# Characterization of Polysulfone and Polysulfone/Vanillin Microcapsules by H-1 NMR Spectroscopy, Solid-State C-13 CP/MAS-NMR Spectroscopy, and N-2 Adsorption Desorption Analyses

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RESEARCH ARTICLE

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# Characterization of Polysulfone and Polysulfone/Vanillin Microcapsules by $^{1}H$ NMR Spectroscopy, Solid-State $^{13}C$ CP/MAS—NMR Spectroscopy, and $N_2$ Adsorption—Desorption Analyses

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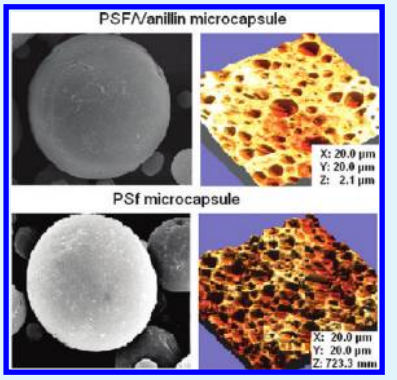
**ABSTRACT:** Textile detergent and softener industries have incorporated perfume microencapsulation technology to improve their products. Perfume encapsulation allows perfume protection until use and provides a long-lasting fragrance release. But, certain industrial microcapsules show low encapsulation capacity and low material stability. Polysulfone capsules have been already proposed to solve these drawbacks. Among them, PSf/Vanillin capsules were considered as a desirable system. They present both good material stability and high encapsulation capacity. However, several factors such as the final location of the perfume in the polymeric matrix, the aggregation state that it has in the capsule and its interaction with the capsule components have not been studied yet. These factors can provide vast information about the capsule performance and its improvement. With the aim to characterize these parameters, the physical and chemical properties of PSf/Vanillin capsules have been investigated by nuclear magnetic resonance (NMR) spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), and $N_2$ adsorption—desorption measurements. AFM micrograph and $N_2$ isotherms confirm that the presence of vanillin modify the physical structure of PSf/Vanillin microcapsules as it is trapped in the capsule porosity. NMR results show that vanillin is present in solid state in PSf/Vanillin microcapsules.




**KEYWORDS:** microcapsule, polysulfone, vanillin, NMR, $N_2$ sorption—desorption

## 1. INTRODUCTION

The use of microcapsules has been considerably increasing in the last years. Encapsulation technology presents numerous applications for a vast number of industrial products, such as metal removal, separation of organic acids, immobilization of anaerobic microbial cells, protection of food ingredients, release of perfume agents and drugs, isolation of solvents, etc.[1−7]

Capsules are produced from a large number of different materials. Among them, polymeric materials are mostly used. In this case, phase inversion method is one of the synthesis techniques more frequently employed.[1−8]

The controlled release of fragrances is a challenge for the industries that use perfumes in their products. Perfumes present compounds that may be lost because of their high volatility;[9−11] but, by encapsulation, they can be protected during storage and until the final use of the product.

Currently, the encapsulation of perfumes is being used for the development of textile products in order to offer a long-lasting fragrance release. It has been demonstrated that the aroma perception is maintained for several days in fabrics if these are impregnated with capsules containing perfume.[4,12,13]

Textile detergents and softeners industries have been incorporating in their processes the perfume microencapsulation technology as it allows to preserve the fragrance until the final use, as well as to provide a long lasting fragrance release.[14] The industrial perfume-containing microcapsules are fabricated mainly using interfacial polymerization with melamine-formaldehyde. They present a number of problems such as, low material stability and low perfume encapsulation capacity. Moreover, with the microencapsulation process used it is not possible to encapsulate hydrophilic perfumes.

With the aim to solve these problems polysulfone (PSf) microcapsules prepared by phase inversion precipitation technique were proposed.[2]

PSf macrocapsules containing vanillin, a polar component commonly used in perfume and cosmetic formulations,[15,16] have been investigated previously.[2,3] They showed promising results related to perfume encapsulation capacity, release behavior, and material stability.

In a previous work with PSf/vanillin films, it was observed that after immersing PSf/Vanillin films in aqueous solutions at different temperatures, the porosity on the porous surface of the membranes increased. It was concluded that the presence of perfume in the structure of PSf films changed the original morphology of the films.[17] However, a clear description about how and why the perfume alters the structure of the PSf material was not provided. Therefore, with the aim to understand and

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improve the capsule performance, it becomes necessary to determine how the perfume is located in the polymeric matrix, how it is encapsulated, which interactions it can have with the other capsule components, and finally, how this factors could affect the capsule performance.

The location of the active compound in the capsule material is an important aspect that governs the coating physical properties. Nuclear magnetic resonance (NMR) is one of the most versatile techniques used to determine chemical structures at atomic level resolution. NMR chemical shifts depend on the molecular environment of the atom nuclei, so changes in chemical shifts provide precise information on the position and interaction of the molecules' atoms.[18−25]

In the encapsulation technology, the core material release is the key factor that controls the requirements of industrial applications. In this case, the morphology of the capsules material is one of the main factors to determine the capsule performance. The pore size and the pore size distribution determine the capsules morphological parameters. Electronic microscopy techniques are widely considered to investigate morphological structure of different materials, including polymers. Scanning electron microscopy (SEM) offers a suitable method to examine in detail the morphological structure of capsules.[26] Besides, atomic force microscopy (AFM) is a good method to characterize the structure of membrane surfaces.[27−30]

Gas adsorption−desorption is a well-known technique for determining pore size and pore size distribution in porous materials, being nitrogen ($N_2$ at 77 K) the most widely used adsorptive.[31−36]

Because of the fact that PSf/vanillin microcapsules are a well-established chemical system for the production of microcapsules, for perfume release of hydrophilic substances, they have been here investigated by scanning electron microscopy (SEM), atomic force microscopy (AFM), proton nuclear magnetic resonance ($^1$H NMR) spectroscopy, solid-state carbon-13 cross-polarization/magic-angle spinning (CP/MAS) nuclear magnetic resonance (NMR) spectroscopy ($^{13}$C CP/MAS NMR) and $N_2$ adsorption−desorption measurements, with the purpose to elucidate the vanillin influence in the physical and chemical properties of PSf/Vanillin capsules and its relationship with their performance.

## 2. MATERIALS AND METHODS

**2.1. Materials.** Polysulfone (PSf) and vanillin were purchased from Sigma-Aldrich (Spain). NN Dimethylformamide (DMF) was obtained from Scharlau (Spain), whereas deuterated water ($D_2O$) with purity greater than 99.9% was from sigma-Aldrich (France).

**2.2. Microcapsule Preparation.** *2.2.1. Microcapsule Preparation for Chemical and Physical Characterization.* Two different polymeric solutions were prepared by dissolving (a) 15% w/w of PSf and 10% w/w of vanillin in DMF or (b) 15% w/w of PSf in DMF. Both of them were stirred during 24 h at room temperature with a stirring rate of 500 rpm, in a SBS multipoint magnetic stirrer. Microcapsules were obtained by phase inversion (immersion) precipitation technique;[8] by dispersing the polymeric solution, in order to form microdroplets, into a water bath containing 100 mL of $D_2O$. Microdroplets precipitation occurred because of an exchange of $D_2O$ and DMF, leading to vanillin encapsulation. Finally, the microcapsules were recovered, from the precipitation bath, by filtration and afterward analyzed by $^1$H NMR, $^{13}$C CP/MAS NMR, SEM, and $N_2$ absorption−desorption.

