Sulfonation of Microcapsules Containing Selective Extractant Agents

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Abstract-Microcapsules from P(St-EGDMA) and P(St-DVB) containing di(2-ethylhexyl) phosphoric acid (DEHPA) as core material has been prepared by suspension-like polymerization technique by using two different recipes. These materials were synthesized by using percentage mass ratios of 0.1 wt.% and 18.6 wt.% for EGDMA/St and DVB/St, respectively. Toluene was required as diluent to produce microcapsules from P(St-DVB) due to the high reactivity of the crosslinking monomer (DVB) since polymerization reaction without toluene yielded to compacted block. Microcapsules containing DEHPA were obtained using the above shell materials having a smooth and spherical shape, a particle size in the range of those reported for commercial resins but the amount of encapsulated DEHPA was larger when P(St-DVB) was used, 34.86 wt.% respect to the 28.15 wt.% obtained for the P(St-EGDMA). Attending to this higher DEHPA content, P(St-DVB) was selected as shell material to develop microcapsules combining the advantages and capabilities of the ion exchange and the solvent extraction technologies. Once the extractant agent has been encapsulated, different sulfonation agents -chlorosulfonic and sulfuric acid- and the applicability of swelling agents to minimize the sulfonation treatment impact on the microcapsules were carried out to attribute them ion exchange properties. Swelling agents release the DEHPA from the microcapsules whereas the chorosulfonation treatment leads to a cracked material. Thus, the effect of the sulfonation by sulfuric acid on DEHPA and sulfur contents and swelling degree of microcapsules as function on the particle size was studied. Sulfonation results showed that sulfuric acid at 50ºC did not damage the microcapsules but it had big influence on the DEHPA content. Results showed that sulfur and swelling increased whereas the DEHPA decreased in a linear way with the sulfonation time. From the slopes of these curves, it was found that sulfonation process was dependent on the particle size and DEHPA was less released from particles having a particle size of 500 m and incorporating an enough amount of sulfonic groups in the shell material (-6.43 g_{DEHPA}/g_S). Besides, attending to the low sulfonation required for this material, a maximum time of 20 min is recommended to introduce a 30% of the sulfonic groups commonly found in commercial resins.

Keywords- Microcapsules; Extractant Agent; Sulfonation; Suspension-Like Polymerization; Heavy Metals

I. INTRODUCTION

Industrial effluents (e.g. electroplating, battery and chemical manufacture, mining, metal finishing, forging or petroleum refining) can constitute not only a potential source of many valuable and scarce metals but also a serious environmental problem[1]. Thus, the recovery or removal of heavy metals such as chromium, nickel, zinc, copper or lead and their compounds, which have been classified in the List II of the families and groups of substances of the Directive 2008/105/EC[2] on pollutant caused by certain dangerous substances discharged into the aquatic environment of the community, is of great importance.

Different technologies have been applied to eliminate heavy metals from aqueous systems: chemical precipitation[3–5], electrodyalisis[6–8], reverse osmosis[9–11], adsorption on organic and inorganic materials[12–17], aluminium and iron coagulation[18, 19], electrocoagulation[20, 21], filtration[22, 23], ultrafiltration[24–26], solvent extraction[27–29], ion exchange[30, 31] and biomass[32–35]. At low metal concentrations, the practical application of enumerated methods can be ineffective, economically unfavourable or technically complicated.

Solvent extraction and ion exchange are currently the major industrial-scale techniques used for that purpose[36–39]. However, they present limitations when applied to aqueous effluent treatments. In the case of solvent extraction, multistage cycles of extraction and back-extraction and the use of organic solvents are required to attain a favorable separation. On the other hand, ion exchange resins have low selectivity in the extraction of metal ions and are highly saturated with ions different to those of interest, thus decreasing the yield. Even highly selective chelating ion exchange resins have slow kinetics in ion removal.

Polymeric adsorbents impregnated with liquid ligands[40-41] extractants in supported liquid membranes[42-43] and polymeric microcapsules containing extractants[39, 44-45] are three methods and processes for separating and concentrating metal ions to overcome the aforementioned limitations of conventional methods. However, some disadvantages have been documented and these include the loss of extractant and steric hindrance for solvent impregnated resins[37, 44, 46] and slow kinetics and low stability for liquid membranes[47-48].

An interesting alternative to overcome such limitations is the microencapsulation of extractants. Kiyoyama et al.[49] Kamio et al.[39] Araneda et al.[45] and Barassi et al.[50] have developed microcapsules with permeable non-functionalized polymeric shells from poly(divinylbenzene) -P(DVB)- or poly(styrene-co-ethylene glycol dimetacrylate) -P(St-EGDMA)- containing an extractant agent by polymerization. This kind of material had a large interfacial area, a high selectivity for the metallic ions

similar to those of the pure extractant agent solvents and easy separation of metal-loaded microcapsules[45, 50-51] but the mass transfer kinetics were still slow and the maximum adsorption capacity was smaller than those of conventional and commercial ion exchangers.

All of these developed microcapsules showed high selectivity to heavy metal ions. However, these systems do suffer from several drawbacks, such as relatively slow kinetics and small loading capacity compared with conventional ion exchange resins. The introduction of active sulfonic acid sites ($-SO_3^-H^+$) in the resin matrix overcomes these limitations. It has been well documented since the 1960s that hydrophilic moieties can be introduced into the hydrophobic matrix of the resins by the incorporation of ionic groups such as $-SO_3^-H^+$. This matrix is elastic and can be expanded. Hence the resins can swell by taking up solvent. The degree of crosslinking determines the mesh width of the matrix and thus the swelling ability of the resin and the mobilities of the counter ions in the resins. The latter characteristic, in turn, determines the rates of ion exchange[52]. In this process the negative charge of the sulfonate groups will attract metal cations to the surface of the microcapsule. Once at the surface, these cations enter to the polymeric shell with water, which enhances their mobility and thus favours mass transfer of the metallic ions from the liquid phase to the core of the capsule.

The encapsulated extractant forms the selective part of the microcapsule and this will form a strong complex with heavy metals, a property that makes the system highly selective. In fact, a non-sulfonated extractant microcapsule will not exchange metal cations at all, since the polymeric shell acts as a barrier between the extractant and the metal solution. As a result, mass transfer will be less favorable than in the system with a functionalized shell.

