but the air flow rate effect is dependent on the pH level. At air flow rates, a better selectivity is achieved when pH is on the high. In contrast, at higher flow rates, the selectivity is not greatly affected by the pH change.

The adequacy of the model was further verified by checking the coefficient of determination (R^2), the adjusted R^2 , predicted R^2 and the adequate precision. The results are shown in Table 16.

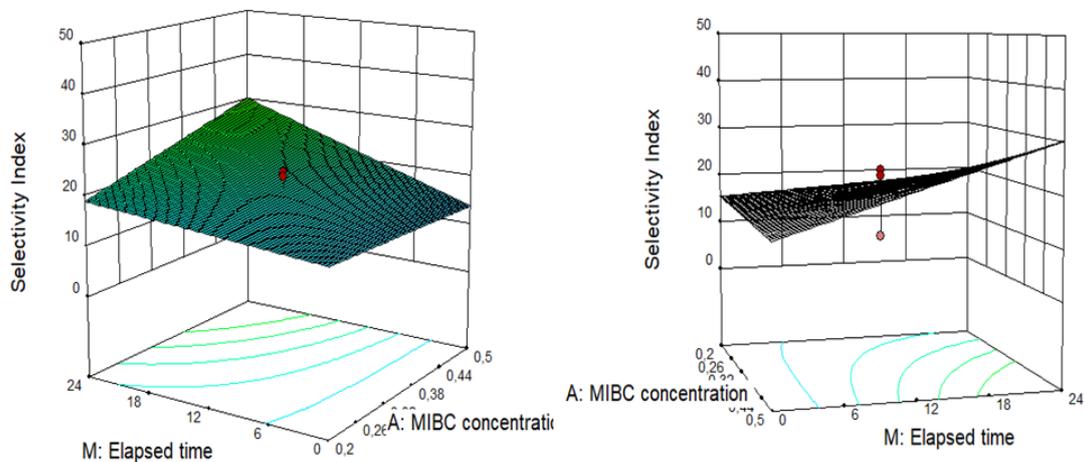


Figure 20: Model surfaces for MIBC concentration and elapsed time interaction

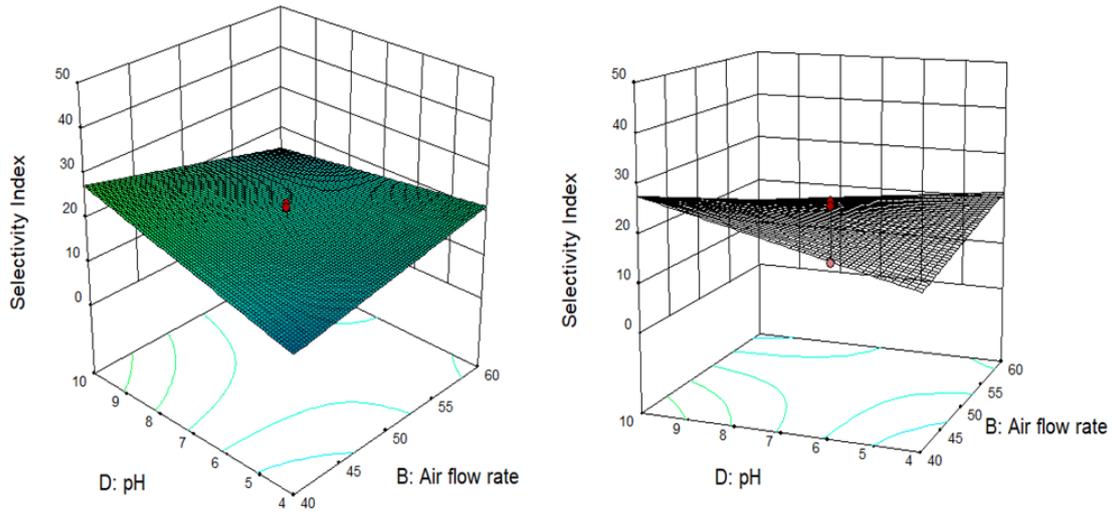


Table 16: ANOVA results for Selectivity Index model adequacy

R^2	0,8855
Adjusted R^2	0,7936
Predicted R^2	0,6506
Adequate precision	11,266

To validate the assumptions of the model, the normal plot of residuals (Figure 22), the residuals vs. predicted values plot (Figure 23) and the residuals vs. run number plot (Figure 24) were used.

Design-Expert® Software
 Selectivity Index
 (adjusted for curvature)

Color points by value of
 Selectivity Index:
 48,67
 6,61

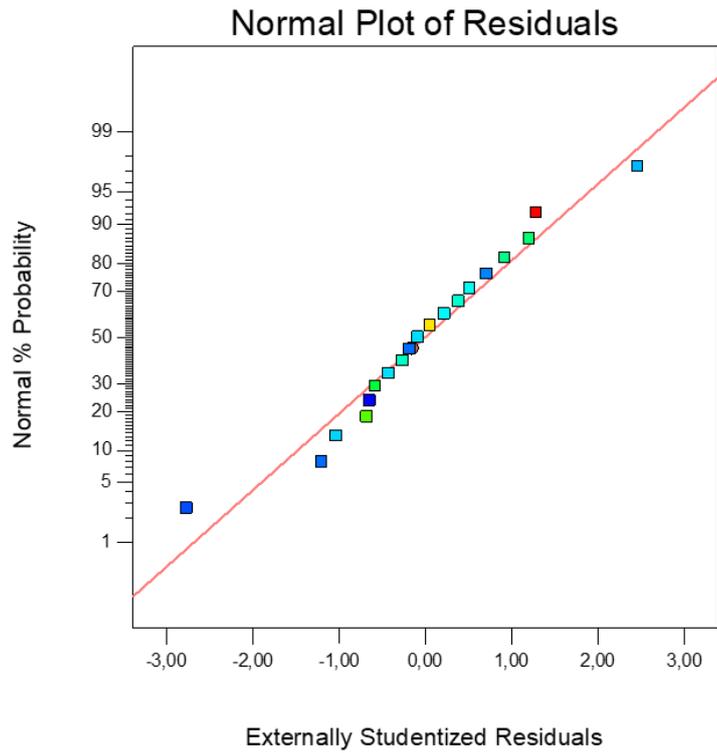


Figure 22: Normal probability plot of residuals

Design-Expert® Software
 Selectivity Index
 (adjusted for curvature)