*2.2.2. Microcapsule Preparation with Different Vanillin Concentration.* As DMF is the solvent of the polymer, it is added into the polymeric solution in a considerable quantity and during the capsule formation a part of it is encapsulated together with the vanillin.[2,3] This represents a considerable problem, as DMF is harmful and toxic.[37,38] Decreasing the amount of DMF in the polymeric solution, within a limit that does not affect the capsule formation, and correspondingly increasing the vanillin concentration could reduce DMF encapsulation. Thus, with the purpose to prove this hypothesis, several PSf/vanillin microcapsules were prepared with different concentration of vanillin. In this way, four polymeric solution, with different vanillin concentration, were prepared by dissolving (a) 15% w/w of PSf and 5% w/w of vanillin in 80% w/w of DMF, (b) 15% w/w of PSf and 10% w/w of vanillin in 75% w/w of DMF, (c) 15% w/w of PSf and 15% w/w of vanillin in 70% w/w of DMF, and (d) 15% w/w of PSf and 20% w/w of vanillin in 65% w/w of DMF. All the solutions were stirred during 24 h at room temperature with a stirring rate of 500 rpm in a SBS multipoint magnetic stirrer. Microcapsules were obtained by phase inversion (immersion) precipitation technique, as mentioned above.

**2.2. Membrane Preparation (AFM Analyses).** Due to the shape and size of the microcapsules, AFM analyses cannot be carried out directly; therefore PSf and PSf/Vanillin films have to be used instead.

PSf and PSf/Vanillin membranes were prepared by phase inversion (immersion) precipitation technique[10] from two different polymeric solutions by dissolving (a) 15% w/w PSf, 10% w/w vanillin, and 75% DMF or (b) 15% w/w PSf and 85% DMF. Both polymeric solutions were mixed during 24 h at room temperature at a stirring rate of 500 rpm.

Membrane films were produced by spreading the polymeric solution onto a glass surface ($20 \times 20$ cm$^2$) using a casting knife, providing 50 $\mu$m thick films, which was pushed by an applicator (K-Paint applicator, United kingdom) at a constant velocity of 3 m/min. Afterward, the glass with the liquid polymeric film on top was immersed into a coagulation bath of Milli-Q water at 25 °C. Finally, precipitation took place because of an exchange of water and DMF obtaining as a result films with dimensions of $20 \times 20$ cm$^2$.

**2.3. Sample Preparation for Chemical and Physical Characterization.** To carry out microcapsules characterization in terms of morphology, chemical composition, and pore structure, we prepared samples according to Table 1.

For proton NMR analysis 8 samples were employed: (1) 1 g of PSf/vanillin microcapsules suspended in 2 mL of $D_2O$ solution that contained 0.01 and 0.03 g of vanillin and DMF respectively. It was done in this way for two reasons: first; for determining differences between DMF and vanillin present both in the external solution and inside the capsule and second; because in a previous investigation it was found that both vanillin and DMF were encapsulated together during the capsule formation.[2,3] Additionally, it was observed that PSf/Vanillin capsules released vanillin and DMF in water.[2,3] Thus, vanillin and DMF were added to $D_2O$ to avoid a release of the vanillin and DMF encapsulated in $D_2O$ during the analyses. (2) 0.1 g of vanillin dissolved in 2 mL of $D_2O$, (3) 0.02 g of vanillin dissolved in 2 mL of $D_2O$, (4) 0.6 g of DMF dissolved in 2 mL of $D_2O$, and (5) 0.06 g of DMF dissolved in 2 mL of $D_2O$.

With the purpose to avoid interferences in the detection of the capsule components, PSf/Vanillin microcapsules, without being immersed in a vanillin-DMF solution and conveniently dried, were also analyzed. In these analyses the only liquid compounds used were benzene and TMS standards. In this way, samples 6−9 were prepared by drying 1 g of PSf/vanillin microcapsules under vacuum at room temperature during 0, 5, 10, and 15 min, respectively. Samples 3 and 5 were also analyzed by $^{13}$C NMR.

For $^{13}$C CP/MAS NMR, four samples were studied: sample number 6 (described above), (10) 1 g of PSf microcapsules (without perfume), (11) 1 g of solid vanillin, and (12) 1 g of PSf microcapsules dried under a vacuum at 50 °C during 12 h.

**Table 1. Sample Preparation Conditions for Each Analysis**

| | | characterization techniques | | | | |
|---|---|---|---|---|---|---|
| no. | sample preparation | $^1$H NMR | $^{13}$C NMR | $^{13}$C CP/MAS NMR | SEM | $N_2$ adsorption−desorption |
| 1 | PSf/vanillin microcapsules were suspended in a $D_2O$ solution that contained 0.01 g of vanillin and 0.03 g of DMF. | * | | | | |
| 2 | 0.1 g of vanillin were dissolved in 2 mL of $D_2O$ | * | * | | | |
| 3 | 0.02 g of vanillin were dissolved in 2 mL of $D_20$ | * | | | | |
| 4 | 0.6 g of DMF were dissolved in 2 mL of $D_2O$ | * | * | | | |
| 5 | 0.06 g of DMF were dissolved in 2 mL of $D_2O$ | * | | | | |
| 6 | PSf/vanillin microcapsules without drying treatment | * | | * | * | |
| 7 | PSf/vanillin microcapsules were dried under vacuum at room temperature during 5 min | * | | | | |
| 8 | PSf/vanillin microcapsules were dried under vacuum at room temperature during 10 min | * | | | | |
| 9 | PSf/Vanillin microcapsules were dried under vacuum at room temperature during 15 min | * | | | | |
| 10 | PSf microcapsules | | | * | * | |
| 11 | solid vanillin | | | * | | |
| 12 | PSf microcapsules were dried under vacuum at 50 °C for 12 h | | | * | | * |
| 13 | PSf/vanillin microcapsules were dried under vacuum at 50 °C for 12 h | | | | | * |
| 14 | PSf/vanillin microcapsules were dried under vacuum at 50 °C for 12 h, were added in a release treatment with water during 96 h and were dried again under vacuum at 50 °C for 12 h. | | | | | * |

Samples 6 and 10 were analyzed by SEM. PSf and PSf/vanillin membranes were used for AFM studies as microcapsule configuration makes complicated the analysis. Membranes were analyzed immediately after being prepared.

$N_2$ adsorption−desorption analyses were performed with three samples: (12) described above, (13) 1 g of PSf/vanillin microcapsules dried under vacuum at 50 °C for 12 h, and (14) 1 g of PSf/vanillin microcapsules dried under vacuum at 50 °C during 12 h, afterward immersed in Milli-Q water during 96 h with an stirring rate of 700 rpm (release experiment), and finally dried again under vacuum at 50 °C during 12 h.

**2.4. NMR Spectroscopy.** *2.4.1. $^1$H NMR.* Proton NMR spectra of samples, prepared according to Table 1, were obtained at 400.13 MHz with a digital resolution of 0.06 Hz/data point using a Bruker DRX 400 NMR spectrometer. The NMR measurements were performed at 303 (± 0.1) K. The average number of scans recorded for all the samples analyzed, was 128. The 90° pulse length was typically 10 $\mu$s and the relaxation time (t1) was 6s. Chemical shifts ($\delta$) were determined from two external references of residual protons in fully deuterated benzene ($\delta$ = 7.157 ppm) with an aliquot of tetramethylsilane (TMS) ($\delta$ = 0.000 ppm) contained in wilmad coaxial insert capillaries (1 mm o.d.). NMR spectra were locked with $D_2O$.