There are two methods of introducing the sulfonic acid group during the synthesis of cation exchange resins. The first approach involves the synthesis of the polymeric beads with sulfonated monomers[53–57]. The second approach involves functionalization of the resin (after its synthesis) using sulfonating reagent like sulfur trioxide[58-59], sulfuric acid, chlorosulfonic acid or acetyl sulfate[60–62]. Sulfuric acid and chlorosulfonic acid have been widely used in the sulfonation of styrene-divinylbenzene P(St-DVB) macroporous resins[63–75]. On the basis of the results reported by Rabia et al.[69], and Lee et al. (2009)[76], these latter two sulfonating agents were employed for the functionalization of microcapsules.

The choice of the shell material for the microencapsulation of extractants plays an important role in improving the structure, permeability of the ions and mechanical stability of the microcapsules, as well as their chemical stability for the functionalization process. Thus, the goal of this work is the development of sulfonated microcapsules from shells such as P(St-EGDMA) or P(St-DVB) containing DEHPA as core material. The synthesis of microcapsules containing DEHPA was performed by suspension-like polymerization technique[77] and the sulfonation was accomplished by known methods trying that the attack of the sulfonation reagents to the microcapsules was as light as possible to maintain the intact the integrity of the particles. This kind of sulfonated microcapsules containing extraction agents has not been previously described in literature.

II. EXPERIMENTAL

A. Materials

1) Synthesis of Microcapsules:

The monomers, styrene (99 wt.%, Sigma-Aldrich Chemical Co.) and divinylbenzene of technical grade (containing 80% DVB isomers, Fluka Chemical Co., Ltd.), were purified by washing with aqueous sodium hydroxide solution and using calcium chloride as a desiccant. Ethylene glycol dimethacrylate (97 wt.%, Fluka Chemical Co., Ltd) was purified by passing it through a column packed with activated basic alumina. PRS® paraffin wax, with an energy storage capacity of 202.6 J g^{-1} (produced and commercialized by Repsol YPF, Spain), and the extractant agent DEHPA (97 wt.%, Aldrich Chemical Co.) were used as core materials. Benzoyl peroxide (97 wt.%) was used as the initiator (Fluka Chemical Co., Ltd.). Arabic gum of reagent grade (Sigma-Aldrich Chemical Co.), polyvinylalcohol (10-98, Mw 61.000 g mol^{-1}) of analytical grade and reagent grade polyvinylpyrrolidone (K30, Mw 40,000 g mol^{-1}) of reagent grade, supplied by Fluka Chemical Co., Ltd., were used as stabilisers. Toluene of analytical grade (BDH Prolabo, VWR Co.) was used as inert diluent.

Water with a conductivity of 1 µS cm^{-1} was purified by distillation and subsequent deionisation using ion-exchange resins (Milli-Q water). Nitrogen was high-purity grade (99.999 %).

2) Sulfonation of the Polymeric Shell Using HClSO$_3$ or H$_2$SO$_4$:

Chlorosulfonic acid (98 wt.%, Fluka Chemical Co., Ltd.), boric acid (Fluka Chemical Co., Ltd.), sulfuric acid (96 wt.%, Sigma-Aldrich Chemical Co.) and fuming sulfuric acid (20 wt.%, Sigma-Aldrich Chemical Co.) were of reagent grade. Microcapsules were washed with distilled and deionized water. An aqueous sodium hydroxide solution 1.25 N was used to absorb and neutralize acid gases.

B. Procedure for the Synthesis of Microcapsules

Microencapsulations were carried out by suspension-like polymerization technique in a 1 L glass reactor equipped with a temperature-controlled oil bath, a stirrer, a reflux condenser and a nitrogen gas inlet tube. A schematic diagram of this experimental set-up was described elsewhere[77].

The synthesis process involves two phases: a continuous phase containing water and suspending agents and a discontinuous phase containing the monomers, the core material (PRS® paraffin wax or DEHPA), benzoyl peroxide and toluene. The discontinuous phase was then added into the continuous phase and maintained under vigorous agitation at a constant temperature. The polymerization process was carried out under a nitrogen atmosphere.

The recipe reported in a previous study[77] was employed in this work to produce microcapsules having different shell and core materials. The formulation is summarized in Table 1. Once the reaction had ceased, the product was discharged into water at room temperature. This product was purified by repeated washing with water and finally dried at room temperature.

TABLE I RECIPE AND EXPERIMENTAL CONDITIONS FOR THE MICROCAPSULES CONTAINING PRS® PARAFFIN WAX OR DEHPA

	Ingredients	P(St-EGDMA) PRS	P(St-EGDMA) DEHPA	P(St-DVB) DEHPA
Continuous phase (g)	Water (Milli-Q)	377.40		400
	Polyvinylpyrrolidone	3.77		-
Discontinuous phase (g)	Arabic gum:polyvinylalcohol	-		8.16
	Benzoyl Peroxide	1.26		2.06
	Styrene	78.32		7.56
	Secondary monomer (wt.%)	0.08–1.57 (0.1–2)	0.08 (0.1)	1.41 (18.6)
	PRS® paraffin wax	27.04	-	-
	DEHPA	-	27.04	4.56
	Toluene	-		13.60
Reaction conditions	Temperature (ºC)	98		80
	Stirring rate (rpm)	850		400
	Reaction time (h)	5		

C. Sulfonation of the Polymeric Shell with HClSO₃

Sulfonation reactions were performed in a 0.25 L jacketed glass reactor equipped with a fritted glass disk at the bottom, a reflux condenser, an acid gas scrubber system and a vacuum filtering connection to take out the liquid from the reactor. The sulfonation reaction was done at the desired temperature by means of a thermostatic bath.

