Separation of WEEE plastics resorting gravity separation and froth flotation

Mara Raquel Simões Dias

Thesis to obtain Master of Science Degree in Geological and Mine Engineering

Instituto Superior Técnico, Technical University of Lisbon, Lisbon, Portugal

Abstract

The aim of this research was to separate plastics from WEEE, using gravity concentration techniques (fluidization and heavy liquid separation) and froth flotation.

By using fluidization, from eight mixed-plastics wastes including polypropylene (PP), acrylonitrile-butadiene-styrene (ABS), styrene-acrylonitrile (SAN), polystyrene with ($PS_{c/}$) and without ($PS_{s/}$) mineral fillers, polyamide 6 (PA_6), polyoxymethylene (POM) and polyvinylchloride (PVC) resulting in a pure product of PP and two polymer blends: ABS+$PS_{s/}$+SAN and POM+PVC+$PS_{c/}$, not getting through a simple diagram of fluidization a product of PA_6.

Froth flotation was the second technique applied, in order to separate the blends obtained before. It was studied the mixtures ABS/$PS_{s/}$ and POM/PVC, with the recovery of 67% of ABS in the floated product, contaminated by some PS, and a product of POM, with about 4% contamination by PVC.

In flotation using sodium hydroxide as heavy liquid, was obtained a pure product $PS_{S/}$ in the non-floated product and ABS with some contamination by $PS_{s/}$ in the float product.

INTRODUCTION

Traditional materials as wood, metal, ceramic and glass have being replaced by plastic, since plastics materials are cheap, functional, easy to produce, light and versatile. (Burat, *et al.*, 2009) As the consumption increased the plastic waste increases as well, becoming a major problem in waste management, from the 47 million tonnes of plastics consumption in E.U. in 2011, 25,1 million tonnes ends up in the waste stream (PlasticsEurope, 2012).

The increasing amount of plastic waste is placing great pressure on limited landfill space; hence most polymers take hundreds of years old to decompose when being place in landfill. (Takoungsakdakun, *et al.*, 2007) Plastic waste need to be recycled for both economic and environmental reason (Burat, *et al.*, 2009), in order to do that in an efficient way, plastic waste is separated accordingly to their origin.

Waste electrical and electronic equipment (WEEE) makes one of the most complex stream, hence electrical electronic equipment (EEE) covers a wide variety of products, ranging from mechanical devices such as microwaves ovens to highly integrated systems such as computers and mobile phones (Martinho, *et al.*, 2012) contained on average 30% of plastics materials (WRAP, 2009).

The plastic recovery from WEEE is challenging because of the presence up to 15 different types of engineering plastics, and the numerous additives (organic and inorganic) capable of changing the material properties. (Martinho, *et al.*, 2012)

The experimental work presented, described the study of the separability of polypropylene (PP), acrylonitrile-butadiene-styrene (ABS), styrene-acrylonitrile (SAN), polystyrene (PS) – with ($PS_{c/}$) and without ($PS_{s/}$) mineral fillers –, polyamide 6 (PA_6), polyoxymethylene (POM) and polyvinyl chloride (PVC), from small WEEE by minerals processing techniques: gravity concentration and froth flotation. This study was include in the project "", financed by *Fundação para a Ciência e Tecnologia* (FCT). The partners of the project was CERENA, a research center if *Instituto Superior Técnico*, PIEP, a research center of Minho University, *Recielectric*, a recycling unit, responsible for the collection of WEEE.

In this research were used 2 techniques of gravity concentration: the fluidization bed technique and the flotation using NaOH as heavy liquid, and froth flotation. Fluidization bed in order to separate different specific weight plastics from the eight mixed-plastic, froth flotation in order to separate the blends obtained as product of the fluidization bed and flotation using NaOH as a heavy liquid in order to separate a mixture of ABS/PS without mineral fillers.

Fluidization bed is the cheapest gravity separation technique and has the simplest methodology as well. A column full with water with an ascending flow of water (hydraulic flow - Q_H) drags the particles, according their shape, size and density, to the overflow product. This technique is very effective in the separation of materials with different specific weight, not so much with materials with a similar one.