*2.4.2. Liquid-State $^{13}$C NMR.* Liquid state $^{13}$C NMR measurements of samples prepared according to Table 1 were performed at 303 (±0.1) K using a Bruker spectrometer. All chemical shifts were recovered from the external references: deuterated benzene ($\delta$ = 128.39 ppm) with an aliquot of tetramethylsilane (TMS) ($\delta$ = 0.000 ppm) contained in wilmad coaxial insert capillaries (1 mm o.d.). $^{13}$C NMR spectra were obtained at 100.732 MHz with a digital resolution of 0.36 Hz/data point. The 90° pulse length was typically 10 $\mu$s with a relaxation time ($t_1$) of 1 and 2000 scans.

*2.4.3. Solid-State $^{13}$C CP/MAS NMR.* The cross-polarization magic angle spinning (CP/MAS) $^{13}$C NMR spectra of the solid samples, prepared according to Table 1, were collected with an ASX-300 Bruker spectrometer at 75.47 MHz with a contact time of 4 ms, a 10 kHz spinning rate and 13 000 accumulations with an interval of 5 s. All the CP/MAS $^{13}$C NMR measurements were performed at 300 (±0.1) K.

**2.5. Morphological Characterization.** The morphology of PSf/Vanillin and PSf microcapsules was determined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The SEM used was a JEOL JSM-6400 Scanning Microscopy Series, with an acceleration voltage of 15−20 KV and the AFM used was a Digital Instruments 3400 series.

Cross-section SEM micrographs were obtained by cryogenic breaking and afterward analyzed using SEM[26]

**2.6. $N_2$ Gas Adsorption−Desorption.** BET specific surface areas and pore size distribution of PSf and PSf/vanillin microcapsules were determined by $N_2$ gas adsorption−desorption at 77 K with a Micrometrics ASAP-2020 device. Prior to adsorption measurements, the samples were vacuum degassed for 12 h at 50 °C.

**2.7. Release Experiments.** *2.7.1. Determination of the Vanillin Influence in the Encapsulation of Polymer Solvent.* The effect of vanillin in the encapsulation of DMF was studied using five different PSf/Vanillin microcapsules: (1) with 5% w/w of vanillin, (2) with 10% w/w of vanillin, (3) 15% w/w of vanillin, (4) 20% w/w of vanillin, and (5) capsules without vanillin. For all the experiments, 1 g of PSf/vanillin microcapsules was added into 80 mL of Milli-Q water and stirred (SBS multipoint magnetic stirrer, Spain) at 700 rpm during 96 h. Medium samples of 1 mL were withdrawn and hermetically stored until the quantitative analysis.

*2.7.2. Vanillin Release after $N_2$ Gas Adsorpition−Desorption Analysis.* With the aim to determinate if vanillin stills remaining into PSf/Vanillin microcapsules after $N_2$ gas adsorption−desorption analysis, a vanillin release experiment was performed. With this purpose, 1 g of PSf/Vanillin microcapsules, (see Table 1, sample 12) were added into 80 mL of Milli-Q water and stirred (SBS multipoint magnetic stirrer, Spain) at 700 rpm during 96 h. Release medium samples of 1 mL were periodically withdrawn and hermetically stored until they were analyzed.

Table 2. $^1$H NMR Shifts of Vanillin in Different Systems

| | vanillin proton resonance (ppm) | | | | |
|---|---|---|---|---|---|
| system | $H_3CO$(a) | H(b) | H(c) | H(d) | CHO(e) |
| PSf/vanillin microcapsules | 3.887 | 6.981− 7.001 | 7.458−7.463 | 7.485−7.491<br>7.506−7.511 | 9.641 |
| vanillin concentrated | 3.801 | 6.899−6.919 | 7.279−7.284 | 7.355−7.359<br>7.375−7.379 | 9.553 |
| vanillin less concentrated | 3.818 | 6.912−6.932 | 7.302−7.306 | 7.372−7.376<br>7.392−7.396 | 9.566 |

Table 3. $^1$H NMR Shifts of DMF in Different Systems

| | DMF protons resonance (ppm) | | |
|---|---|---|---|
| system | $CH_3$ (a) | $CH_3$(b) | H(c) |
| PSf/vanillin microcapsules | 2.8224−2.825 | 2.941 | 7.899 |
| PSf microcapsules | 2.937 | 3.089 | 8.041 |
| DMF concentrated | 2.937 | 3.089 | 8.041 |
| DMF less concentrated | 2.855 | 2.981 | 7.932 |

**2.9. Analytical Determination of Vanillin and DMF.** The concentration of DMF and vanillin in water medium samples was determined by High-performance liquid chromatography (HPLC) using an Agilent 1100 with photodiode array detector. The column used was a supelcosil LC-8 (SUPELCO). The mobile phase was 80:20 water:acetonitrile. For all analysis, the flow rate was set at 1 mL/min, the column temperature was 40 °C, the analysis time was 8 min and the injection volume was 4 $\mu$L. DMF and vanillin concentration was determined at 229 nm, showing a typical retention time of 2−2.5 and 4.2−4.5 min, respectively.

## 3. RESULTS AND DISCUSSION

PSf microcapsules both with and without vanillin were characterized morphologically, physically, and chemically.

**3.1. Chemical Characterization.** *3.1.1. $^1$H NMR.* The interaction of vanillin and DMF in PSf/Vanillin microcapsules system was investigated by $^1$H NMR spectroscopy with the following purposes: (1) to elucidate the aggregation state that they have inside of the microcapsules and (2) to understand the interactions between them.

The $^1$H NMR spectra of two different samples of vanillin (sample 2 and 3) and DMF (sample 4 and 5) were recorded in $D_2O$ and compared with the spectrum of PSf/Vanillin microcapsules suspended in a $D_2O$ solution containing vanillin and DMF (sample 1). Results are collected in Tables 2 and 3.

As may be observed PSf/Vanillin microcapsules, suspended in a $D_2O$ solution containing vanillin and DMF, show five kind of protons corresponding to vanillin and another three corresponding to DMF.

As can be seen in Tables 2 and 3, all the resonance of PSf/vanillin microcapsules were shifted down in the case of the vanillin signals and shifted up in the case of the DMF signals. Both, downfield and upfield proton shifts were more notorious in the more concentrated systems. Hence, two factors play an important role in the chemical shifts of the capsule components: (1) their concentration and (2) the presence of the microcapsules.

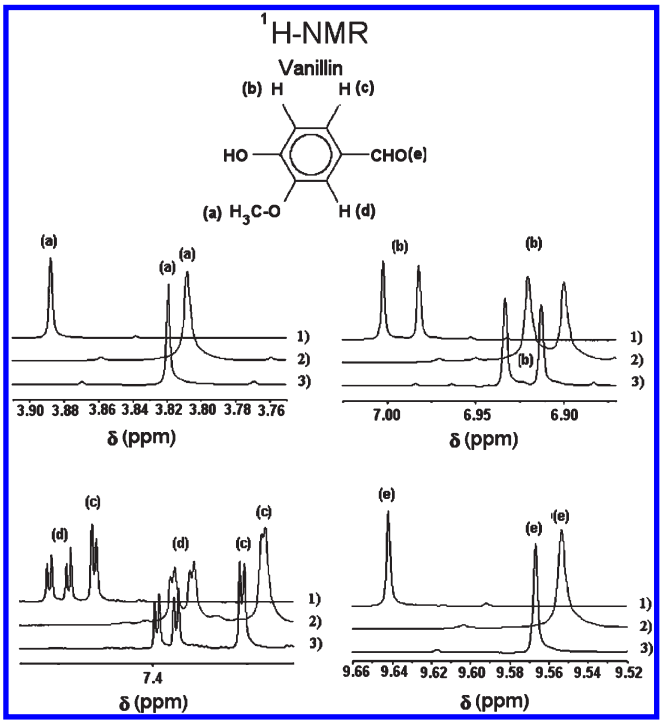


**Figure 1.** $^1$H NMR spectra. Vanillin resonance. (1) PSf/vanillin microcapsules in a DMF/vanillin/$D_2O$ solution, (2) concentrated vanillin/$D_2O$ solution, and (3) diluted vanillin/$D_2O$ solution.