Two different sulfonation times (10 and 30 min) were studied. In each sulfonation experiment 2.0 g of solid microcapsules were brought in contact at 20ºC with a liquid mixture of 26 mL of $HClSO_3/SO_3$ with a volume ratio of 3:1 and containing 1.20 g of dissolved H_3BO_3[78]. According to Amick[78] the chlorosulfonation of the P(St) yields between 70 and 85% the chlorosulfonated form P(St)-SO₂Cl and between 15 and 30% the sulfonated one P(St)-SO₃ (Equation (1))[79]. Thus, once the solid-liquid mixture was filtered sulfuric acid was added dropwise -at a rate of 10 mL per min- to the solid material to promote the formation of sulfonated form instead of chlorosulfonated one. The resultant liquid was also filtered under vacuum and finally, sulfonated microcapsules were washed thoroughly with deionized water and dried at room temperature for 24 h.

$$(1)$$
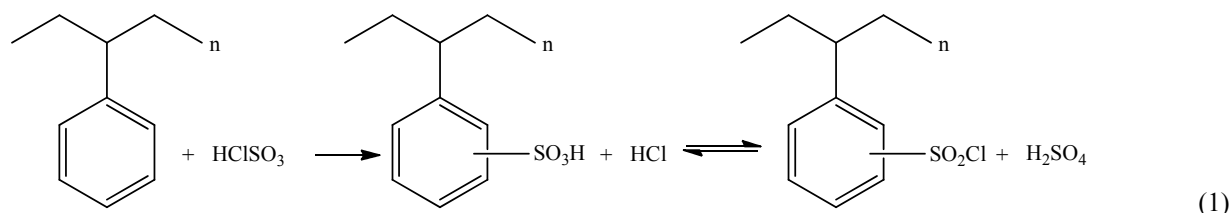
D. Sulfonation of the Polymeric Shell with H₂SO₄

Sulfonation reactions using H_2SO_4 were performed in an experimental setup similar to the one that has been described previously for $HClSO_3$ sulfonations. But in this case, the jacketed reactor was replaced with an ordinary reactor, where the reactions were performed at the required temperature under agitation (250 rpm) by means of a heat plate/magnetic stirrer.

Initially, 200 mL of sulfuric acid were introduced into the reactor and heated up to the desired temperature. Then 2.0 g of microcapsules were added and the mixture was stirred for the selected reaction time. Once the reaction had subsided, the reaction mixture was filtered under vacuum to separate the solid product. Sulfonated microcapsules were washed thoroughly with deionized water and dried at room temperature for 24 h.

E. Microcapsule Characterization

1) Microscopy Observations:

The morphology and the surface features of sulfonated and non-sulfonated microcapsules were observed by Optical and Environmental Scan Electron Microscopy using an Axio Imager. A1 (Carl Zeiss) optical microscope and a XL30 (LFD) ESEM, respectively. Optical Microscopy was also used to determine the percentage of broken microcapsules after the sulfonation process.

2) Thermogravimetric Analyses:

The thermal stability and DEHPA and water contents of the synthesized microcapsules were obtained by using a TA instruments SDT Q600 Simultaneous DSC-TGA from room temperature to 700°C at a heating rate of 10°C min^{-1} under a nitrogen atmosphere.

3) Particle Size and Particle Size Distribution:

The average particle size of the microcapsules in number (dpn$_{0.5}$) and volume (dpv$_{0.5}$) were determined by Low Angle Laser Light Scattering (LALLS) using a Mastersizer Hydro 2000 with dilute dispersions of the paraffin particles in methanol and a Mastersizer 2000 equipped with a Scirocco 2000 unit that works with air as dispersing agent. In the same way, the particle size-weight distribution was obtained by sieving the synthesized product using different mesh sizes (from 250 to 1000 μm).

4) Swelling Percentage:

The swelling percentage was determined leaving the microcapsules in contact with water at 25ºC during 24 h. The swelling degree of sulfonated and non-sulfonated microcapsules was determined gravimetrically by the following equation:

$$Sw(\%) = \frac{W_s - W_0}{W_0} 100 \qquad (2)$$

where Sw is the swelling percentage, W_0 is the initial weight of the microcapsules and W_s is the final weight of swollen microcapsules.

5) Determination of Sulphur Content:

Sulfur content (S) of the sulfonated microcapsules was measured with an elemental analyzer for solid samples, Multi EA 4000 (Analytik-Jena). Microcapsules were burned up to 1200ºC under an oxygen atmosphere in order to convert sulphur in sulphurous anhydride. That gas was measured with a NDIR sensor.

III. RESULTS AND DISCUSSION

In previous works the synthesis of P(St) and P(St-MMA) microcapsules containing PRS$^{®}$ paraffin wax have been accomplished using the suspension-like polymerization technique, obtaining microcapsules with core material percentages of 20.56 and 43.17, respectively[77, 80].

It is necessary to improve the chemical and mechanical stability of the polymeric shell to allow the production of microcapsules that resist the acid attack during sulfonation. Thus, a proper shell formulation is required to provide toughness to the structure while maintaining an adequate level of permeability and thermal stability after attacking by the sulfonating reagents and alkaline solutions.

It is well known that the mechanical and chemical stability of a polymer can be enhanced by adding a crosslinking agent[81]. According to Araneda et al.[45] the use of EGDMA and DVB should improve the shell resistance by introducing a certain degree of crosslinking. Thus, in this work, the mentioned crosslinkers have been studied.

Taking advantage of our previous experience in the development of microcapsules containing PCMs[77, 80, 82-83], the synthesis of microcapsules of P(St-EGDMA) and P(St-DVB) containing PRS$^{®}$ paraffin wax was carried out prior to DEHPA encapsulation .

A. Study of the Synthesis of PCMs Microcapsules with Different Shell Materials

1) Encapsulation of PRS$^{®}$ Paraffin with P(St-EGDMA):

The EGDMA/St mass ratio percentage was varied between 0.1 and 2 wt.% with the aim of studying how a crosslinking agent improves the mechanical and chemical resistance of the shell. The synthesis was carried out according to the procedure reported by Sánchez et al.[77] and the experimental conditions are reported in Table 1.