Color points by value of
 Selectivity Index:
 48,67
 6,61

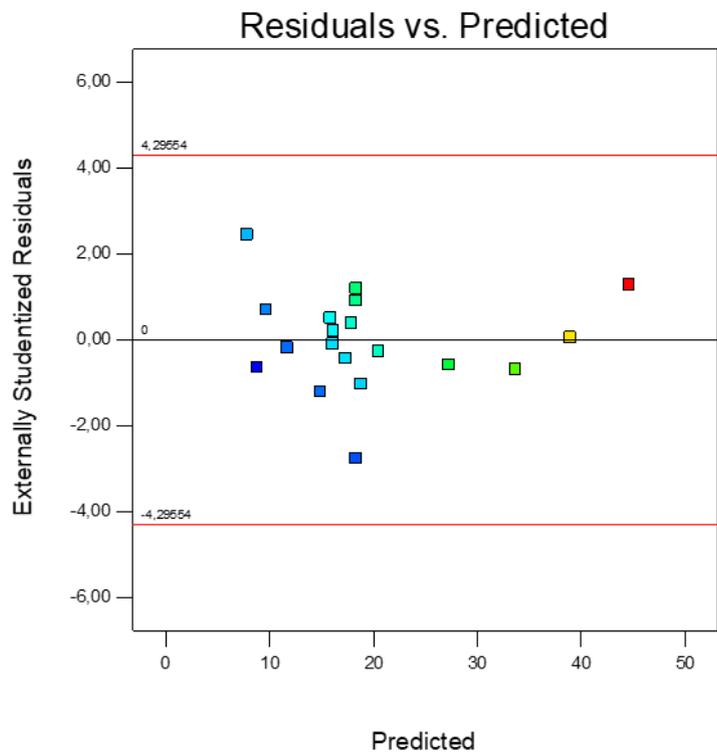


Figure 23: Predicted values vs. residuals

Design-Expert® Software
 Selectivity Index
 (adjusted for curvature)

Color points by value of
 Selectivity Index

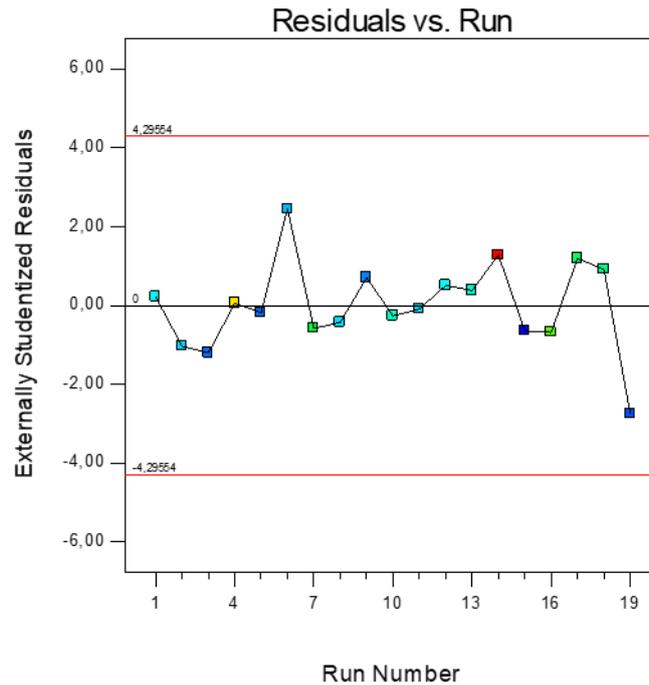


Figure 24: Residuals vs. run test order

From the previous figures, it can be concluded that the residuals follow a normal distribution, have constant variance and are independent. Therefore, the ANOVA assumptions are fulfilled, and the ANOVA is valid.

Data variability and results have characterized the experimental work. Indeed, the L16 orthogonal array of experiments includes three replicates at the centre point and as depicted in the previous sub-chapters even though operating conditions were the same, produced different responses. Considering the centre point projection in the response model highlighted in, the variability between results is also clear.

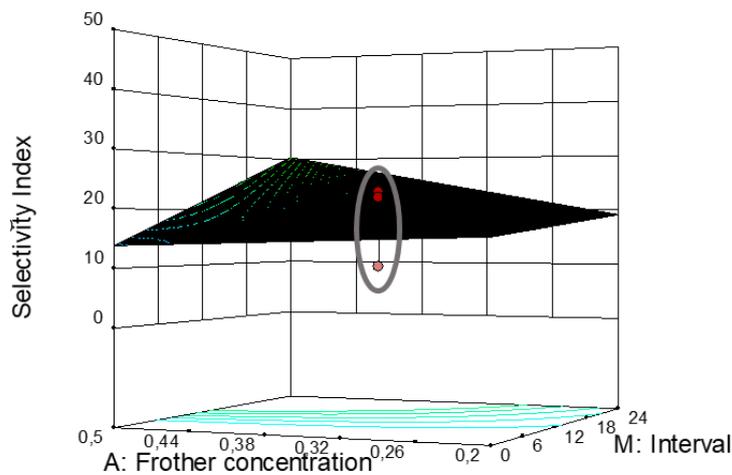


Figure 25: Response model with highlighted centre point replicates

The factors that may be behind the evident variability could be mishandled variables or an uncontrolled and undisclosed noise variable.

The sources of variability could be the surface chemistry of the particles and lack of uniformity in size and shape. This physical characteristic has an important role in the flotation process, as mentioned in the third chapter. Some operating errors or even some cell hydrodynamic issues may be affecting the results. Despite that, the heating treatment presented itself as an effective way to separate ABS and PS plastics since it was possible to obtain an average ABS recovery in the floated product of 98% and the PS recovery ranged from 3 to 55%, indicating that under the treatment conditions PS was depressed while the overall floatability of ABS was slightly altered.

The Taguchi method allowed the identification of the most influencing factors in the experimental work. However, more tests should be carried out to make the model even more robust. It was not possible to model PS response due to its high variability, therefore only the Selectivity Index was modelled. The model with statistical significance which couples the Selectivity Index response with the manipulated variables and interactions is a linear which follows Equation 4 previously shown.

6. Treatment evaluation methods

In light of the results obtained in the experimental work, some supplementary analysis was carried out to understand the different flotation recoveries for both plastics obtained with the treatment. The physical conditioning technique developed and tested in the present dissertation, intended to selectively alter the surface of one of the plastics. Contact angle measurements were taken to evaluate surface wettability changes in both plastics that would affect their floatability. In order to understand the scale of the change, an image analysis tool was developed to analyse surface roughness before and after the treatment. Both plastics were also analysed by thermogravimetry analysis, to evaluate their degradation and study the presence of additives, since they can be a hindering factor for plastic recycling.

6.1. Contact angle results

Contact angle measurements were carried out to evaluate the wettability characteristics of the plastic samples, using the sessile drop method with a goniometer. The apparatus consisted on a JAI CV-A50 video camera with a Wild M3Z microscope and coupled to a frame grabber (Data Translation DT3155), an adjustable light source and a movable support for the syringe and the sample (Figure 26).



Figure 26: Goniometer

The plastic samples had regular shape and size, and at least a flat surface to drop the bubble (Figure 27). The treated plastic samples were heated separately in water at 80°C for 80 minutes.

Samples were cleaned with distilled water separately for the contact angle measurement and left to dry out for 24h. The contact angle was determined by placing a droplet of water on the plastic samples surface. The droplet was illuminated to produce an image with clear edges, which was then reproduced by a video camera.