However, it is not possible to conclude if those signals correspond to the DMF and the vanillin encapsulated. Thus, separated analysis of both vanillin and DMF signals were done.

Figure 1 shows the amplification of the vanillin signals in the spectra of the following samples: (1) PSf/vanillin microcapsules suspended in a $D_2O$ solution of vanillin and DMF, (2) a concentrated $D_2O$ solution of vanillin, and (3) a diluted $D_2O$ solution of vanillin.

Vanillin exhibits five kind of protons in this $^1$H NMR spectrum: one belonging to the methoxy group (a), three belonging to the phenol group (b, c, d), and one belonging to the aldehyde group (e). As may be seen in Figure 1, when the vanillin solution is less concentrated, all the vanillin proton resonances are shifted to the downfield. Similar results were previously reported. It was stated that vanillin was involved in a self-association process through stacking interactions.[39] The proton shifts can be attributed to a solvent effect. As the diluted vanillin solution presents a major quantity of $D_2O$, probably certain transient ionic interactions took place between the $D_2O$ and the vanillin protons.

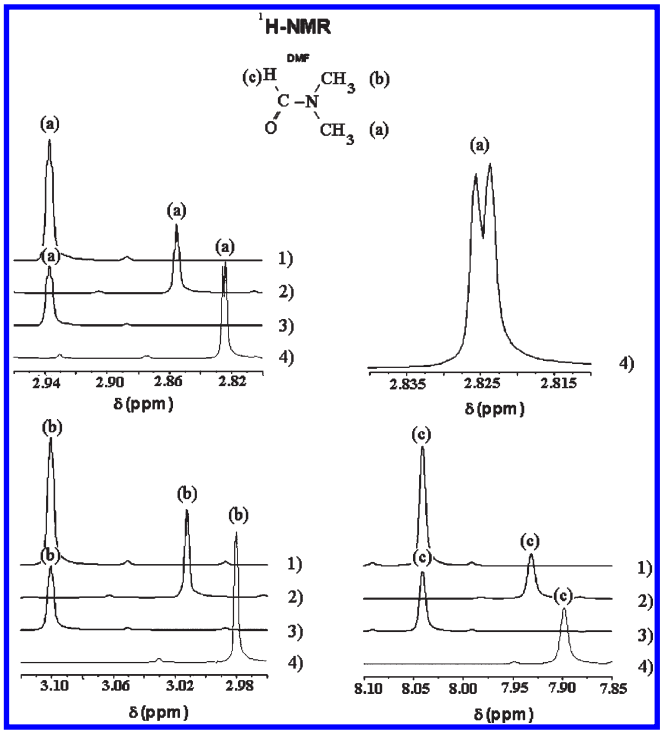


**Figure 2.** $^1$H NMR spectra. DMF resonances. (1) Concentrated DMF/$D_2O$ solution, (2) diluted DMF/$D_2O$ solution, (3) PSf microcapsules in a DMF/$D_2O$ solution, (4) PSf/vanillin microcapsules in a DMF/Vanillin/$D_2O$ solution.

In the case of the vanillin signals detected in PSf/vanillin microcapsules sample, not only $D_2O$ was present as a solvent but also DMF. Moreover, the presence of the capsules changed the environmental system. These factors favored the displacement to the downfield of the vanillin resonance.

In a previous investigation, it was found that vanillin was in liquid state into PSf/vanillin macrocapsules[2] and therefore two kind of vanillin in PSf/vanillin microcapsules system were expected: vanillin from the external solution and vanillin encapsulated, but duplicate signals were not encountered. Thus probably, those interactions could correspond to vanillin of the external solution and not to the vanillin of the capsule.

In the case of the DMF, its protons resonance were analyzed from four samples: (1) PSf/vanillin microcapsules suspended in a $D_2O$ solution containing vanillin and DMF, (2) PSf microcapsules suspended in a $D_2O$ solution containing DMF, (3) a concentrated DMF/$D_2O$ solution (sample 4), and (4) a diluted DMF/$D_2O$ solution (sample 5). Figure 2 shows the spectra of the samples and Table 3 the proton shifts of DMF.

As can be seen in Figure 2, the signals of the diluted system and the signals of PSf/vanillin microcapsules are shifted to the upfield. Although the DMF signals of the concentrated system and of the PSf microcapsules are exactly the same

As in the case of vanillin, a solvent interaction due to the DMF concentration was observed. Moreover, an ionic interaction could happen during the NMR analyze because DMF was more solvated. Probably an attraction between the $D_2O$ protons and the carbonyl or the amide groups of the DMF took place during the analysis.

In PSf/vanillin microcapsules, a particular case was observed. The first signal of DMF that corresponds to the methyl (a) resolves in two well-defined peaks (Figure 2). A similar phenomenon was observed in sodium dodecyl sulfate (SDS)/phenol micelles in which the nine bulk methylene protons of SDS shown two peaks, one at 1.20 ppm and the other at 1.28 ppm. The splitting of the signal was attributed to an approach of a part of methylene to polar groups and another part to a hydrophobic area of the micelle.[40] In another work, it was found that methylene protons resolved in two peaks in surfactants solutions containing acetophenone and benzophenone. It was attributed to the fact that acetophenone and benzophenone penetrate more deeply into the micellar core, shielding the half of the methylene protons.[41]

In the case of PSf/vanillin microcapsules, a splitting of the methylene signal was observed; one corresponding to the DMF of the external solution and another corresponding to the DMF encapsulated. The splitting may take place because of an interaction between the DMF encapsulated and the vanillin dissolved in the external solution. Previous investigations, demonstrated that the oxidation of DMF by hepatic cytochrome P450 takes place only in the same methylene (a) where in this work the splitting was observed.[42] Thus, that is why the splitting phenomena was only observed in the methylene (a) of DMF.

The existence of DMF in PSf/vanillin microcapsules was probed. Also the interaction vanillin−DMF was elucidated. However, the presence of vanillin in PSf/vanillin microcapsules was not observed by $^1$H NMR.

To corroborate if vanillin signals are detected by $^1$H NMR and with the propose to avoid any interference of the solution in which PSf/vanilin microcapsules were suspended, we carried out another $^1$H NMR analysis, consisting of analyzing samples of PSF/vanillin microcapsules, without being dissolved in a vanillin/DMF solution and dried under vacuum at different periods of time (0, 5, 10, and 15 min) as shown in Table 1 (sample 6−9). In these analyses, the only liquid compounds used were the external references of benzene and TMS. The results are shown in Figure 3.

As can be seen in Figure 3, a wide peak was observed in the PSF/vanillin microcapsules without drying treatment. This signal seems to correspond to water absorbed into the capsule surface. However, in comparison with the normal $D_2O$ spectrum, it was displaced to the downfield. This displacement is related to the volume magnetic susceptibility, which is a susceptibility-induced field caused by the interface of fluid and solid, of the absorbed water downfield-shifted. Similar results were found in bovine rib bone, in which a diamagnetic shift of the water resonance was observed because of the water absorption in bone samples.[43] The water absorbed in the capsule surface does not have freedom to move, thus it leads to a widening of the water signal. The signal of water disappears progressively when the drying period increases, finding in the spectrum only the external references signals. However, no signals of vanillin were detected.

