PREPARATION AND CHARACTERIZATION OF PSF/VANILLIN CAPSULES
Brisa Marisol Peña Castellanos

PREPARATION AND CHARACTERIZATION OF PSF/VANILLIN CAPSULES

Thesis presented at the chemical engineering department to acquire the grade of doctor by the *Universitat Rovira i Virgili*

BRISA MARISOL PEÑA CASTELLANOS

Thesis supervised by Dr. Tània Gumí Caballero

METEOR
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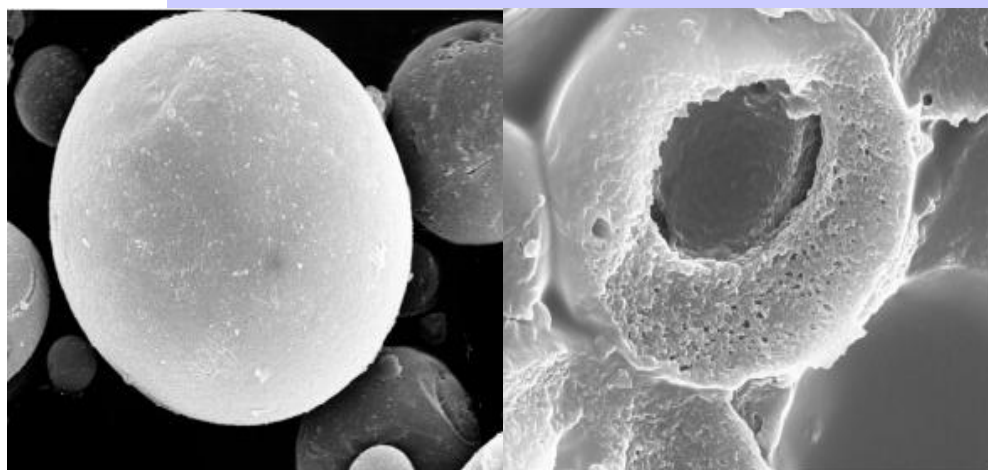
DOCTORAL THESIS

PREPARATION AND CHARACTERIZATION OF PSf/VANILLIN CAPSULES

Presented by:

Brisa Marisol Peña Castellanos

Universitat Rovira i Virgili
Departament d'Enginyeria Química

UNIVERSITAT ROVIRA I VIRGILI

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I, Dr. Tània Gumí Caballero,

CERTIFY

That the present study, entitled "Preparation and Characterization of PSf/Vanillin capsules" presented by Brisa Marisol Peña Castellanos for the award of the degree of Doctor, has been carried out under my supervision at the Chemical Engineering Department of this university.

Tarragona, 25 April 2012

Universitat Rovira i Virgili

Departament d'Enginyeria Química

Escola Tècnica Superior d'Enginyeria Química

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To acquire the grade of:

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Thesis directed by:

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Brisa Peña

When wisdom enters into your heart and

knowledge itself becomes pleasant to your

very soul, thinking ability itself will keep

guard over you and discernment itself will

safeguard you

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ABBREVIATIONS

Å	Angstrom
A_o	Original Cross-sectional Area
AFM	Atomic Force Microscopy
ASTM	American Society for Testing and Materials
ATR-IR	Attenuated Total Reflectance Infrared
Ca^{2+}	Calcium
C^{13}	Carbon-13
°C	Celsius degree
°C/min	Celsius degree per minute
cm	Centimeter
cm^2	Square Centimeter
cm^3	Cubic Centimeter
CP/MAS	Cross-Polarization/ Magic-Angle Spinning
D_2O	Deuterated Water
DMA_C	Dimethlyacetamide
DMF	Dimethylformamide
DFP	Dimethylsulfoxide
ε	Engineering Strain
E	Young's Modulus
F	Force
g	Gram
gMC	Gram of macro or microcapsule
Hz	Hertz
HPLC	High Performance Liquid Chromatography
^1H	Hydrogen Proton
H	Hysteresis
h	Hour
IFME	*Interpretació de Fotografies de Microscòpia Electrónica*
J_1	Nonsolvent Flux
J_2	Solvent Flux
K	Kelvin Celsius
KHz	Kilohertz
Kv	Kilo Volt
L	Liter
L	Original Distance between the gauge marks
l_0	Distance between the gauge marks after Force applied