It was not possible to obtain a microcapsule containing PRS$^{®}$ paraffin wax when a percentage of EGDMA respect to St of 1 or 2 wt.% was used. The product of these reactions was a solid material that had the appearance of a compacted block. This

physical form could be related to the high reactivity between EGDMA and St at high concentrations, which leads to mass polymerization. Nevertheless, as shown in Figure 1, microcapsules of $dpv_{0.5} = 547.00$ µm containing 18 wt.% of paraffin wax were obtained when an EGDMA/St mass ratio percentage of 0.1 was employed.
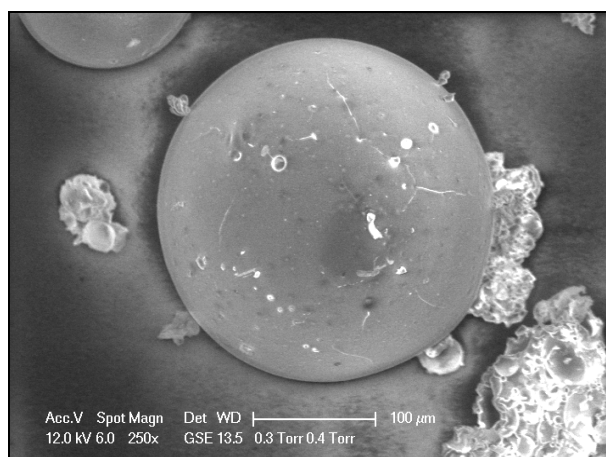

Figure 1 ESEM micrograph of a microcapsule formed by P(St-EGDMA) containing
PRS® paraffin wax

2) Encapsulation of PRS® Paraffin with P(St-DVB):

In the same way, different proportions of DVB/St 0.1, 1.0, 3.0, 6.0 and 9.0 wt.% were assayed. Polymerization products indicated that %DVB/St higher than 3.0 yielded to a compacted block and lower values gave rise to the formation of non-spherical materials.

The encapsulation success depends on multiple factors related with the thermodynamic and kinetics. EGDMA is more reactive and has higher crosslinking ability than DVB[45]. Nevertheless this fact does not guaranty the encapsulation success. The higher hydrophobic character of DVB and its lower reactivity can even favour the shell formation and consequently improving the encapsulation efficiency.

Thus, if microcapsules from P(St-DVB) are desired, the dispersed phase should be diluted with an organic solvent to decrease the reaction rate.

B. Study of the Synthesis of DEHPA Microcapsules with Different Shell Materials

1) Encapsulation of DEHPA with P(St-EGDMA):

Microcapsules containing DEHPA were prepared by copolymerization of St and EGDMA for an EGDMA/St mass ratio of 0.1 wt.% and using the above commented recipe and experimental conditions. Figure 2 shows the ESEM micrograph for microcapsules containing DEHPA. As can be seen, the appearance of this material is similar to that obtained when the PRS® paraffin was encapsulated, being spherical with a smooth surface and exhibiting an average particle size of 353.15 µm which is in the range of those reported for commercial resins[84].
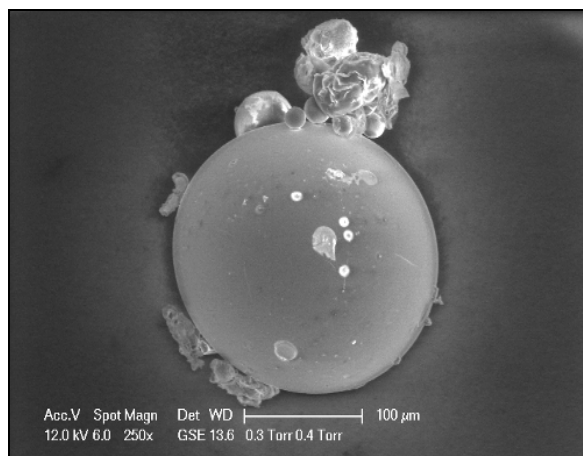

Figure 2 ESEM micrograph of microcapsule formed by P(St-EGDMA) containing DEHPA

The amount of DEHPA encapsulated was quantified by thermogravimetric analysis. The TG and DTG curves for pure DEHPA, the polymer P(St-EGDMA) and the microcapsules containing the extractant (P(St-EGDMA)-DEHPA) are shown in Figure 3.
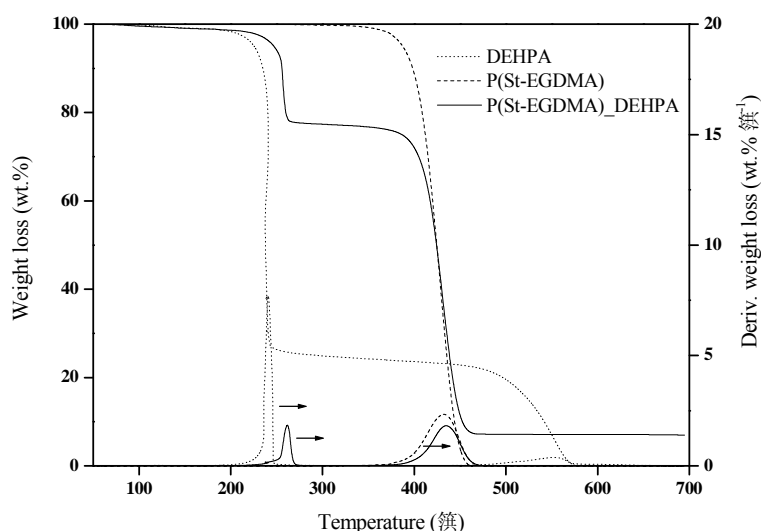
Figure 3 TG and DTG curves of pure DEHPA, P(St-EGDMA) and microcapsules from P(St-EGDMA) containing DEHPA

The TG plot for pure DEHPA indicates that this compound evaporates between 180 and 265ºC, leading to a weight loss of 75.25 wt.%. On the other hand, the polymer did not show any weight loss within this range. Thus, the total weight loss (21.18 wt.%) shown by the microcapsules in this temperature range can be related with the amount of DEHPA encapsulated. The synthesized microcapsules therefore contain approximately 28.15 wt.% of DEHPA. Besides, weight loss of the microcapsules between 334 and 477ºC can be related with the amount of remaining DEHPA and the decomposed polymer. The success of the microencapsulation process was therefore demonstrated.

2) Encapsulation of DEHPA with P(St-DVB):

As it is said before if microcapsules from P(St-DVB) wanted to be obtained, it is necessary the use of diluents in order to decrease the reaction rate of the organic mixture. In this way, Nishihama et al.[36-37] and Araneda et al.[45] have reported the use of kerosene, benzene and toluene as porogen agents to synthesize microcapsules from P(St-DVB) or P(St-EGDMA) containing extractant agents. Besides, it is important to point out that these compounds are also employed in the conventional liquid-liquid extraction to form the organic liquid phase. Thus, in order to accomplish the synthesis of microcapsules containing DEHPA with a shell of P(St-DVB), a recipe based on that proposed by Araneda et al.[45] was employed. This recipe was modified and the resulting formulation has been also included in Table 1.