To try achieving a successful separation of similar specific weight plastics, froth flotation was applied. Similarly to the froth flotation of minerals, the physical separation of the plastics is achieved by creating an adequate physic-chemical environment to carry on a selective modification of the plastics surface. Since plastics are naturally hydrophobic materials, the separation between plastics types can be achieved by increasing the wettability of plastic surface selectively. (Carvalho, *et al*., 2012) According with Shent, *et al.* (1999), froth flotation of plastics can be divided in 4 methods: (1) gamma flotation, reduction of the liquid surface tension to a value between the critical surface tension of the two plastics; (2) selective wetting by chemical conditioning (adsorption of wetting agents); (3) selective wetting by physical conditioning such as plasma treatment or corona discharge; (4) selective hydrophobic modification by chemical conditioning. In this work, was used the method of selective wetting by adsorption of wetting agent. Some authors applied an alkaline treatment to the plastics, stirring the plastics in a strongly alkaline solution (usually NaOH), controlling the treatment time, base concentration and temperature. (Carvalho, *et al*., 2012)

Flotation using NaOH as a heavy liquid is another well-known and commonly used gravity concentration technique. Two materials with different specific weight are separate using a liquid with specific weight between them; this technique can be classified as "static" or dynamic whether gravitational forces are applied or centrifugal forces are applied as well, respectively. In this work, was used a "static" separation.

MATERIALS

Sample

Experimental work began by collecting samples of 8 types of post-consumer plastic from WEEE in Recielectric (a Portuguese recycling unit) from the small WEEE operational line, after manual dismantling and before shredding. Each plastic type came from a different WEEE and with different color (Table 1), in order to minimize the uncertainty of the identification before and after the separation. The procedure used to identify the plastics was based, initially, on the resin identification code (RIC) of the Society of the Plastics Industry, and in order to ensure that the type polymer was identified correctly, some randomly selected pieces were sent to PIEP for a chemical analysis, confirming the type polymer and measuring the density of each sample (Table 1).

Table 1 – Characterization of the sample used.

Polymer	Provenance	Color	Measured density (g/cm^3)
Polypropylene (PP)	Espresso machine cups	Yellow	0,90 ± 0,00
Acrylonitrile Butadiene Styrene (ABS)	Vacuum cleaners	Orange	1,03 ± 0,00
Polystyrene without mineral fillers (PS_{sl})	Printers	Grey	1,04 ± 0,01
Styrene Acrylonitrile (SAN)	Blender cups	Violet/crystal clear	1,06 ± 0,00
Polyamide 6 (PA_6)	Printers support	Dark grey	1,13 ± 0,00
Polystyrene with mineral fillers (PS_{cl})	Sound speakers (front)	Metallic grey	1,22 ± 0,01
Polyoxymethylene (POM)	Toothed wheels	White with greasy shine	1,39 ± 0,02
Polyvinyl Chloride (PVC)	Freezer friezes	White	1,43 ± 0,04

Sample processing was made in CERENA's laboratory, following the procedure present: (1) shredding in a cutting shredder (Retsch SM 2000) equipped with a screen with 10 mm aperture; (2) dry sieving in a vibratory sieve shaker (Fritsch Analysette). The particle fraction used in the experiments corresponded to 2-4 mm.

Results Analysis

The evaluation of the composition of the results obtained was made by manual sorting in CERENA and for the best results (visual evaluation), chemical analysis in PIEP.

Each process studied was evaluated by calculating the recovery (1) and grade (2) of each polymer in each process product. After each experiment the products were dried in an incubator for 24 hours, weighed and analyzed.

$$\eta_{k,i}\,(\%) = \frac{m_{k,i}}{m_i} * 100 \quad (1)$$

$$g_{k,f}(\%) = \frac{m_{k,i}}{m_k} * 100 \quad (2)$$

Where: $m_{k,i}$ is the mass of the polymer *k* in the product *i*, m_i is the total mass of the product *I* and m_k is the mass of polymer *k* in the feed.

GRAVITY CONCENTRATION IS POSSIBLE IN THE MIXED POST-CONSUMER PLASTICS PRESENTED?

"Concentration criteria" (2) is a parameter used in mineral processing to evaluate the suitability of the application of gravity concentration processes in the separation of a minerals mixture.

$$CC = \frac{D_h - D_l}{D_l - D_f} \quad (2)$$

Where: D_h is the specific gravity of the "heavy" specie, D_l is the specific gravity of the "light" specie and D_f is the specific gravity of the fluid. In the case studied the fluid was water.

According to the concentration criteria, the separation should be easy for CC>2.50, for a particle size down to 75 µm and impossible at any size when CC<1.25. (Wills, 1998)

Since other facts besides gravity and size, such as particle shape, can be a strong effect on the separation, this criterion should be considered only as a guideline and once this criterion was created for minerals, apply it in plastics can be challenging.