As no vanillin signals were detected by $^1$H NMR it is possible to say that vanillin is in a solid state inside of capsules. As during the capsule precipitation,a great amount of DMF was lost into the coagulation bath, precipitation of vanillin inside the capsules could have taken place.

*3.1.2. Solid-State $^{13}$C−CP/MAS−NMR.* With the aim to confirm the physical state of vanillin in PSf/vanillin capsules, a solid-state $^{13}$C−CP MAS NMR analysis was performed.

The spectra were recorded for the following solid samples: vanillin, PSf/Vanillin microcapsules, PSf microcapsules (without vanillin) and PSf microcapsules (without vanillin) dried at 50 °C

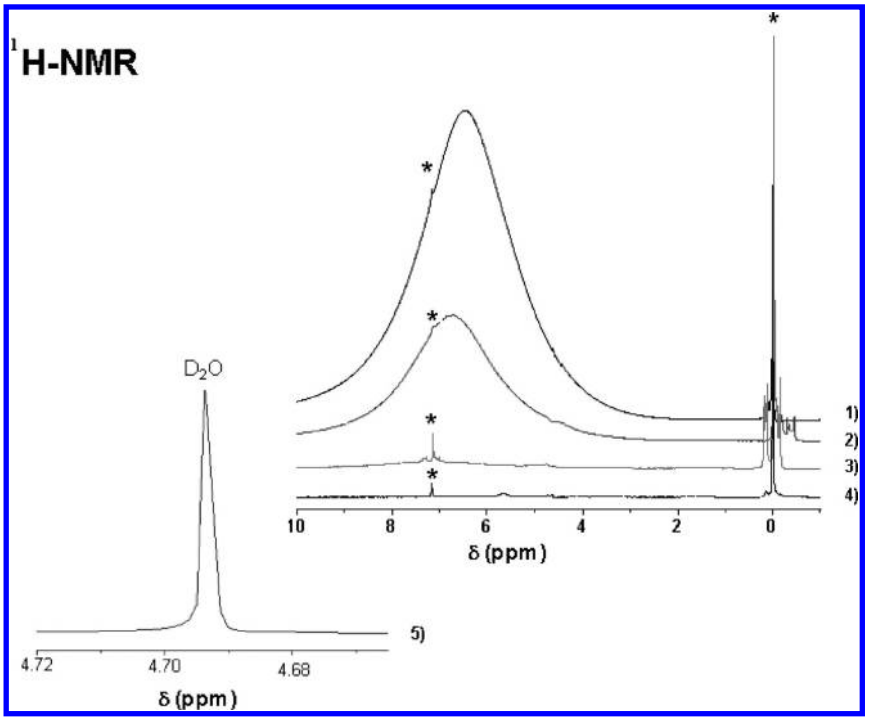


**Figure 3.** $^{1}$H NMR spectra. (1) PSf/vanillin microcapsules dried at room temperature spectrum. (2) PSf/vanillin microcapsules dried at room temperature under vacuum during 5 min spectrum. (3) PSf/vanillin microcapsules dried at room temperature under vacuum during 10 min spectrum. (4) PSf/vanillin microcapsules dried at room temperature under vacuum during 15 min spectrum. (5) $D_2O$. * External references.

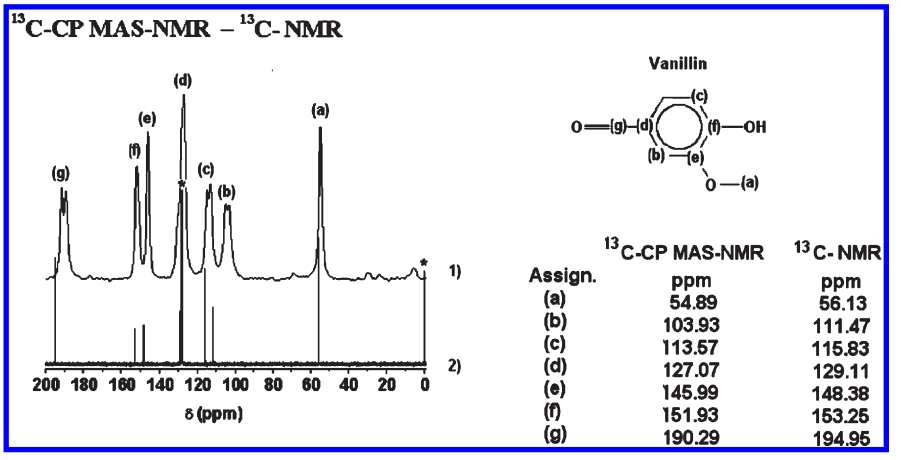


**Figure 4.** Solid-state $^{13}$C−CP MAS NMR and $^{13}$C NMR spectra of vanillin. (1) $^{13}$C−CP MAS NMR spectrum of vanillin. (2) $^{13}$C NMR spectrum of vanillin. * External references.

under vacuum during 12 h. All the samples were prepared according to Table 1. Figures 4−6 show the sample solid-state $^{13}$C−CP MAS NMR spectra.

$^{13}$C−CP MAS NMR and $^{13}$C NMR spectra of vanillin were compared in order to identify vanillin peaks and afterward to recognize them in the $^{13}$C−CP MAS NMR spectrum of PSf/vanillin microcapsules. Figure 4 shows the comparison between vanillin peaks obtained by $^{13}$C−CP MAS NMR and those obtained by liquid- state $^{13}$C NMR.

Vanillin shows six typical peaks in both spectra; however, they were slightly displaced from one spectrum to the other.

Figure 5 shows the spectra of dry PSf microcapsules without vanillin, PSf/vanillin microcapsules, and vanillin. As can be seen in Figure 5, two characteristic peaks of vanillin were encountered in PSf/vanillin microcapsules. Therefore, the presence of these peaks corroborates that vanillin is in solid state inside of PSf/vanillin microcapsules. Moreover, in the $^{13}$C−CP MAS NMR spectra of PSf/vanillin microcapsules it is possible to observe peaks that could correspond to the DMF resonance.

A sharp signal was observed in the range of 30 to 40 ppm. That signal could correspond to the DMF peak detected in the $^{13}$C NMR spectrum of DMF. With the aim to see if DMF remains inside of the capsules, the solid-state $^{13}$C−CP MAS NMR spectra of PSf/Vanillin microcapsules, PSf microcapsules and PSf microcapsules dried at 50 °C were compared with the liquid-state $^{13}$C NMR spectrum of DMF Figure 6 shows the results.

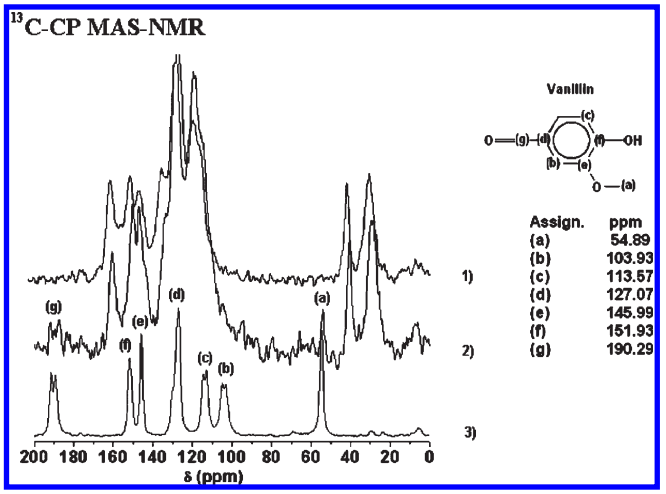


**Figure 5.** Solid-state $^{13}C-CP$ MAS NMR spectra. (1) Dry PSf microcapsules spectrum. (2) PSf/vanillin microcapsules spectrum. (3) Vanillin spectrum.