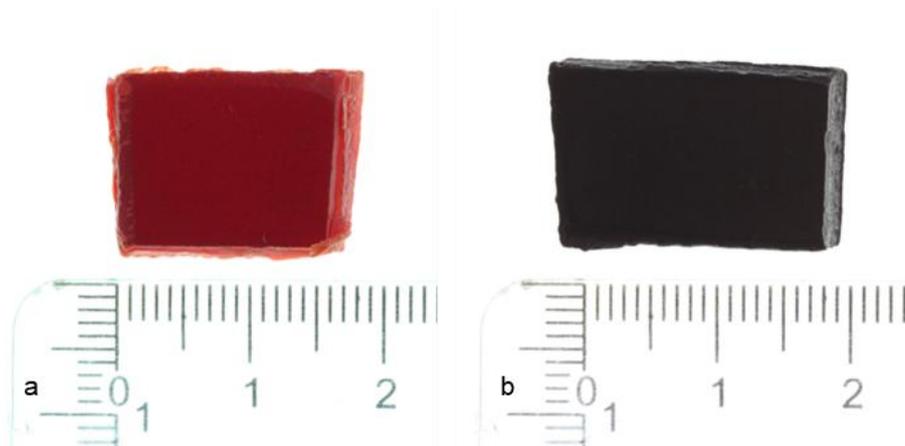
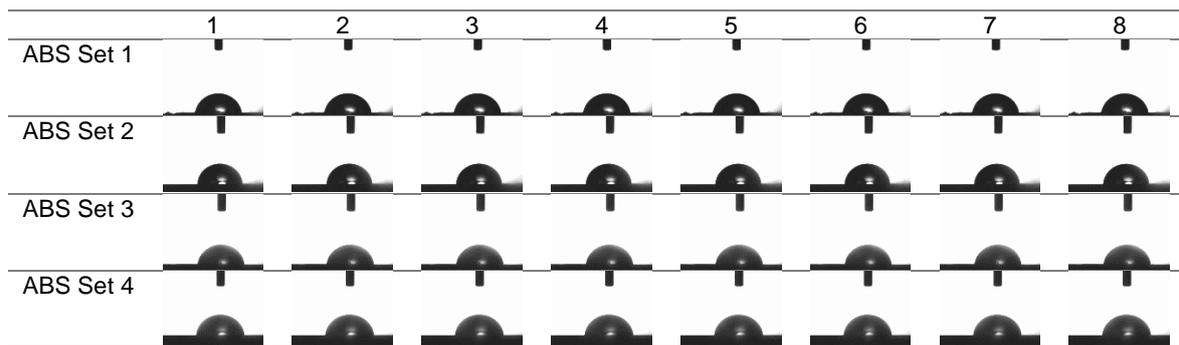


Figure 27: Plastic pieces used to contact angle measurements (a-ABS;b-PS)

A set of four samples of each plastic (treated and untreated) was tested, each sample measured eight times. The plastic contact angle value is an average of the 24 measurements. The images were captured and treated using Matlab. In Table 17 are presented the pictures used to calculate the experimental contact angle for ABS. The measurements can be found in Annex III.

Table 17: ABS contact angle pictures



The experimental contact angles are listed in the Table 18 below, as well as contact angles for ABS and PS from WEEE found in literature for reference.

Table 18: Experimental contact angles for ABS and PS plastics without treatment and treated at 80°C for 80 minutes; contact angles for reference (Shent et al. 1999)

Samples		Experimental contact angle (°)	Contact angle (°) (Shent et al, 1999)
Untreated	ABS	81,9	83,7
	PS	82,0	86,3
Treated	ABS	78,5	-
	PS	75,0	-

Both plastics presented close experimental angles for the untreated samples, which explains the results obtained in the control set. The differences between these results and the ones obtained by Shent et al.

(1999) may be due to different additives present in the plastics for both studies. These results strengthen the case for the presence of different additives in plastics from WEEE.

It is observed a decrease in the contact angle with for both plastics. ABS contact angle decreased from $81,9^\circ$ to $78,5^\circ$ with the treatment, showing a difference of 4% equivalent to $3,4^\circ$. PS contact angle showed a difference of 8,5%, equivalent to 7° . This variation explains different flotation recoveries for both plastics after going through the treatment and the reason why there are significant differences between flotation recovery without the heating treatment. These results also attest that the physical conditioning effectively changes the surface the surface of plastics, rendering PS more hydrophilic than ABS. The slight differences between contact angles of the treated samples (they differ only by $3,5^\circ$) do not fully explain the recovery differences between both plastics. More factors may be interfering, namely MIBC adsorption mechanism on the plastic surfaces. These unknown factors may be behind the high variability that prevailed in the experimental work.

6.2. Image analysis

The image analysis tool was developed in Matlab, using the Image Processing toolbox functions to characterize the texture of the plastic particles. The image analysis using digital image processing was based on the premise that it would obtain comparable results with the contact angle measurements. It should be noted that the present study has an exploratory character and that the validity of the results may be limited. The developed code can be found in Annex IV.

The tool used several texture analysis functions that filtered the provided images using statistical measures. These statistics characterize the texture based on the provided information on the local variability of the intensity values of pixels in the image, quantifying intuitive qualities like roughness as a function of the spatial variation in pixel intensities. For example, in areas with smoother texture, the range of values in the neighbourhood around a pixel is a small value, in areas with rougher texture, this range is larger (Mathworks, 2019).

The analysis consisted in the following steps:

Experimental data acquisition

The images were acquired using a Canon 500 Dequipped with a Canon MACRO 100mm objective lens, placed at 45,2 cm perpendicular to the sample as shown in Figure 28, using a Polaroid MP-4 Land Camera apparatus. Images were acquired in the same light conditions. The plastic samples used for this analysis were of the size fraction 2-4 mm. The treated plastic samples were heated separately in water at 80°C for 80 minutes. The plastics were placed over a table top horizontal light film viewer. Three

images of each plastic were taken, homogenising the sample before each picture was taken to ensure a greater representativeness of the results.



Figure 28: Image acquisition apparatus

Image processing

1. Masking (Figure 29)

The background was removed prior to texture analysis, so that it would not interfere with the results. The background removal was performed first by creating a binary mask image for each image. First, the contrast of the grayscale version of the original image was adjusted. Then, using the histogram, the threshold value of the pixels to include in the mask was defined. Pixels with gray levels over to 220 represented the background, so they were removed. Smaller objects in the mask that did not correspond to particles were eliminated using Matlab built-in function `bwareaopen`. The border of the particles was smoothen using a morphological closing operation with the Matlab built-in function `strel`. The mask was then finally applied to the images, to perform the texture analysis over the image objects.