However, the application of this criteria to mixtures of PP, ABS, $PS_{s/}$, SAN, PA_6, $PS_{c/}$, POM and PVC in study, by direct use of the densities included in Table 1, are present in Table 2.

Table 2 – Application of the concentration criteria to the plastics in study.

PP	---							
ABS	-0,30	---						
$PS_{s/}$	-0,40	1,33	---					
SAN	-0,60	2,00	1,50	---				
PA_6	-1,30	4,33	3,25	2,17	---			
$PS_{c/}$	-2,20	7,33	5,50	3,67	1,69	---		
POM	-3,90	13,00	9,75	6,50	3,00	1,77	---	
PVC	-4,30	14,33	10,75	7,17	3,31	1,95	1,10	---
	PP	**ABS**	**$PS_{s/}$**	**SAN**	**PA_6**	**$PS_{c/}$**	**POM**	**PVC**

EXPERIMENTAL

FLUIDIZATION BED

Variables affecting the process are the particle size, velocity of the pulp, overflow volume fraction of solids, overflow and underflow pulp densities.

Equipment

The experiments were carried out in a fluidized bed separator shown in Fig. 1, with 80 cm height and 9 cm diameter. The device is fed with a suspension of particles in water by a variable speed peristaltic pump from a stirred tank at a constant flow rate of 30 l/h (Q_A) and a supplementary flow of "hydraulic water" (Q_H) is added near the bottom of the device column. Flow rate of "hydraulic water" should be adequate in order to particles with lower settling velocities can be carried to the "overflow" and the particles with higher settling velocities sink, being recovered in the "underflow" product.

Fig. 1 – Fluidized bed separator used.

Experimental procedures

Tests were carried out with a flow rate of hydraulic water between 100 and 2000 l/h.

In a first phase, separability tests were carried out to determine the optimal flow rate of hydraulic water needed to separate each binary mixture of the eight plastics in study. Forty grams of each plastic, in a total of eighty grams was placed in the tank and the equipment was continuously operated for 20 minutes with a predetermined flow rate of hydraulic water, starting with 100l/h and ending with the flow rate capable of transport one of the samples to the overflow product. After that time, overflow and underflow products were collected and after manual sorting they were evaluated in terms of grade e recovery.

In a second e third phases, separation tests were conducted in continuously mode with the eight plastics in order to determine the optimal flow rate of hydraulic water needed to separate the mixture. For second phase, ten grams of each plastic, in a total of eighty grams was placed in the tank and for third phase, feed composition was based in the data received by Recielectric (Table 3). As before, in these two phases the equipment was continuously operated for 20 minutes. After that time, overflow and underflow products were collected, the underflow product was placed again in the tank and the test restarted. Bests results obtained for a mixture, by visual comparison, was sent to PIEP for chemical analysis, the other was submitted to manual sorting. All results were evaluated in terms of grade e recovery.

Table 3 – Feed composition of the third phase of fluidization bed experimental work.

Polymer	$PS_{C/}$	$PS_{S/}$	ABS	SAN	PVC	PP	POM	PA_6
% Weight	10	10	40	2	4	30	2	2

*R*ESULTS AND DISCUSSION

In separability tests was determined the flow rate of hydraulic water needed to carry one of the polymer to the overflow product. Table 4 present the results obtained for each binary mixture.

Table 4 – Flow rates of hydraulic water in result of the separability tests.

<table>
<tr><th></th><th>PP</th><th>ABS</th><th>$PS_{s/}$</th><th>SAN</th><th>PA_6</th><th>$PS_{c/}$</th><th>POM</th></tr>
<tr><td>ABS</td><td rowspan="7">100 l/h</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>$PS_{s/}$</td><td>---</td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>SAN</td><td>700 l/h</td><td>700 l/h</td><td></td><td></td><td></td><td></td></tr>
<tr><td>PA_6</td><td rowspan="4">700 l/h</td><td rowspan="4">700 l/h</td><td>800 l/h</td><td></td><td></td><td></td></tr>
<tr><td>$PS_{c/}$</td><td rowspan="3">900 l/h</td><td>1200 l/h</td><td></td><td></td></tr>
<tr><td>POM</td><td>1200 l/h</td><td rowspan="2">1500 l/h</td><td></td></tr>
<tr><td>PVC</td><td>1600 l/h</td><td>---</td></tr>
</table>

PP was separated from the other polymers with a flow rate of hydraulic water of 100 l/h, the mixtures POM+PVC and ABS+PS_s/ could not be separated with this equipment and with the mixtures ABS+SAN, $PS_{S/}$+SAN, PA_6+PVC and PA_6+POM was not obtained pure products.