Figure 4 shows the microcapsules of DEHPA prepared with P(St-DVB) (P(St-DVB)-DEHPA)). As can be seen, they exhibit a spherical shape with a regular surface and a particle size appropriate to be used as ion exchanger, confirming that this recipe is suitable to produce microcapsules with the required physical properties.
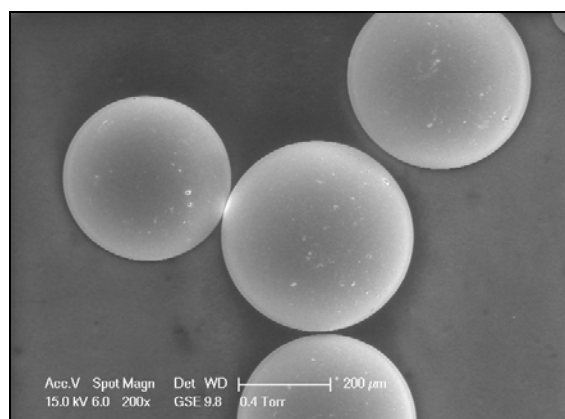

Figure 4 ESEM micrograph of microcapsules from P(St-DVB) containing DEHPA

The synthesized microcapsules have a particle size that fall in the range of those used in fixed bed columns, $dpn_{0.5} = 340.83$ μm. These particles are somewhat larger than those reported by Araneda et al.[45] and Barassi et al.[50] that used a similar recipe, with an average particle size of 67 μm at 600 rpm and 20 μm at 500 rpm, encapsulating PC-88A and the commercial quaternary ammonium salt Aliquat 336, respectively.

Thermogravimetric analyses were carried out to determine the amount of DEHPA encapsulated in PS-DVB particles. Thermogravimetric analysis shown in Figure 5 indicates that a 34.86 wt.% of the particle mass correspond to the DEHPA encapsulated, being this value a 23.84% higher than that exhibited by the microcapsules synthesized using P(St-EDGMA) as shell material and similar to those amounts reported by Araneda et al.[45] (between 32.2 to 36.7 wt.%) and Barassi et al.[50] (35.7 wt.%).
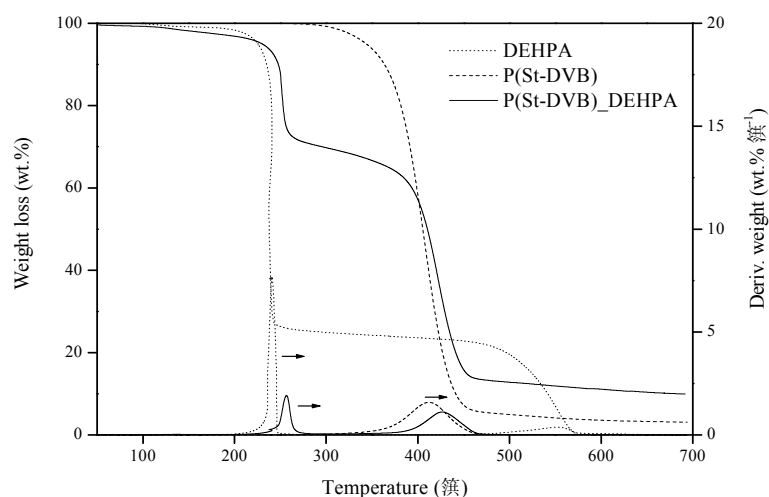
Figure 5 TG and DTG curves of pure DEHPA, P(St-DVB) and microcapsules from P(St-DVB) containing DEHPA

Thus, attending to the above DEHPA content that microcapsules from P(St-DVB) exhibit respect to those from P(St-EDGMA), P(St-DVB) was selected as the proper shell material to encapsulate this extractant agent.

C. Sulfonation of the Polymeric Shell

1) Sulfonation Using HClSO₃:

Functionalization of the P(St-DVB) shell by chlorosulfonic acid was carried out following the recipe proposed by Amick[78], who found that the use of boric acid allows developing the reaction at temperatures lower than 25ºC limiting the increase of cracked particles. Hence a temperature of 20ºC was selected with the aim of decreasing the aggressiveness of the sulfonating agent attack.

Figure 6 shows the optical micrographs for the microcapsules containing DEHPA sulfonated during 0, 10 and 30 min. They have been named MD, S10MD and S30MD, respectively.
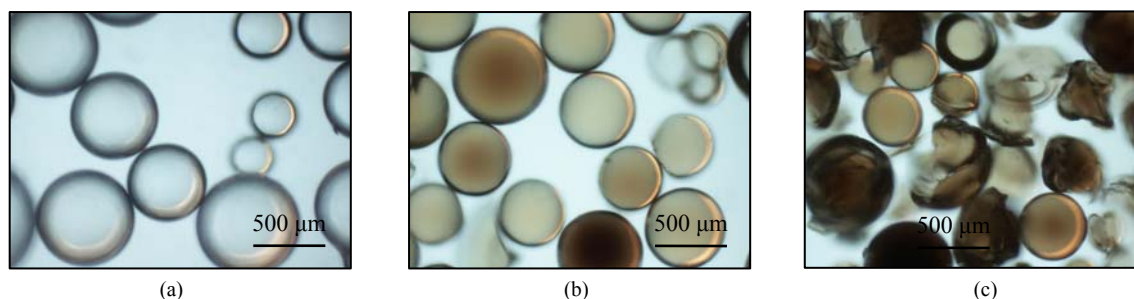

| (a) | (b) | (c) |

Figure 6 Optical micrographs of synthesized microcapsules:a) S0MD, b) S10MD and c) S30MD

As can be seen as longer is the sulfonation time the particles turn on a darker brown color. A sulfonation time of 10 min did not affect noticeably the microcapsules morphology (Figure 6b), whereas for a sulfonation time of 30 min an appreciable number of cracked microcapsules are observed (Figure 6c). The quantification of cracked microcapsules indicates that this material increases from 24.49 to 75.36 wt.% raising the sulfonation time from 10 to 30 min.

These results suggest that the presence of DEHPA into the microcapsules decreases the chemical resistance of the polymer, since only 1.0 wt.% of cracked solid particles from P(St) were obtained by Amick[78] following this sulfonation procedure. Hence, another sulfonating or swelling agent must be studied to minimize the number of cracked particles.