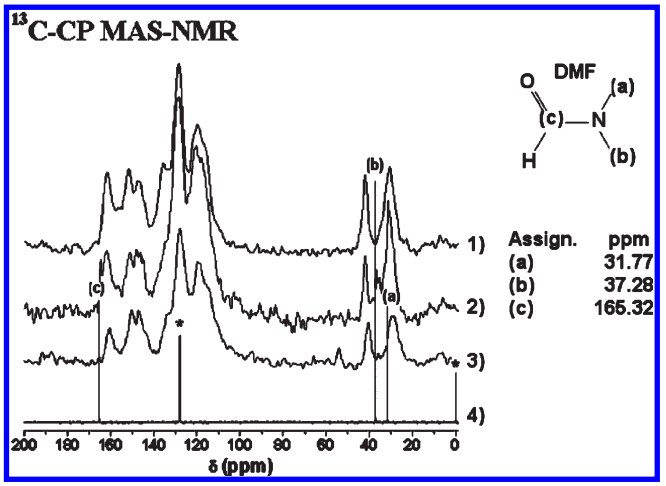


**Figure 6.** Solid-state $^{13}C-CP$ MAS NMR spectra of (1) PSf microcapsules dried at 50 °C under vacuum. (2) PSf microcapsules. (3) PSf/Vanillin microcapsules. (4) DMF/$D_2O$ solution. * External references.

As can be seen in Figure 6, DMF signals in dried PSf capsules (under vacuum for 12 h at 50 °C) were not detected. In a previous investigation, it was proposed the use of a vanillin-saturated solution to eliminate DMF from the capsules.[2] Hence, a combination of a drying treatment followed by a vanillin solution treatment could be used to improve the elimination of DMF encapsulated.

In the case of PSf microcapsules some sharp peaks, which nearly correspond with those DMF signals detected by liquid-state $^{13}C$ NMR, were clearly appreciated. While in PSf/Vanillin microcapsules only one signal was appreciated, Thus in the case of PSf/Vanillin microcapsules it is not possible to ensure that the signal corresponds to DMF.

DMF was detected in PSf/Vanillin microcapsules by $^{1}H$ NMR, but the conditions of the sample were totally different than the conditions of the samples analyzed by $^{13}C-CP$ MAS NMR. In $^{1}H$ NMR, the capsules were suspended in a solution with vanillin and DMF in order to preserve the components of the capsules. In $^{13}C-CP$ MAS NMR, the capsules were dried at room temperature in a desiccator. This, fact could involve a DMF release from the capsules. In the case of PSf microcapsules, the capsules were also dried as PSf/Vanillin microcapsules but curiously they showed the typical signals of DMF. Therefore, it is possible that the presence of vanillin determines the encapsulation of DMF. As PSf microcapsules do not contain vanillin, the amount of DMF is high and well-detected by $^{13}C-CP$ MAS NMR even after the drying treatment.

This information could be used to control the amount of DMF inside the capsules. It suggests that increasing the amount of vanillin in the polymeric solution it would decrease the DMF encapsulated. Thus, it was proposed to analyze the effect that the increment of the vanillin amount in the polymeric solution has on the encapsulation of DMF.

**3.2. Determination of the Vanillin Concentration Influence in the DMF Encapsulated.** Several experiments were performed to determine the influence of vanillin in the encapsulation of DMF. Table 4 shows the results obtained.

As may be seen in Table 4, the increment of the vanillin into the polymeric solution barely decreases the amount of DMF encapsulated. The amount of DMF released is quite similar in all the cases in which vanillin was added into the polymeric solution. However, when vanillin was not added into the polymeric solution, the quantity of DMF released had a significant increase.

Probably during the capsule formation, vanillin has a high tendency to be trapped into the polymeric matrix, blocking immediately its pores. Hence, DMF does not have the same freedom to be encapsulated because vanillin compacts the polymeric shell. Thus the amount of DMF encapsulated decreases.

On the other hand, the amount of vanillin released has a notorious increment when more vanillin was added into the polymeric solution. It seems that the extra vanillin added into the polymeric solution it is not lost during the capsule formation. Vanillin tends to be encapsulated. Moreover, the encapsulation capacity of PSf/vanillin microcapsules is higher than expected. Comparing with a previous investigation,[2] PSf microcapsules were not filled until their maximum capacity[2] as they allowed more incorporation of vanillin.

**3.3. Morphological Characterization.** Morphological characterization of PSf microcapsules with and without vanillin was carried out by SEM and AFM analysis.

Figure 7 shows SEM micrographs of PSf and PSf/vanillin microcapsules. SEM micrographs show that PSf microcapsules present diameters around 30 $\mu$m and a well-defined spherical shape. In addition, individual capsule formation without evidence of material collapse was observed. Also, cross-section micrographs show an empty space. At the same time, the presence of the polymer matrix throughout the whole capsule volume provides good material stability. Significant differences between both capsules were not observed.

On the other hand, as can seen in Figure 8, by AFM analysis, developed with the WSxM 5.0 software,[44] it is possible to distinguish clearly the differences between the films prepared with and without vanillin. PSf films present a higher amount of small pores, whereas PSf/vanillin films show less pores but with a larger size. It suggests that a part of vanillin occupies the capsule porosity, giving as a result a reduction in the amount of pores. Moreover, it seems that during the preparation of the films, a quantity of vanillin was located in certain pores deforming them. When the films were collected from the precipitation bath, the trapped vanillin was probably released and therefore led to larger pores.

**3.4. Physical Characterizations.** *3.4.1. $N_2$ Adsorption−Desorption.* Figure 9 shows the adsorption−desorption isotherms of PSf microcapsules, PSf/Vanillin microcapsules, and PSf/vanillin microcapsules after release treatments. As can be seen in Figure 9, all the samples exhibited type IV profile according to the BET classification,[28−30,32] which is represented by a mono and multilayer adsorption plus capillary condensation. Besides, each isotherm shows a hysteresis loop, as the resulting curves are in the form of a loop. The hysteresis loop observed in the isotherms can be associated to capillary condensation of the adsorbate in mesopores (>2 nm). This hysteresis loop belongs to the H4-type that characterizes mesoporous adsorbents with strong affinities.[31−33,35] However, in all the cases, isotherms were no longer reversible in the low-pressure region, thus a steep fall on the desorption branch was not detected. This phenomenon can be due to the presence of mesopores connected to the surface by narrow slitlike pores with a diameter in the range of the micropores (<2 nm).

On another hand, notorious differences are appreciated in the amount of micro and meso-pores. As may be seen in panels a and b in Figure 9, PSf microcapsules present more micro and macro pores than those microcapsules prepared with vanillin. As aforementioned, a part of vanillin precipitates into the capsule porosity blocking the pores. Therefore, vanillin reduces considerably the porosity of the capsules, and it is able to block both micro- and mesopores.