In the second phase were determined two flow rates of hydraulic water series, in Fig. 2 are showed the results for both series.

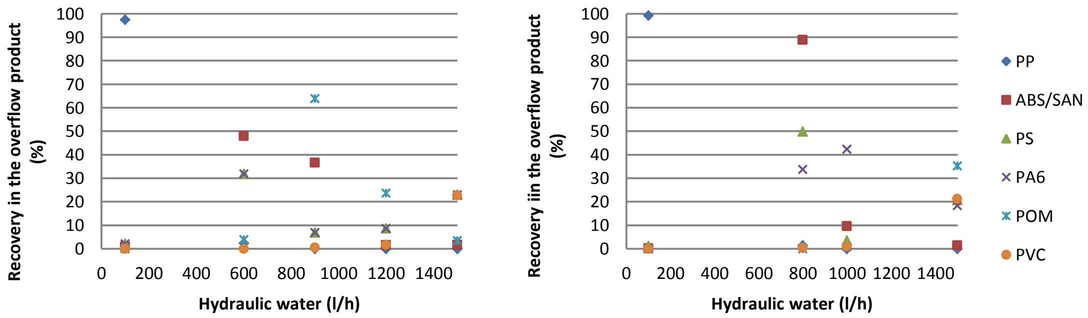
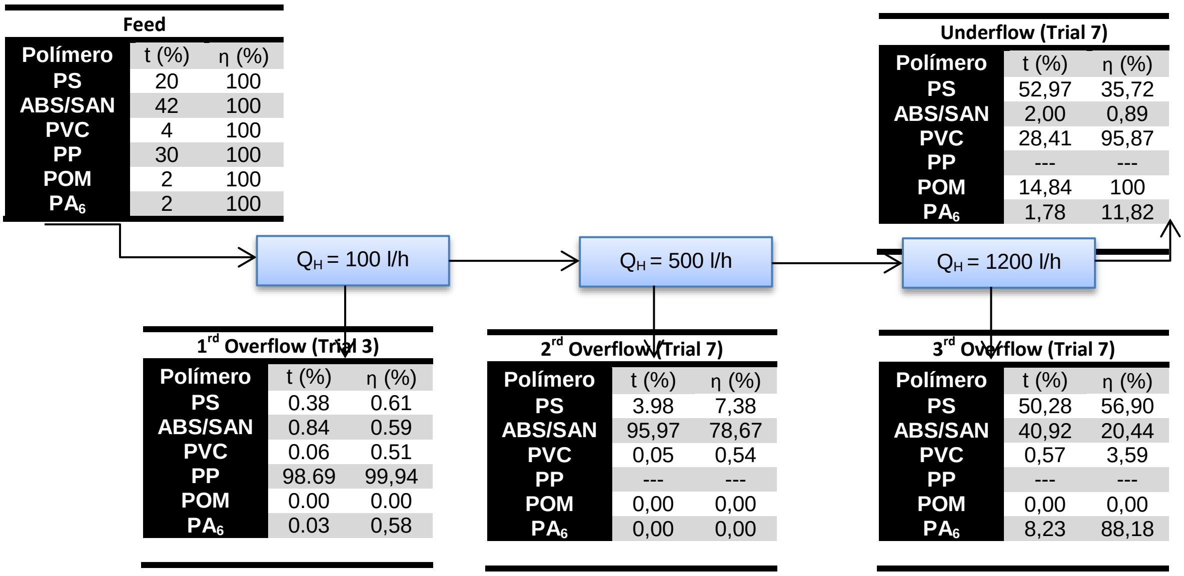


Fig. 2 – Separation results for both series of hydraulic water flow rates.

ABS and SAN are found together because chemical analysis is not able to discriminate one of the other, same things happens with PS with and without mineral fillers. From this study were obtain mixtures of polymers with similar density, like as expected. PP are completely separated from the other polymers in the mixture.

In the third phase of the study a complex fed of plastics was tested, the results for a diagram of treatment by fluidization bed with 3 flow rates, for obtaining four products are showed in

Fig. 3. The diagram combines two different trials, once was proved that PP was removed from the mixture at 100 l/h, for saving money and time; PP was removed from the feed in the remaining trials.