2) Sulfonation Using Swelling Agents:

Swelling agents are usually used to soften the reaction conditions during the sulfonation, since they reduce the effects of osmotic shock and maintain the spherical form of the bead[85]. Cyclohexane and chloroform have been used in literature to swell P(St-DVB) and P(St) particles, respectively, avoiding the particle damage after the sulfonation process[86, 87].

The stability of the microcapsules to this kind of agents was checked by means of the following procedure: 0.2 g of MD were added to 5 mL of chloroform and cyclohexane and keep under agitation during 24 h. After this period of time, microcapsules treated with chloroform (MD-CHCl₃) and cyclohexane (MD-cC₆) were separated from the liquid by filtration and dried at room temperature. Figure 7 shows the TG analyses of these materials in order to check if the amount of DEHPA had changed.
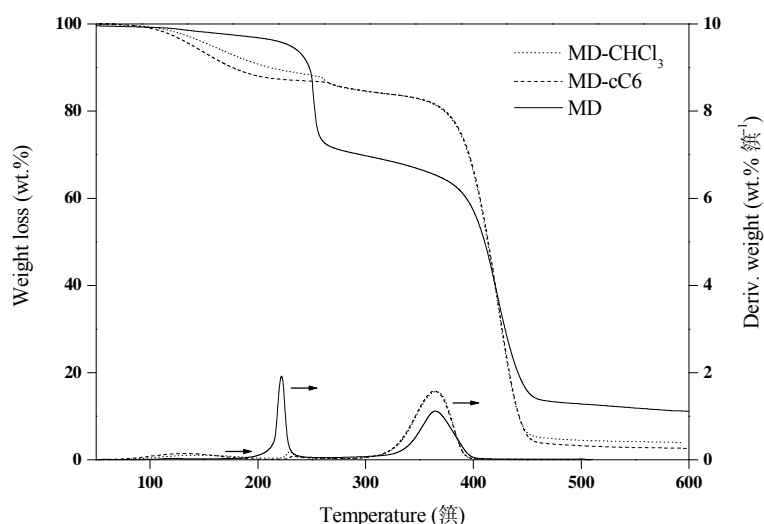
Figure 7 TG and DTG curves of microcapsules containing DEHPA treated with swelling agents

This figure shows a decrease in the weight loss at 250ºC when MD are treated with solvents indicating that DEHPA is released from the shell material by the solvents. It is also confirmed by the residue content, which is similar to that obtained for particles from P(St-DVB), being lower than that for MD. Attending to these results, the use of swelling agents to decrease the damage of microcapsules was discarded prior to the sulfonation process.

3) Sulfonation Using H_2SO_4:

Lee et al.[76] employed sulfuric acid for the functionalization of P(St) particles and determined that their ion exchange capacity was smaller than that obtained when chlorosulfonic acid is used. However, there were not changes in their morphology. For this reason, H_2SO_4 as sulfonating agent has been studied for the sulfonation process. Sulfonation reactions were carried out at 25, 50 and 75ºC and at different times from 1 to 30 min.

The sulfonation time and temperature effect on the surface morphology and integrity of the microcapsules was analyzed by means of an optical microscope and results are shown in Table 2.

TABLE II INFLUENCE OF SULFONATION TEMPERATURE AND TIME WITH H_2SO_4 ON THE MORPHOLOGY OF THE MICROCAPSULES

As previously observed using the chlorosulfonation process, the higher the sulfonation time the greater the brown coloration of the obtained microcapsules. Attending to microcapsule appearance the minimum sulfonation is obtained at 25ºC whereas at temperature of 75°C the microcapsules are cracked even for 10 min of reaction time being this temperature so high for this purpose. On the contrary, at 50ºC the microcapsules are stable and seem to have been sulfonated. This temperature was selected as the proper sulfonation temperature to attribute ion exchange characteristics to microcapsules.

Once the temperature has been selected, this research was focussed in the determination of the adequate sulfonation time and in the study of its influence on the properties of MD and the particle size. Thus, these microcapsules were synthesized in a reactor of 10 L to produce enough amount of microcapsules. Produced microcapsules were sieved to separate them into fractions and using sieves between 355 and 710 μm. DEHPA content and average particle in volume of each fraction are reported in Table 3.

TABLE III LARGE-SCALE MICROCAPSULES PRODUCTION

Mesh size (μm)	DEHPA (wt.%)	$dpv_{0.5}$ (μm)
355	30.88	461.02
500	31.27	560.29
600	31.47	625.35
710	31.15	691.94

These results indicate that particle size does not have influence on DEHPA content and the synthesized product in a large scale has a DEHPA content similar to that obtained in the laboratory scale (34.86 wt.%).

The effect of the sulfonation time on the MD as function of the particle size by using optical microscope is shown in Table 4.