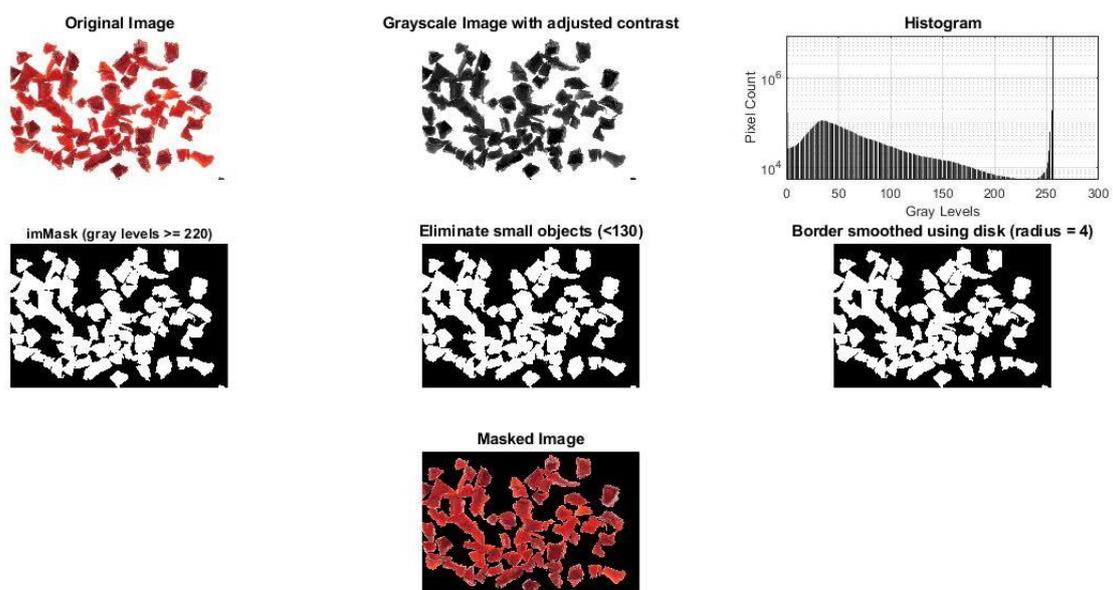


Figure 29: Masking original image of ABS plastics, prior to texture analysis

2. Texture analysis (Figure 30)

The texture analysis was performed over the masked original image. The masked image of the plastics was sharpened to increase image contrast and then converted to grayscale. Afterwards, the built-in function `entropyfilt` was used to filter the grayscaled image. This texture filter function detected regions of texture based on the variation in the grey-level values. Surface contours display more texture and therefore the entropy filter made the edges and contours more visible. The entropy function was used on the texture filtered image, returning a scalar value that represented the degree of randomness in the image. The texture analysis was carried for each plastic type separately.

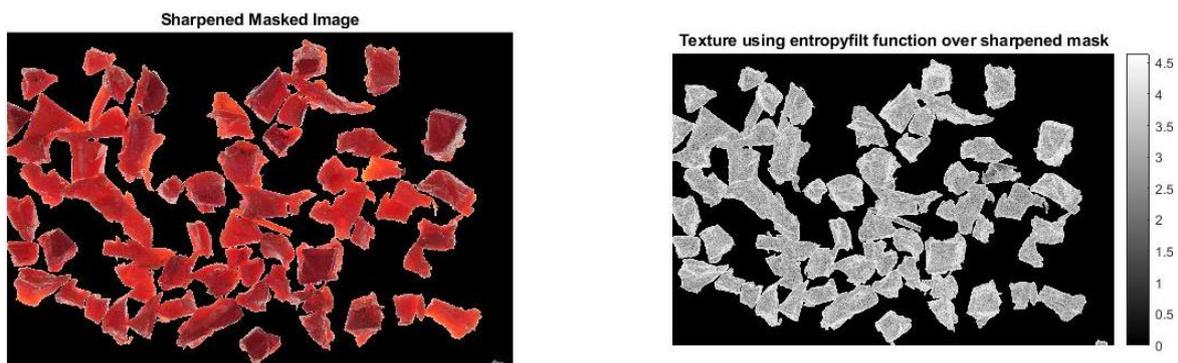


Figure 30: Sharpened image of ABS plastics and texture filtered using `entropyfilt`

The entropy results are listed in Table 19 below. An additional analysis was made for samples treated at 100°C for 80 minutes to contrast the results with the samples treated at 80°C.

Table 19: Entropy results for PS and ABS plastics ABS and PS plastics without treatment and treated at 80°C and 100°C for 80 minutes

Samples		Entropy
Untreated	ABS	1,02
	PS	0,90
Treated 80°C	ABS	1,04
	PS	1,04
Treated 100°C	ABS	0,95
	PS	0,93

From entropy results for the untreated ABS and PS samples, it could be taken into consideration that PS particles surface is smoother, presenting low entropy values. From Figure 9 presented in Chapter 4, slight differences between the surface of both plastic types strengthen this case. PS particles surface appears to be smoother than ABS particles surface and therefore bubbles will attach differently in the flotation process.

However, considering entropy values can vary within the interval $[0, +\infty[$, and that the acquired images entropy values ranged only between 0,90 and 1,04 and that no evident trend can be inferred from the measured alterations, some hypothesis may be drawn:

- The scale of the surface alteration is below the camera resolution ($197,1 \mu\text{m}^2/\text{pixel}$);
- Particles three-dimensionality and the angle on which images were taken may be a drawback on using two-dimensional images to determine a three-dimensional parameter like roughness due to the way light will reflect differently on the different surfaces of the same particle when the sample is agitated between image acquisitions;
- The selective influence of the treatment is attributed to different molecular mobility of the polymer chains, as suggested by Wang et al. (2014c).

6.3. Thermogravimetry analysis

The samples in the size fraction $<2\text{mm}$ were investigated by thermogravimetry analysis coupled with differential scanning calorimetry (TG/DSC) in a crucible under air flow, on the scope of project PTDC/EQU-EQU/29614/2017. Samples of ABS and PS plastics without treatment and treated at 80°C for 80 minutes were analysed, to evaluate whether there was plastic degradation with the treatment and therefore its applicability to the recycling industry.

The obtained TG (mg) and DTG curves (mg/minute/ $^\circ\text{C}$) are presented below.

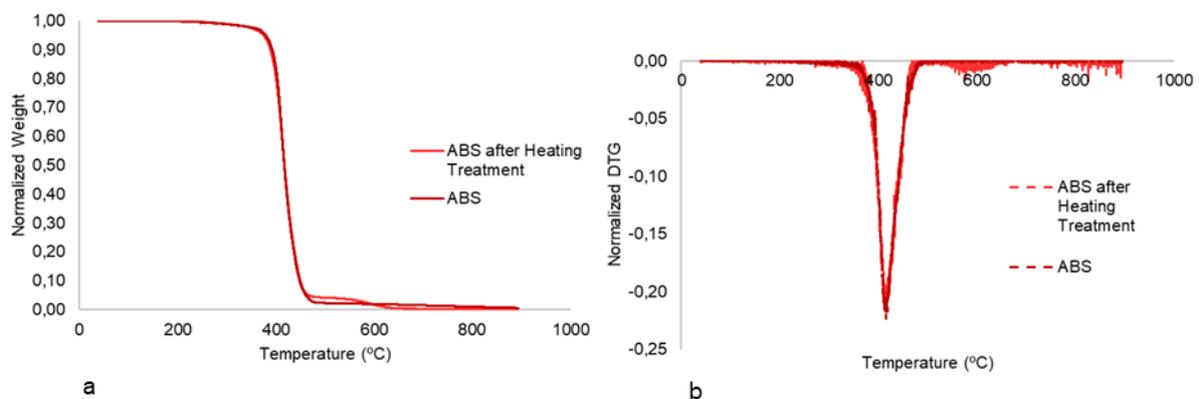


Figure 31: a - TG, b - DTG from ABS treated and untreated samples

Regarding Figure 31, the ABS samples kept a similar degradation profile. The ABS untreated samples degradation profile was also compared with other ABS samples from WEEE and with other TG and DTG curves concerning the homologous virgin and waste plastic (Figure 32 and Figure 33).