Feed

Polímero	t (%)	η (%)
PS	20	100
ABS/SAN	42	100
PVC	4	100
PP	30	100
POM	2	100
PA_6	2	100

Underflow (Trial 7)

Polímero	t (%)	η (%)
PS	52,97	35,72
ABS/SAN	2,00	0,89
PVC	28,41	95,87
PP	---	---
POM	14,84	100
PA_6	1,78	11,82

1rd Overflow (Trial 3)

Polímero	t (%)	η (%)
PS	0.38	0.61
ABS/SAN	0.84	0.59
PVC	0.06	0.51
PP	98.69	99,94
POM	0.00	0.00
PA_6	0.03	0,58

2rd Overflow (Trial 7)

Polímero	t (%)	η (%)
PS	3.98	7,38
ABS/SAN	95,97	78,67
PVC	0,05	0,54
PP	---	---
POM	0,00	0,00
PA_6	0,00	0,00

3rd Overflow (Trial 7)

Polímero	t (%)	η (%)
PS	50,28	56,90
ABS/SAN	40,92	20,44
PVC	0,57	3,59
PP	---	---
POM	0,00	0,00
PA_6	8,23	88,18

Fig. 3 – Diagram of treatment by fluidization bed for obtaining four products with a complex fed.

FROTH FLOTATION

Reagents´

For froth flotation tests were used the following reagents: Calcium Lignosulfonate (CaLS) as depressant, Sodium Hydroxide (NaOH) for alkaline treatment of the samples and for pH control, Sulfuric Acid (H_2SO_4) for pH control and Methyl Isobutyl Carbinol (MIBC) as frother.

Equipment

The experimental work was carried out in a Leeds flotation cell, with 5 liters volume (Fig. 4). The cell is equipped with airflow rate and impeller's speed control, the impeller is driven from the bottom of the cell. It was imposed a rotational speed of approximately 650 rpm, in order to avoid high turbulence on the top of the cell.

Fig. 4 . Flotation cell used in the experimental work.

Experimental procedures

The experimental work was carried out for the mixtures ABS+$PS_{s/}$ and POM+PVC, both unable to be separated with the fluidization bed process. It was experiment several variables: CaLS and MIBC concentration, pH, alkaline treatment, conditioning time of CaLS, air flow rate and flotation time. The procedure followed was obtaining optimal interval results of one variable keeping all others constant, followed with testing other variable in the interval predetermined. The first variable studied was CaLS concentration. The fed in both scenarios, ABS+$PS_{s/}$ and POM+PVC, was kept invariable 10 grams of each plastic, in a total of 20 grams for trial.

The flotation procedure adopted for all tests was as follows: (1) Sample stirred in tap water for 10 min, this step was remove when alkaline treatment was in placed, in that case, sample was stirred for 20 min in a solution of 40 mg/l of NaOH at 90ºC. (2) Flotation cell filled up with tap water, agitation was started at ≈ 650 rpm and the sample was placed inside. (3) Added CaLS and wait the predetermined conditioning time. (4) Added MIBC and wait 2 min. (5) Turn on the air flow. (6) Froth flotation with predetermined time.

RESULTS AND DISCUSSION

ABS+$PS_{s/}$

The experimental work began with the study of the effect of CaLS concentration, leaving all the other variable constants: 0.4 ml MIBC, 70l/h air flow rate, conditioning and flotation time of 10 minutes, no alkaline treatment and pH ≈7.5. CaLS is a strong depressant of ABS and $PS_{s/}$, being the best results found for concentrations between 2.5 and 5 mg/l of CaLS.

The study of the effect of MIBC concentration was made for 2.5 mg/l and 5 mg/l of CalS, leaving all the other variables constants. The results obtained demonstrating that 0.4 ml of MIBC and 5 mg/l of CaLS were the best combination.

Using a combination of 5 mg/l of CaLS and 0.4 ml of MIBC, the effect of alkaline treatment was studied. The results obtained shows a rapidly depletion of the floatability of both polymers, this test was made for several pH and always was verified a depletion of floatability. The alkaline treatment was forsaken.

The effect of pH was studied was the results benefit the use of a basic pH, approximately 11.2.

Once again, the effect of air flow rate was studied keeping the other variables constant: 0.5 mg/l CaLS, 0.4 ml MIBC, no alkaline treatment, pH at 11.2, conditioning time 10 minutes. Best results were found for an air flow rate of 70 l/h.