TABLE IV INFLUENCE OF SULFONATION TIME ON THE MORPHOLOGY OF THE MICROCAPSULES
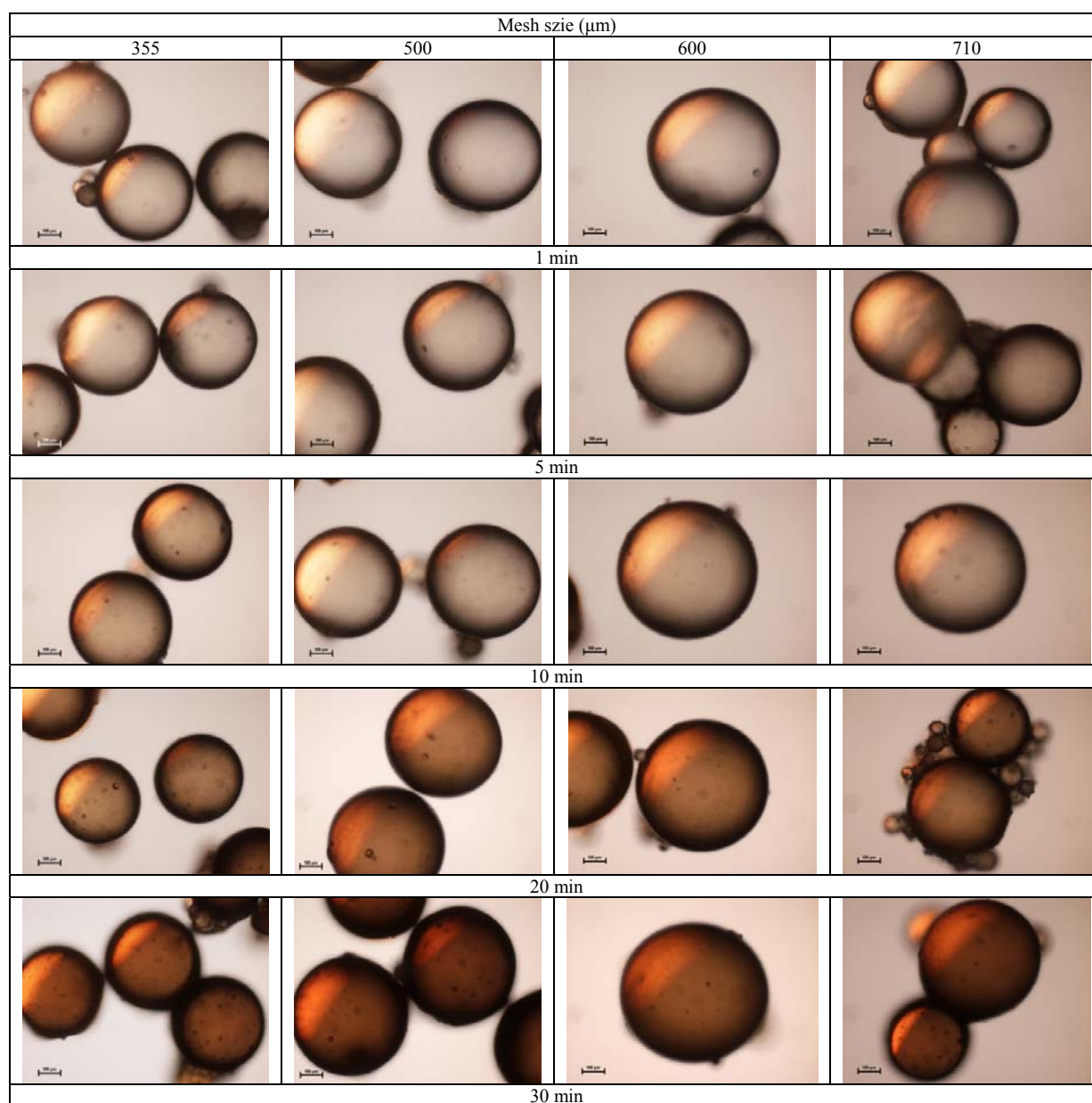
As can be seen, there are not cracked microcapsules and thus, this sulfonation procedure seems to be less aggressive than the chlorosulfonic method. It is also observed independently on the particle size that the longer the sulfonation time is, the more colorful the material is due to presence of sulfur.

To determine the presence of sulfonic groups in the polymeric shell, sulfur content and swelling degree were quantified.

For sulfonated microcapsules it is not possible to analyze DEHPA content by means of thermogravimetric measurements since after sulfonation there is a weight loss from 200 to 350ºC related to the desulfonation process[88-89]. This range temperature coincides with DEHPA descomposition, thus TG results would not be representative. For this reason, the way to check if they suffer the loss of the extractant after the sulfonation, it was necessary an exposure of the material to acetone. This solvent is capable of extracting DEHPA from microcapsules and thus, DEHPA loss can be determined gravimetrically taking into account the mass of microcapsules before and after the exposure to acetone.

Figure 8 shows Sw(%), S and DEHPA contents for each particle size after the sulfonation process. It can be observed that all of these parameters exhibit a linear behaviour over time for every particle size. In the case of S and Sw(%) the effect of time of reaction is positive, while the effect for DEHPA percentage is negative. Thus, as higher is the sulfonation time the content of sulfur becomes greater reaching values higher than 50 g kg^{-1} for 30 min of reaction. This S content is much lower than that measured for the commercial resin Amberlite IR-120 (136 g kg^{-1}). But, the main goal of this process is not the total sulfonation, is to attribute ion exchange properties to microcapsules keeping a high seletivity to heavy metals, increasing the mobility of the ionic species inside the polymeric matrix.
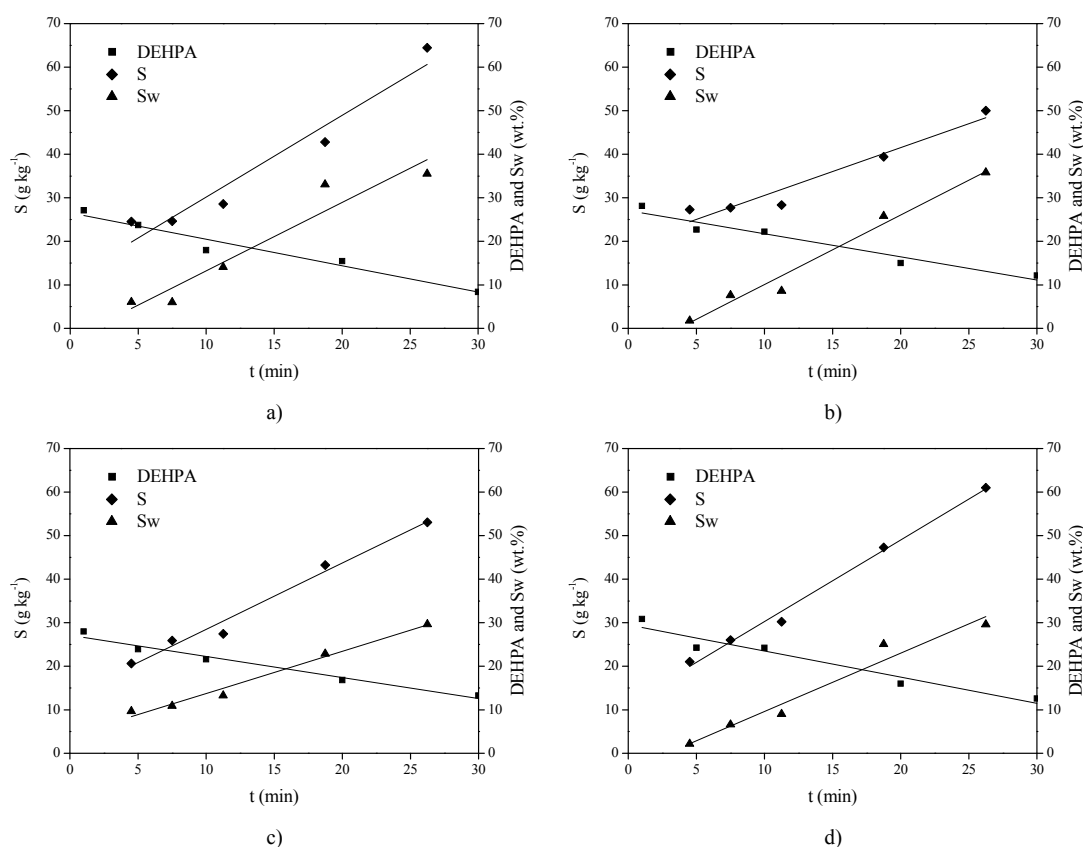