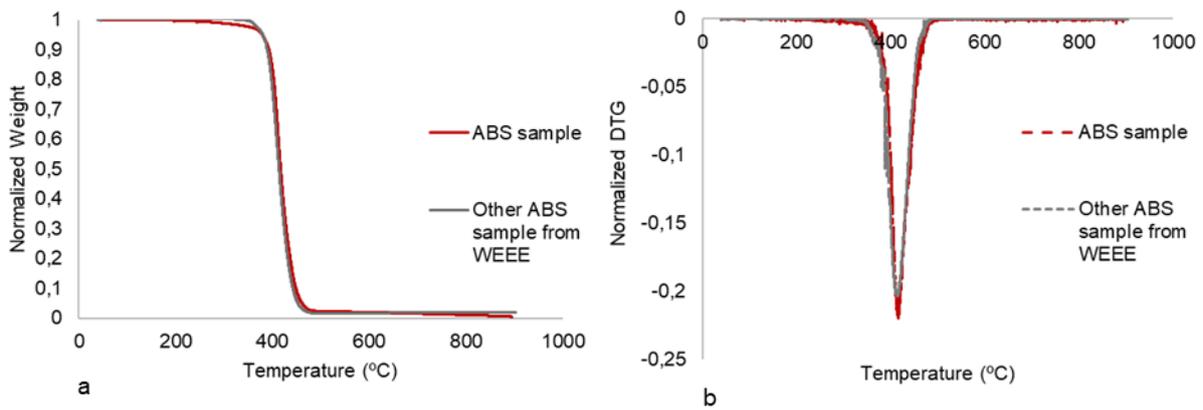


Figure 32: a - TG, b - DTG from ABS untreated samples and another ABS samples from WEEE

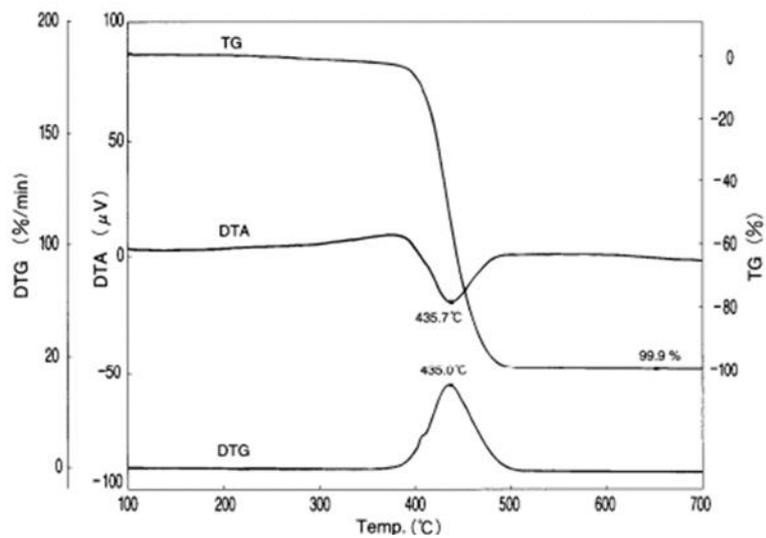


Figure 33: TGA and DTG of virgin ABS (Source: https://www.hitachi-hightech.com/file/global/pdf/products/science/appli/ana/thermal/application_TA_066e.pdf)

The TG and DTG of the thermal degradation curves of the ABS sample was indistinguishable from other ABS samples from WEEE (Figure 32) and also compatible with other TG and DTG curves concerning the homologous virgin plastic (Figure 33).

Additives present in the ABS plastics are not causing a different degradation profile and the treatment is affecting ABS behaviour.

The obtained TG and DTG curves for PS are presented below.

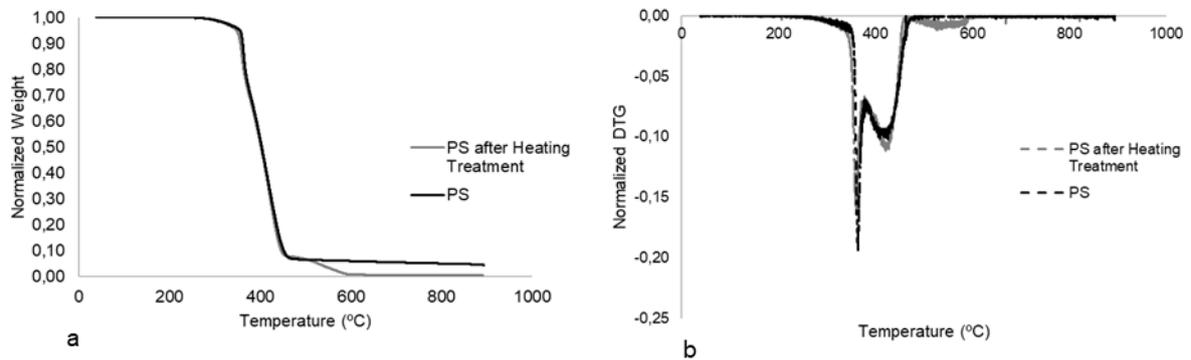


Figure 34: a - TG, b - DTG from PS treated and untreated samples

PS thermal degradation profile, observed in Figure 34, denotes slightly larger differences than the ones observed between ABS. It can be observed that treated PS samples present faster thermal decomposition than the untreated ones. An analysis of other PS samples from WEEE and virgin PS was also carried out. The results are presented in Figure 35.

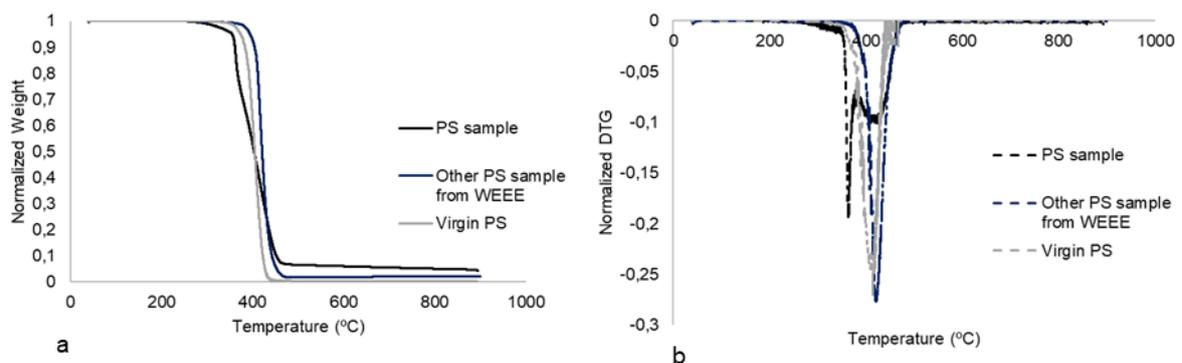


Figure 35: a - TG, b - DTG from PS untreated samples, another PS samples from WEEE and virgin PS

The observed differences between the PS plastics, namely between the original sample and both virgin and from other WEEE might be due to the presence of additives in the plastic, and strengthen the same hypothesis drawn from the differences between contact angles of untreated PS plastics from WEEE.

7. Conclusions and future works

7.1. Conclusions

The thesis framework allows that different conclusions in terms of separation efficiency and statistical analysis can be drawn.

The separation between the two waste plastics ABS and PS was studied, using froth flotation combined with physical conditioning treatment. This treatment consisted in heating in tap water both plastics before the flotation test. Using the treatment, it was possible to obtain an average ABS recovery in the floated product of 98% and the PS recovery ranged from 3 to 55%, indicating that under the treatment conditions PS was depressed while the overall floatability of ABS was slightly altered. These results do not meet Wang et al. (2014c), on which the treatment used was based. This could be either to the different frother used (MIBC instead of terpineol) or different additives present in the plastics in both works.