After the drying treatment of PSf/vanillin microcapsules, it was expected to obtain similar isotherms between PSf and PSf/

**Table 4. Vanillin Concentration Influence in the Encapsulation of DMF**

| % (w/w) of vanillin in the PSf polymeric solution | ppm of DMF released in a aqueous solution | ppm of vanillin released in a aqueous solution |
|---|---|---|
| 20 | 335.7 ± 0 | 697.5 ± 0 |
| 15 | 346.9 ± 3 | 517.4 ± 10 |
| 10 | 355.2 ± 3 | 451.3 ± 12 |
| 5 | 371.6 ± 4 | 272.1 ± 11 |
| 0 | 880.5 ± 3 | 0 |

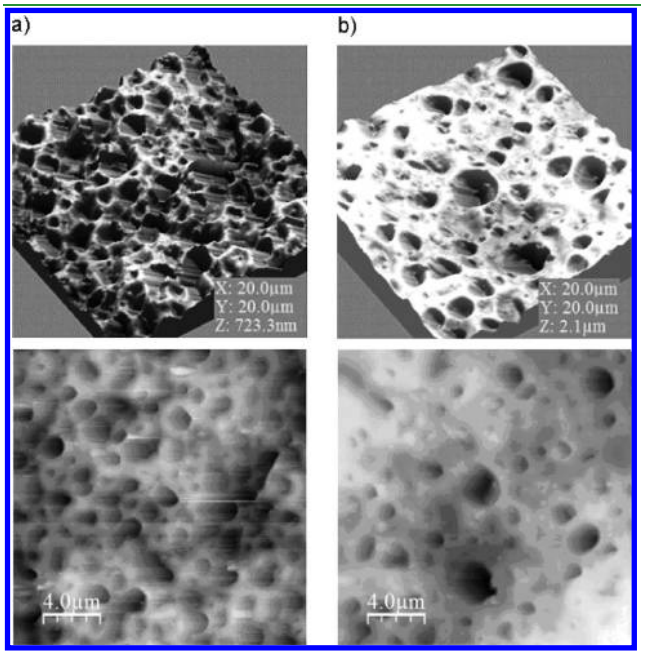


**Figure 8.** AFM micrographs. From left to right: (a) PSf films and (b) PSf/vanillin films.

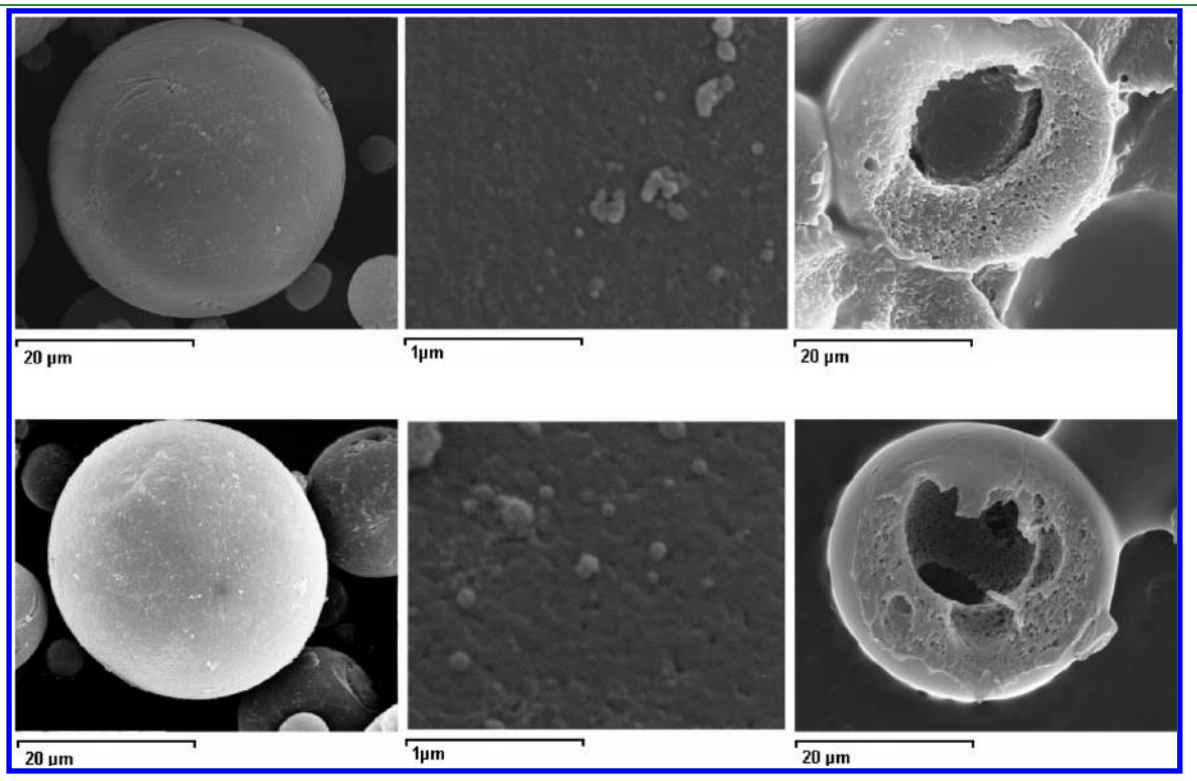


**Figure 7.** SEM micrographs (top, PSf/vanillin microcapsules; bottom, PSf microcapsules).

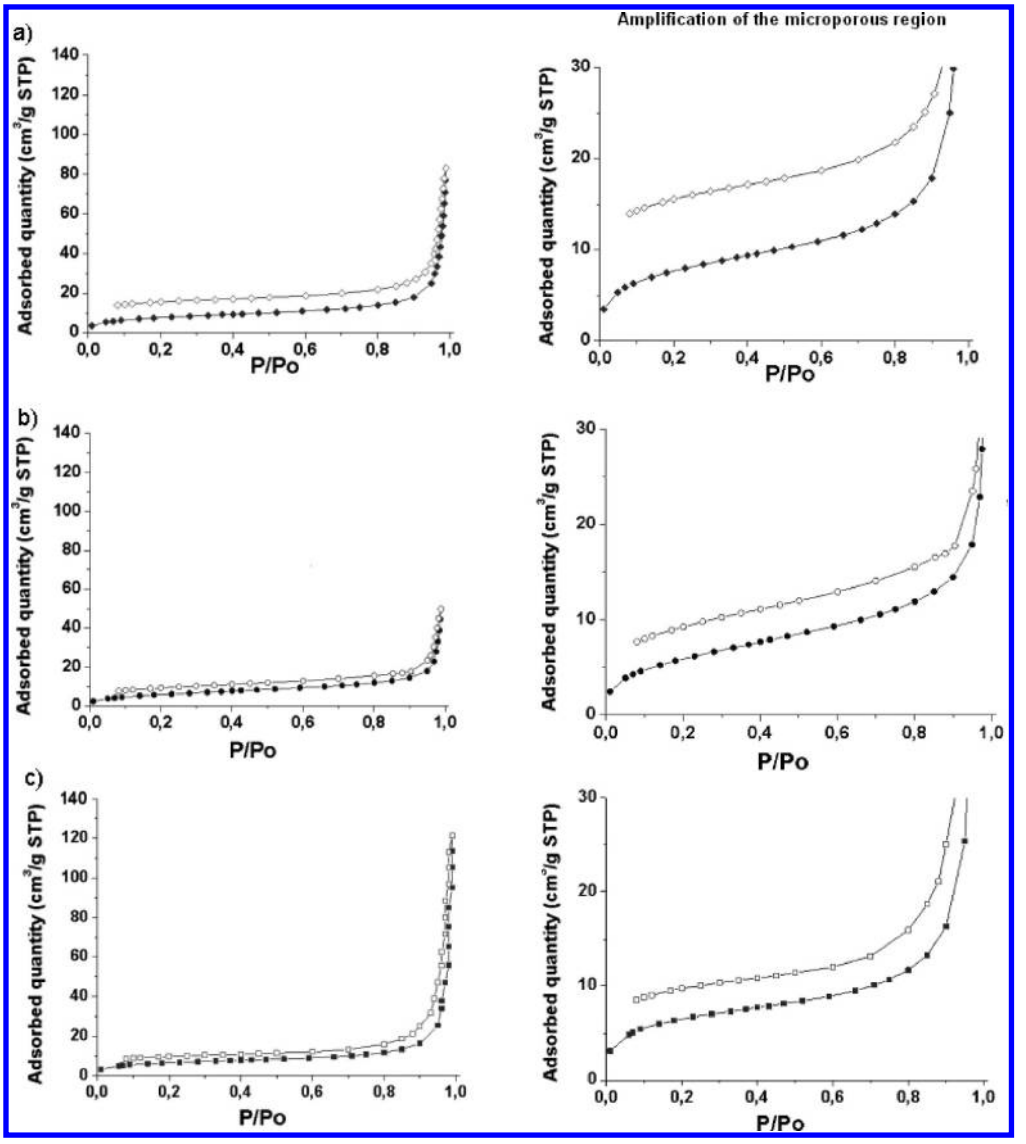


**Figure 9.** Adsorption−desorption isotherms. (a) PSf microcapsules dried at 50 °C under vacuum. (b) PSf/vanillin microcapsules dried at 50 °C under vacuum. (c) PSf/vanillin microcapsules dried at 50 °C under vacuum, afterward immersed in water for a release treatment, and finally, dried again at 50 °C under vacuum. Right images: normal adsorption−desorption isotherms. Left images: amplification of the microporous region.

vanillin microcapsules. However it was not possible. It indicates that vanillin is strongly trapped into the capsules, which is in fact a desirable factor that ensures perfume preservation and a long lasting fragrance release

It was not possible to obtain the same isotherm than PSf microcapsules even after heating the PSf/Vanillin capsules at 50 °C under vacuum during 12 h. It means that vanillin still remains in the capsules porosity. To corroborate this, a release experiment using PSf/Vanillin microcapsules previously dried (Table 1, sample 14) was performed and compared with the corresponding experiment with PSf/Vanillin microcapsules without drying treatment. Figure 10 shows the results.

As can be observed in Figure 10, vanillin is released from PSf/Vanillin microcapsules even after the drying treatment. In fact the release behavior is quite similar than that of capsules that were not dried. Vanillin is rapidly released during the first 10 h of experiment. After that, a plateau is reached. It seems that the release mechanism of PSf/Vanillin microcapsules is due to the dissolution of vanillin in the water present on the surface of the microcapsules and in the aqueous solution penetrating the microcapsule porosity. Moreover, the stirring enhances the release, because it helps to remove the vanillin molecules from the capsule surface to the bulk solution media. On the other hand, those capsules that were not dried have released a higher amount of vanillin. It seems that with the drying treatment, a part of vanillin was removed. However, even working under vacuum conditions, the amount of vanillin removed was not so high. Therefore, it is proved that capsules can protect the perfume offering a long lasting perfume release.