Figure 8 Swelling degree, sulfur and DEHPA contents after the sulfonation process for particle size: a) 355 μm, b) 500 μm, c) 600 μm, d) 710 μm

The incorporation of sulfonic groups (−SO$_3$H) to the polymeric network transforms its hydrophobic nature into one with a hydrophilic character. Consequently, the higher the sulfonation time is, the higher the amount of retained water is. In this way swelling degree increases up to 35 wt.% for 30 min of sulfonation. This solvation must favour the mobility of the ions inside the polymeric shell, enhancing the diffusion of the ions into this polymeric membrane[52].

As can be observed in this figure, even for 1 min of reaction time the amount of DEHPA is reduced by almost a 10 wt.% and decreasing to the half of its initial concentration at 30 min. This is due to the fact that sulfuric acid not only functionalizes the polymeric shell but also elutes DEHPA from the microcapsules. Hence, the higher the sulfonation time, the greater the loss of extractant agent due to the higher contact time with the acid.

These results let us conclude that although sulfonation with sulfuric acid seems to be a non destructive method to functionalize microcapsules, it produces the loss of the extractant agent during the process even just for 1 min of reaction. Nevertheless, it is necessary a minimum sulfonation time of 20 min to introduce into the shell a 30 % of sulfonic groups that a

commercial resin presents by using this method.

From the slope of the above straight lines for each particle size it is possible to obtain the sulfonation rate looking for the minimum effect on the DEHPA reduction. Gradients of sulfur and DEHPA contents respect to sulfonation time and DEHPA respect to sulfur are shown in Figure 9 as function on the particle size.
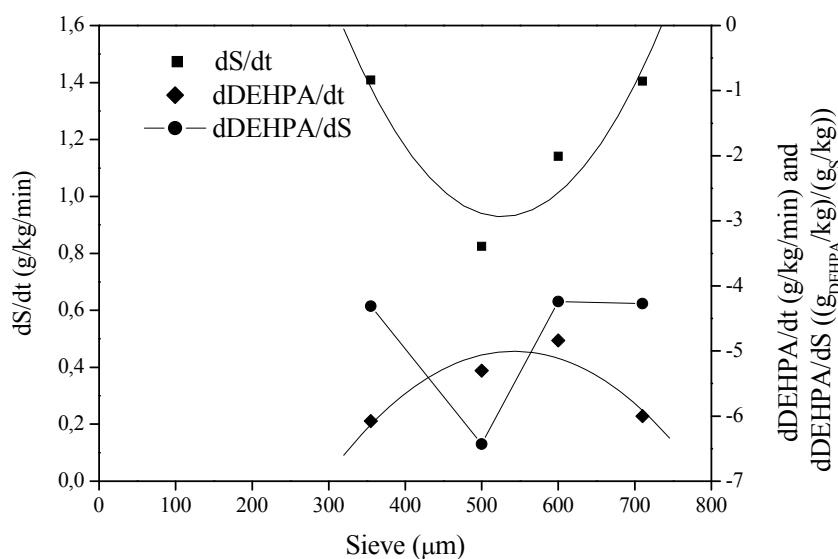

Figure 9 Influence of particle size on sulfonation and DEHPA loss rates and loss of DEHPA respect to sulfur incorporation

According to this figure, there is a minimum incorporation of the sulfonic groups into the polymeric shell for particles having an average diameter of 500 μm. In the same way, the more negative the gradient value (dDEHPA/dt), the faster the DEHPA elution from the microcapsule. This indicates that microcapsules of 600 μm are more stable to the sulfonation treatment. However, the gradient dDEHPA/dS, obtained dividing dDEHPA/dt per dS/dt, indicates that microcapsules of 500 μm must be selected for the sulfonation process since they exhibit the minimum value of this relation (-6.43 g_{DEHPA}/g_S). Finally, it can be concluded that sulfonated microcapsules containing DEHPA must be synthesized from P(St-DVB) having a particle size of 500 μm and sulfonated during 20 min with H_2SO_4 to attribute to them ion exchange characteristics.

IV. CONCLUSIONS

The formulation used for the synthesis microcapsules containing PRS® paraffin with a P(St) shell by suspension-like polymerization technique can be employed to microencapsulate a 28.15 wt.% of DEHPA by means of a polymeric shell from P(St-EGDMA). However, it was not a proper recipe to synthesize microcapsules from P(St-DVB) due to the high reactivity of the dispersed phase. Thus, the incorporation of a diluent was necessary in order to decrease the reaction rate. P(St-DVB) microcapsules with a extractant agent content of 34.86 wt.% were developed and selected for further sulfonation experiments, owing to their higher amount of DEHPA encapsulated. Sulfonation by chlorosulfonic acid was discarded since it brought a high percentage of cracked microcapsules (∼25%) even just for 10 min of reaction at 20ºC and swelling agents used in literature to minimize the sulfonation impact released the extractant agent from the polymer shell. On the other hand, sulfuric acid did not change the morphology of the microcapsules and the sulfonation of this material was noticeable at 50ºC. Sulfonation results showed that, regardless of particle size, the higher the sulfonation time, the higher the sulfur content and the swelling degree of the microcapusles due to the greater number of sulfonic groups incorporated in the shell. Likewise, the percentage of DEHPA decreased since it was extracted by contact with the acid.

Microcapsules of 500 μm of mesh size seemed to be the most stable material to the sulfonation process, as DEHPA loss per gram of incorporated S in the shell was the lowest found. Besides, a sulfonation time of 20 min is recommended to incorporate approximately a 30% of sulfonic groups into the shell materials of those observed in commercial products, avoiding a large loss of DEHPA during the sulfonation process.

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