It was possible to achieve both floated and sunken products with high purity in ABS and PS, respectively. After two minutes of flotation, it was possible to achieve 91% ABS in the floated product and 97% of PS in the sunken product. This method achieves a selective separation. The selectivity index was determined. The greatest Selectivity Index was achieved at one minute of flotation, with a value of 28,06. When increasing flotation time, selectivity decreased.

The froth flotation combined with physical conditioning technique is a suitable technique to separate both plastics, at least under the conditions applied in the experimental plan. The Taguchi design presented itself as an adequate experimentation methodology to correctly identify and evaluate the effect of several operating variables and their predicted interactions on the flotation results. In this study, variables had different influences according to plastic type response, therefore the Selectivity Index response was modelled to a better understanding of the most significant factors.

A linear model was found to explain the selectivity index response and it was demonstrated that impeller speed and elapsed time between treatment and flotation tests, as well as interactions between MIBC concentration and elapsed time, and air flow rate and pH have the most influence on the process efficiency. The R^2 coefficient of 0,8852 is good, thus the model fitted the data properly. The SI response model shows an adequate precision of 12,646, meaning that it is relatively robust to noise. However, data variability and results have characterized the experimental work. The experimental plan included three replicates at the centre point and even though operating conditions were the same, different responses were produced. Further tests should be carried out to disclose the source of variability.

The Taguchi design analysis corroborate Salerno et al. (2018) results. Froth flotation is a complex and multivariable method. Hence, results must be analysed considering this information. Most studies fail in providing a detailed analysis, disregarding variables and interactions.

The conducted supplementary analysis allowed to complement the analysis of the statistical results. The contact angle analysis shows that there is a change in the wettability characteristics of both plastics with the treatment, which explains the different floatability results. The image analysis did not provide further information on how the surface was changed. This could be either due to poor camera resolution,

bad implementation of the image analysis tool or even the wettability change happening at a lower scale, namely in changes in the polymeric chain, clearly not observable in the acquired images. The thermogravimetry analysis showed that this method is suitable to produce products from plastics with proper to deliver to the recycling industry, but more studies are needed.

7.2. Future works

In the end, some suggestions for future works are proposed.

To improve the separation of the two plastics, it is suggested to retreat both floated and sunken products to obtain purer products. The applicability of this treatment for other plastic types should also be studied.

More replicates of the design and using more centre points would produce a more robust model. A full factorial plan considering the significant variables and interactions of this work should be carried out. Due to the observed high variability in the PS recovery in the floated product, it would be interesting to study this response in future works, maybe with more replicates,

To study the wetting mechanism of the heating treatment, further analysis are suggested using Fourier-transform infrared spectroscopy, and the obtained results analysed taking into account Wang et al. (2014c). The study of the adsorption of the frothers on plastic surface should be carried out, because it may be the cause of the different floatability results.

Considering the image analysis technique, the three-dimensionality of the particles should be taken into consideration in the image acquisition method. Furthermore, the shape of the plastic particles should be analysed in future works to study the variability in flotation results.

Finally, an economic feasibility study of the entire process is suggested. The recycled plastic demand should be taken into consideration.

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Annex I – Size distribution after fragmentation

Size (mm)	Mass Retained (g)		% Retained		% Cumulative Passing	
	ABS	PS	ABS	PS	ABS	PS
8,0	0,0	0,0	0,0	0,0	100,0	100,0
5,6	10,6	17,0	1,0	1,3	99,0	98,7
4,0	205,3	288,8	18,6	21,4	80,4	77,3
2,0	812,3	929,5	77,3	68,9	6,8	8,4
<2,0	74,6	112,9	6,8	8,4	0,0	0,0

Annex II – Results

OVAT test plan and Results

Test	MIBC concentration	Air flow rate	pH	Treatment temperature	Impeller speed	Treatment time
1	0,2	60	10	80	640	60
2	0,2	60	10	50	640	60
3	0,2	60	10	20	640	60
4	0,2	60	10	40	640	60
5	0,2	60	8	20	640	60
6	0,2	60	8	40	640	60
7	0,2	60	4	80	640	60
8	0,2	60	10	80	600	60
9	0,2	60	10	100	600	60

Test	% Recovery in the floated product						%Recovery sunken product				SI
	1'		2'		4'		8'		(8')		
	PS	ABS	PS	ABS	PS	ABS	PS	ABS	PS	ABS	
1	0,50	60,10	0,20	29,05	0,50	6,33	4,39	2,91	94,42	1,61	32,17
2	1,29	83,72	1,00	13,79	2,19	1,30	8,07	0,30	87,45	0,90	27,71
3	5,47	96,92	7,29	1,09	13,27	0,40	17,33	0,50	56,64	1,09	10,86
4	3,30	96,18	5,60	1,21	6,30	0,40	16,30	1,21	68,50	1,01	14,64
5	32,37	97,69	16,24	0,30	16,14	0,10	15,24	0,20	20,02	1,71	3,79
6	4,97	95,98	4,08	1,31	10,34	1,01	19,98	0,30	60,64	1,41	10,39
7	3,51	94,73	3,71	3,48	14,03	1,39	11,92	0,10	66,83	0,30	25,96
8	0,50	83,60	1,78	12,98	3,17	2,01	23,07	0,60	71,49	0,80	17,58
9	0,49	83,47	1,69	11,06	3,20	2,60	22,06	0,68	73,00	0,90	10,99
Mean	5,82	88,04	4,62	8,25	7,68	1,73	15,37	0,76	66,55	1,08	17,12
Std. Deviation	9,57	11,48	4,64	9,00	5,52	1,80	5,92	0,82	19,95	0,41	8,96

Control set

Test	% Recovery in the floated product						%Recovery sunken product				SI
	1'		2'		4'		8'		(8')		
	PS	ABS	PS	ABS	PS	ABS	PS	ABS	PS	ABS	
1	51,70	95,79	21,70	0,90	5,10	0,70	1,60	0,20	19,90	2,41	3,17
2	81,14	97,48	5,48	0,30	4,06	0,30	0,41	0,10	8,92	1,81	2,31
3	57,88	97,40	16,36	0,60	5,86	0,10	5,45	0,20	14,44	1,70	3,12
4	69,06	97,07	15,47	0,10	3,79	0,30	4,39	0,40	7,29	2,12	1,90
5	63,87	98,59	9,08	0,20	7,78	0,10	1,30	0,00	17,96	1,11	4,43
6	64,89	97,89	9,73	0,90	4,21	0,20	5,72	0,10	15,45	0,90	4,48
7	46,93	96,49	16,41	1,40	12,19	0,40	2,42	0,00	22,05	1,70	4,04
8	81,29	98,10	10,45	0,40	0,70	0,30	0,00	0,00	7,56	1,20	2,60
Mean	64,6	97,4	13,1	0,6	5,5	0,3	2,7	0,1	14,2	1,6	3,26
Std. Deviation	11,7	0,8	4,9	0,4	3,2	0,2	2,1	0,1	5,4	0,5	0,91