To elucidate whether PSf/vanillin microcapsules after the release experiment present a structure similar to those capsules prepared without vanillin, we subjected capsules that were dried and afterward used for a release experiment to another drying treatment (12 h at 50 °C under vacuum) and finally analyzed them by BET. Figure 9c shows the results.

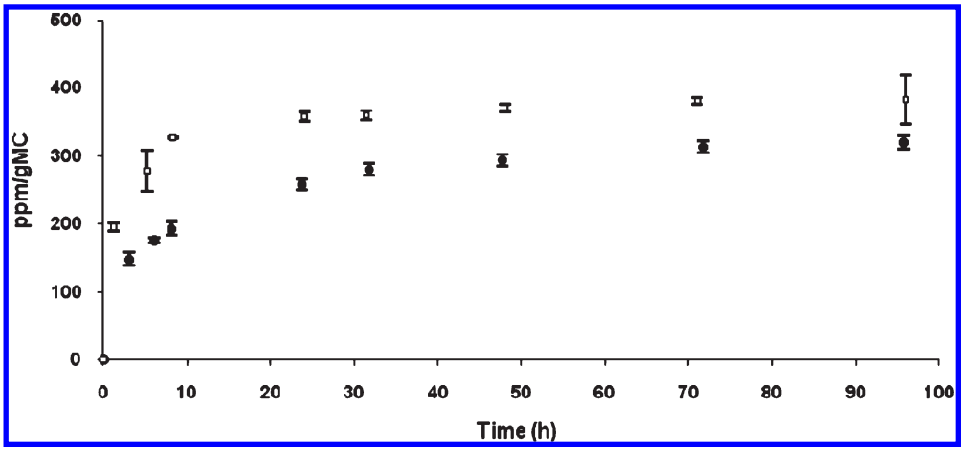


**Figure 10.** Vanillin release from PSf/Vanillin microcapsules. □, PSf/vanillin microcapsules without treatment; ● PSf/vanillin microcapsules after drying treatment.

As can be seen in Figure 9c, the microporous region barely changed in comparison with PSf/Vanillin microcapsules without release treatment. However, a greater number of macropores appears. After the release experiment, the macroporous region of PSf/Vanillin microcapsules (Figure 9c) is even highest than PSf microcapsules (Figure 9a). It means that vanillin is not only trapped into the micro- and macropores, but it is also changing the morphology of the PSf material. Previous analyses already showed that vanillin changed the morphological porosity of PSf membranes.[17] During the capsule formation, vanillin precipitates into the capsule porosity modifying the normal shape of the pores and making them larger.

*3.4.2. Surface Area.* The total surface area of microcapsules was determined by BET method. PSf microcapsules, which showed a higher amount of micro and meso pores than PSf/Vanillin microcapsules, presented a surface area of 27 $m^2/g$ and a total pore volume of 0.1283 $cm^3/g$; whereas the PSf/Vanillin microcapsules shown a surface are of 20 $m^2/g$ and a total pore volume of 0.0721 $cm^3/g$. As was mentioned above, vanillin is trapped in both micro- and mesopores reducing the surface area and the total pore volume of PSf/Vanillin capsules.

After the release treatment, both surface area and total pore volume of PSf/vanillin microcapsules were 23 $m^2/g$ and 0.1878 $cm^3/g$, respectively. Thus, even after the release treatment it was not possible to release all the vanillin from the capsule porosity. In addition, as the total pore volume value was higher than in the case of PSf/Vanillin microcapsules, it is possible to assume that the capsules morphology is considerably affected by the vanillin presence, leading to the formation of larger pores.

## CONCLUSIONS

PSf and PSf/vanillin microcapsules have been successfully prepared and morphologically, chemically and physically characterized.

NMR analysis demonstrates the presence of vanillin and DMF in PSf/vanillin microcapsules; the results show that vanillin exists in a solid state and DMF in a liquid state inside the capsule.

AFM micrographs and $N_2$ isotherms show that the presence of vanillin modifies the physical structure of PSf/vanillin capsules as part of it is trapped into the capsule porosity making the pores larger. Moreover, even heating the capsules at 50 °C under vacuum during 12 h, it was not possible to eliminate all the vanillin from the capsules; thus vanillin is strongly trapped in PSf microcapsule pores, which is in fact a desirable factor that ensures perfume preservation and a long lasting fragrance release.

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