Finally, conditioning time influence was studied; being found that with 10 minutes was obtained the best results.

With the process we were able to recovery 81% of the ABS with 29% contamination in $PS_{s/}$ in the floated product.

POM+PVC

The experimental work began with the study of the effect of CaLS concentration, leaving all the other variable constants: 0.2 ml MIBC, 70l/h air flow rate, conditioning and flotation time of 10 minutes, no alkaline treatment and pH ≈7.5. CaLS is a depressant of POM and PVC, being the best results found for concentrations between 150 and 250 mg/l of CaLS.

The study of the effect of MIBC concentration was made for 150 mg/l and 250 mg/l of CalS, leaving all the other variables constants. The results obtained demonstrating that 0.2 ml of MIBC and 250 mg/l of CaLS were the best combination.

The effect of pH was studied was the results benefit the use of a neutral pH, approximately 7.5.

The effect of alkaline treatment was studied. The results obtained shows a rapidly depletion of the floatability of both polymers with CaLS concentration above 150 mg/l, however for a concentration in CaLS of 150 mg/l was obtained the best results of the study.

With the process we were able to recovery 48.5% of POM with 4.4% contamination in PVC in the floated product without alkaline treatment and 88.5% of POM with 13.4% contamination in PVC.

FLOTATION USING NAOH AS HEAVY LIQUID

Reagents

For the flotation using NaOH as heavy liquid, only Sodium Hydroxide (NaOH) was used.

Equipment

It was used a combined hot-plate magnetic stirrer device (Fig. 5).

Fig. 5 – Device used in flotation using NaOH as heavy liquid experimental tests.

Experimental Procedures

The experimental work was carried out for the mixture ABS+$PS_{s/}$. It was experiment several variables: NaOH concentration, temperature and quantity of the feed.

The flotation procedure adopted for all tests was as follows: (1) Displaced sample in a cup with 400 ml tap water. (2) Turn on the magnetic stirrer at 700 rpm and heat up until predetermined temperature. (3) Added solid NaOH in the system Solids plus water and wait 20 minutes to conditioning. (4) Turn of the magnetic stirrer and wait until stabilized.

RESULTS AND DISCUSSION

To a NaOH concentration of 25 g/l all plastics are recovered on the non-floated product and above 100 l/g all of them are recovered in the floated product, when the feed is composed by 10 grams of each plastic. When the feed is composed by 20 grams of each plastic they are completely recovered in floated product at 75 g/l.

Recovery is similar at any temperature; however at 90ºC was a slight increase of recovery of both plastics in the floated product.

The best result was found for a concentration of NaOH of 87.50 g with a recovery of 100% of ABS with 13.8% contamination in $PS_{s/}$ in floated product, with 10 grams of each plastic in the feed; and for a concentration of 62.5 g/l of NaOH was found a recovery of 100% of ABS with contamination in $PS_{s/}$ of 15.6%.

CONCLUSIONS

Consumption of plastics is in rapidly growth, once they are cheap, light and versatile. WEEE is a important stream of plastics recycling.

Although plastics are one of the most common recycled products found in the waste stream, is up today separated by manual sorting or in some case, by optical sorting. This work showed that minerals processing techniques can be successful applied being able to separate large quantities of small size material.

The experiments were carried out on real post-consumer plastics from WEEE; the collected sample was first subjected to shredding. The size range utilized in the experimental work was 2-4 mm.

In fluidization bed experiments was obtained a pure product of PP, likewise mixtures of polymers with similar specific density: ABS+SAN+$PS_{s/}$ and POM+PVC+$PS_{s/}$. PA_6 showed in all products, except the one carried out with a hydraulic flow rate of 100 l/h.

For the mixtures ABS+$PS_{s/}$ and POM+PVC froth flotation experiments was carried out.

From froth flotation experiments was observed that CaLS is strong depressant of ABS and $PS_{s/}$, being depressant of POM and PVC as well; the alkaline treatment although did not help in the separation of ABS from $PS_{s/}$ was a good option, hence that in combination with CaLS as a depressant increased the recovery of POM in the floated product, obtaining a recovery of POM of 88.5% with 13.4% contamination in PVC.

Flotation using NaOH as heavy liquid was resulting in a pure product of $PS_{s/}$ in the non-floated product and recovered of 100% of ABS with 16% contamination in $PS_{s/}$ in the floated product.

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