Purity

Test	%Purity of the floated product						%Purity of the sunken product			
	1'		2'		4'		8'		(8')	
	PS	ABS	PS	ABS	PS	ABS	PS	ABS	PS	ABS
1	6,09	93,91	82,11	17,89	89,74	10,26	96,97	3,03	98,87	1,13
2	5,47	94,53	69,77	30,23	95,15	4,85	93,86	6,14	98,34	1,66
3	1,75	98,25	45,00	55,00	79,31	20,69	75,00	25,00	98,91	1,09
4	5,87	94,13	68,27	31,73	98,75	1,25	100,00	0,00	98,72	1,28
5	6,58	93,42	92,39	7,61	98,91	1,09	96,50	3,50	97,93	2,07
6	2,13	97,87	65,22	34,78	77,27	22,73	95,65	4,35	97,99	2,01
7	12,36	87,64	90,80	9,20	90,32	9,68	99,50	0,50	96,09	3,91
8	4,21	95,79	57,84	42,16	89,23	10,77	91,14	8,86	98,84	1,16
9	11,42	88,58	63,64	36,36	97,56	2,44	95,45	4,55	97,62	2,38
10	8,56	91,44	87,14	12,86	100,00	0,00	89,19	10,81	98,42	1,58
11	2,48	97,52	7,32	92,68	12,50	87,50	96,55	3,45	99,27	0,73
12	4,00	96,00	37,93	62,07	95,83	4,17	98,07	1,93	98,92	1,08
13	6,02	93,98	98,11	1,89	97,18	2,82	99,05	0,95	97,68	2,32
14	1,14	98,86	21,43	78,57	83,33	16,67	90,00	10,00	97,99	2,01
15	1,02	98,98	64,29	35,71	63,27	36,73	97,25	2,75	98,37	1,63
16	0,60	99,40	12,24	87,76	61,54	38,46	97,49	2,51	98,90	1,10
17	6,47	93,53	53,06	46,94	68,97	31,03	98,33	1,67	98,92	1,08
18	0,51	99,49	38,10	61,90	90,91	9,09	96,30	3,70	98,03	1,97
19	4,53	95,47	91,23	8,77	97,14	2,86	99,45	0,55	97,64	2,36

Test	% Purity over cumulative flotation time															
	1 minute				2 minutes				4 minutes				8 minutes			
	Floated		Sunken		Floated		Sunken		Floated		Sunken		Floated		Sunken	
	PS	ABS	PS	ABS	PS	ABS	PS	ABS	PS	ABS	PS	ABS	PS	ABS	PS	ABS
1	12,36	87,64	95,35	4,65	18,11	81,89	95,84	4,16	26,45	73,55	97,13	2,87	36,01	63,99	96,09	3,91
2	0,60	99,40	86,04	13,96	2,34	97,66	96,67	3,33	5,31	94,69	98,56	1,44	22,61	77,39	98,90	1,10
3	6,09	93,91	96,60	3,40	12,48	87,52	98,17	1,83	15,06	84,94	98,57	1,43	23,37	76,63	98,87	1,13
4	6,02	93,98	97,82	2,18	10,46	89,54	97,80	2,20	15,73	84,27	97,85	2,15	22,59	77,41	97,68	2,32
5	11,42	88,58	94,96	5,04	14,77	85,23	97,34	2,66	17,94	82,06	97,33	2,67	25,17	74,83	97,62	2,38
6	6,47	93,53	95,69	4,31	8,61	91,39	97,95	2,05	10,20	89,80	98,89	1,11	14,77	85,23	98,92	1,08
7	4,00	96,00	93,34	6,66	6,78	93,22	98,42	1,58	14,16	85,84	98,71	1,29	26,89	73,11	98,92	1,08
8	6,58	93,42	97,27	2,73	13,51	86,49	97,80	2,20	19,89	80,11	97,66	2,34	27,85	72,15	97,93	2,07
9	1,02	98,98	96,12	3,88	1,92	98,08	96,56	3,44	4,81	95,19	98,25	1,75	13,59	86,41	98,37	1,63
10	5,87	94,13	95,61	4,39	11,63	88,37	98,86	1,14	17,41	82,59	98,87	1,13	23,38	76,62	98,72	1,28
11	1,75	98,25	96,00	4,00	2,62	97,38	97,01	2,99	4,80	95,20	97,54	2,46	8,45	91,55	98,91	1,09
12	2,48	97,52	94,24	5,76	2,68	97,32	97,80	2,20	2,83	97,17	99,19	0,81	5,41	94,59	99,27	0,73
13	0,51	99,49	96,60	3,40	1,31	98,69	97,82	2,18	2,29	97,71	97,89	2,11	9,30	90,70	98,03	1,97
14	5,47	94,53	96,24	3,76	8,07	91,93	97,45	2,55	15,74	84,26	97,73	2,27	22,68	77,32	98,34	1,66
15	8,56	91,44	96,92	3,08	13,47	86,53	97,71	2,29	16,38	83,62	97,60	2,40	20,75	79,25	98,42	1,58
16	1,14	98,86	95,66	4,34	1,72	98,28	97,82	2,18	2,21	97,79	97,91	2,09	3,08	96,92	97,99	2,01
17	2,13	97,87	96,75	3,25	3,56	96,44	97,48	2,52	5,13	94,87	97,94	2,06	7,10	92,90	97,99	2,01
18	4,21	95,79	93,55	6,45	9,29	90,71	97,51	2,49	13,84	86,16	98,13	1,87	18,84	81,16	98,84	1,16
19	4,53	95,47	97,53	2,47	9,13	90,87	97,92	2,08	19,29	80,71	98,06	1,94	29,70	70,30	97,64	2,36
Mean	4,80	95,20	95,38	4,62	8,02	91,98	97,58	2,42	12,08	87,92	98,10	1,90	19,03	80,97	98,29	1,71
Std. Deviation	2,70	2,70	1,56	1,56	4,34	4,34	0,50	0,50	6,21	6,21	0,46	0,46	7,55	7,55	0,56	0,56

Selectivity

Test	%Selectivity Index as a function of time											
	1 minutes			2 minutes			4 minutes			8minutes		
	PS	ABS	SI	PS	ABS	SI	PS	ABS	SI	PS	ABS	SI
1	96,72	93,71	20,94	98,41	85,91	19,42	98,81	82,42	19,69	99,20	69,63	16,90
2	96,31	94,42	21,02	97,61	91,43	20,87	98,11	81,66	15,19	98,80	70,99	14,22
3	95,88	98,30	36,70	96,99	97,40	34,73	97,59	95,10	28,04	99,00	90,90	31,38
4	95,72	93,98	18,69	99,00	86,86	25,65	99,10	78,94	20,37	99,10	69,51	15,88
5	97,41	93,08	22,50	98,11	84,55	16,85	98,21	75,43	12,97	98,71	61,58	11,06
6	96,70	97,91	37,02	97,50	96,41	32,37	98,00	94,72	29,64	98,10	92,52	25,28
7	95,83	86,37	12,06	96,62	78,46	10,20	98,11	64,43	9,70	98,21	44,29	6,61
8	93,40	95,90	18,18	97,70	89,99	19,54	98,40	84,18	18,09	99,10	76,98	19,19
9	94,78	88,94	12,08	97,44	84,72	14,54	97,56	80,70	12,92	98,11	70,15	11,05
10	97,07	91,04	18,34	97,98	84,96	16,55	97,98	81,08	14,41	98,79	74,50	15,43
11	94,02	97,61	25,36	97,81	97,31	40,21	99,20	97,11	64,73	99,30	94,33	48,67
12	93,13	96,12	18,34	98,51	92,84	29,26	98,91	83,70	21,54	99,30	63,52	15,76
13	97,91	93,73	26,46	98,01	88,56	19,51	98,21	81,69	15,63	98,31	71,34	12,02
14	95,67	98,85	43,64	97,89	98,23	50,64	97,99	97,71	45,52	98,09	96,77	39,17
15	96,02	99,00	48,95	96,52	98,10	37,89	98,31	95,01	33,28	98,61	84,43	19,60
16	83,60	99,50	32,01	96,58	97,72	34,81	98,59	94,55	34,86	99,20	71,49	17,58
17	95,78	93,39	17,92	98,09	90,79	22,52	99,00	88,79	27,94	99,10	82,88	23,04
18	96,51	99,50	74,11	97,81	98,70	58,13	97,91	97,70	44,52	98,21	89,88	22,05
19	97,59	95,37	28,86	98,09	90,14	21,66	98,49	76,46	14,56	98,59	58,35	9,90
Mean	95,27	95,09	28,06	97,72	91,22	27,65	98,34	85,86	25,45	98,73	75,48	19,73
Std. Deviation	3,03	3,53	14,69	0,65	5,83	12,30	0,47	9,02	13,81	0,43	13,45	10,18

Annex III – Contact Angle measurements

No treatment

		1	2	3	4	5	6	7	8
ABS	Set1	78,4134	78,5395	78,4563	78,3176	78,0888	78,604	78,4822	78,4409
	Set2	86,1755	85,7735	85,7981	84,9668	84,8621	84,6216	84,8385	84,4933
	Set3	81,7993	81,7679	81,645	81,7643	81,6228	81,4415	81,498	81,5886
	Set4	82,3067	82,369	82,1393	82,1028	82,661	82,1622	82,1231	82,032
PS	Set1	96,8476	93,0626	89,7579	87,3383	84,992	83,5107	82,5625	81,8145
	Set2	78,4527	77,1529	76,0787	74,8643	74,3501	73,2808	72,3451	
	Set3	89,8998	88,23	84,7845	81,6737	81,3061	81,2308	80,7211	
	Set4	90,538	88,451	83,8349	80,7139	79,1353	77,673	76,1884	74,6182

With heating treatment (treatment temperature 80°C)

		1	2	3	4	5	6	7	8
ABS	Set1	75,1756	74,657	74,9611	74,9242	74,8622	74,9398	74,787	74,8162
	Set2	74,2155	74,1299	74,3133	74,0384	73,873	73,9596	73,8701	73,9844
	Set3	90,4769	88,2248	84,6545	82,9558	81,5506	81,1112	80,0956	79,7985
	Set4	81,6498	81,7097	81,4914	81,5517	81,2666	81,4817	81,348	81,294
PS	Set1	78,7091	77,8441	75,751	73,7576	72,8268	71,9146	70,9188	70,2261
	Set2	82,737	81,4378	80,1114	77,5497	76,3116	75,2715	74,6708	74,506
	Set3	84,5902	80,9321	76,6752	75,2327	74,687	73,8623	73,5229	73,3111
	Set4	80,0358	78,458	74,9517	70,6504	68,9294	67,25448	66,8102	66,6159

Annex IV – Image Analysis Tool code

```
% Adapted from Simple Color Detection - Demo macro to very, very simple
% color detection in RGB color space by ImageAnalyst

% Being tested for red and black particles arranged over a plain with white
% light underneath to remove background

function E = TextureAnalysis(fullImageFileName)

%----- Create Output Folder -----%

% % An output folder with the original image name is created in the Results
% % directory.
% %
temp = strsplit(which(fullImageFileName), '\\');
temp2 = strsplit(temp{end}, '.');
outputFolderName = [temp{end-1}, '\\', temp2{1}];...
% ['C:\Users\Francisca Rey\Dropbox\_Tese\2_Trabalho
Experimental\Results\', ...
% temp{end-1}, '\\', temp2{1}];
mkdir(outputFolderName)

%----- Masking Part -----%

figure;
% Maximize figure
set(gcf, 'Position', get(0, 'ScreenSize'));

% Read in image into an array

[rgbImage, storedColorMap] = imread(fullImageFileName);
[rows, columns, numberOfColorBands] = size(rgbImage);

% Display original image

subplot(3,3,1);
imshow(rgbImage);
title('Original Image', 'FontSize', 11);

G = imadjust(rgb2gray(rgbImage)); % grayscale da imagem original com
contraste ajustado
subplot(3,3,2);
imshow(G);
title('Grayscale Image with adjusted contrast', 'FontSize', 11);

% Compute and plot the grayscale image histogram

% counts count the number of pixels by intensity level - grayLevels
% and its values in the gray scale

subplot(3,3,3);
[counts, grayLevels] = imhist(G);
maxGLValue = find(counts > 0, 1, 'last');
minGLValue = find(counts > 0, 1, 'first');
[maxCountR, positionMaxCount] = max(counts);
bar(counts, 'k');
grid on;
```

```

xlabel('Gray Levels');
ylabel('Pixel Count');
title('Histogram','FontSize',11);

imMask = true(size(G));
imMask(G >= 195) = false;
subplot(3,3,4);
imshow(imMask);
% title('imMask');
title('imMask (gray levels>= 195)');

% Filter out small objects

imMask = bwareaopen(imMask,130);

subplot(3,3,5);
imshow(imMask, []);
title('Eliminate small objects (<130)','FontSize',11);

% Smooth the border using a morphological closing operation, imclose()
% structuringElement = strel('disk',10); % testado para azul e branco

structuringElement = strel('disk',4);
imMask = imclose(imMask, structuringElement);
subplot(3,3,6);
imshow(imMask, []);
title('Border smoothed using disk (radius = 4)','FontSize',11);

% Fill in any holes - do NOT apply when there are a lot of 'empty' spaces
% between objects

% imMask = uint8(imfill(imMask,'holes'));
% subplot(3,4,7);
% imshow(imMask, []);
% title('Regions Filled','FontSize',11);

% imMask = cast(imMask, class(rgbImage)); % imMask was logical

for Ind=3:-1:1
    aux_var{Ind}=rgbImage(:, :, Ind);
    aux_var{Ind}(~imMask)=NaN;
    maskedImage(:, :, Ind)=reshape(aux_var{Ind}, rows, columns);
end
subplot(3,3,8);
imshow(maskedImage);
title('Masked Image','FontSize',11);

%----- Texture Analysis -----%

maskedSharpen = imsharpen(maskedImage);
figure;
subplot(2,1,1);
imshow(maskedSharpen);
title('Sharpened Masked Image','FontSize',11);

rFiltImage = rangefilt(rgb2gray(maskedSharpen));
% Eliminate edges
rFiltImage(rFiltImage>170) = 0;
subplot(2,1,2);

```

```
imshow(rFiltImage);
title('Texture using rangefilt function over sharpened mask',...
      'FontSize',11);

E = entropy(rFiltImage);
title('Texture using rangefilt','FontSize',11);
E = entropy(rFiltImage);

%----- Save Images -----%

save([outputFolderName, '\masks.mat'],...
     'rFiltImage',...
     'maskedImage',...
     'rgbImage')
end
```