Mg^{2+}	Magnesium
MHz	Megahertz
MPa	Megapascal
m	Meter
mm	Millimeter
µm	Micrometer
m^2	Square Meter
mL	Milliliter
µL	Microliter
mmHg	Millimeter of Mercury
min	Minute
ms	Millisecond
nm	Nanometer
N	Newton
N_2	Nitrogen
NMR	Nuclear Magnetic Resonance
n^a	a Number of Times
o.d	Outside Diameter
Pa	Pascal
Ppm	Parts per million
PSf	Polysulfone
pH	Potential of Hydrogen
rpm	Revolutions per Minute
s	Second
σ	Chemical shifts
σ	Engineering stress
SEM	Scanning Electron Microscopy
Tg	Glass Transition Temperature
TGA	Thermogravimetric Analysis
TMS	Tetramethylsilane
w	weight
XRD	X-Ray Diffraction

SUMMARY

The use of encapsulation technology has been considerably increasing in the last years. Its development started in 1950s with the preparation of capsules containing dyes for the manufacture of carbonless copy paper. Nowadays, encapsulation is a well-established scientific technology used by several industrial fields. It presents numerous applications for a vast number of commercial 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.

Encapsulation technology is mainly used to extend the lifetime of labile compounds. From an industrial point of view, the encapsulated compounds are easy to handle as they preserve their properties and stay safety in case of prolonged storage. This stabilization is due to the coating material, which acts as a protective physical barrier.

The resultant product of encapsulation technology is called capsule and it may be defined as spherical membranes with an empty volume inside. They can be classified, according to their diameter size, in nanocapsules (with diameter smaller than 1 µm), microcapsules (with diameter between 1 to 1000 µm) and macrocapsules (with diameter larger than 1000 µm). Capsules may be produced from a large number of different materials. Among them, polymeric materials are mostly used due to its properties and versatility of capsule production. In the latest case, phase inversion precipitation by immersion is one of the most commonly employed techniques for capsules preparation. It is based on the separation (by precipitation) of the polymeric phase from a mixture that contains a solvent and a polymer, by means of thermodynamic processes. The precipitation of the polymer occurs by a diffusion process in which the polymeric solution is immersed into a non-solvent (immersion precipitation). Phase inversion precipitation by immersion is a very well established technique that is not difficult to perform. In addition, it permits to obtain a vast kind of different polymer morphologies, and capsule formation takes place in few seconds without necessity of further stabilization. Moreover, no toxic products are produced and highe temperatures are not required.

Nowadays, the controlled release of fragrances is a challenge for the industries that use perfumes in their products. In general, fragrance ingredients are instable, they tend to degrade over time and it is needed to have tricks to make sure that the best fragrance perception is obtained at the moment that the consumer uses the product. There are several factors that release the desirable volatile molecules.

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Triggers can be pH and temperature, enzymes, oxygen, light or even pressure change. If one would be able to protect the perfume against its hostile environment, the degradation could be stopped or certainly slowed down. Considering that encapsulation technology offers a physical barrier between the perfume and its environment; it is the most appropriate solution to protect the fragrances during storage and until its final use.

Currently, the encapsulation of perfumes is being used for the development of innovative 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.

As the current tendency of consumers is the use of articles that ensure the preservation of the fragrance in the fabrics during drying and storage, textile detergent and softener industries have been incorporating in their processes the perfume microencapsulation technology. This technology allows the protection of the fragrance before and during industrial processes, as well as in the product storage. Moreover, it protects the perfume during the laundry and it provides a long-lasting fragrance release after the drying and storage of fabrics. However, certain current industrial microcapsules present a number of drawbacks such as low material stability, low perfume encapsulation capacity and, in addition, with the industrial encapsulation method presently used it is extremely complicated to encapsulate polar perfumes.

With the aim to solve these problems, in this investigation, polysulfone (PSf) capsules containing vanillin and prepared by phase inversion precipitation technique were proposed.

PSf has been selected as the capsule material due to its high stability (both thermal and chemical) and because it is a well-known polymer broadly used by industries. Vanillin has been selected as a core material because it is a polar component commonly used in perfume and cosmetic formulations; it has antioxidant and antimicrobial activities against yeasts, moulds and bacteria.

Thus, in this investigation PSf/Vanillin capsules have been prepared and chemically and physically analyzed with the aim to prove that PSf capsules may offer a stable system for vanillin encapsulation and that they may ensure a long lasting fragrance release and as well as a good encapsulation capacity.

Due to the simplicity of the capsule preparation, the first attempt of PSf/Vanillin capsules production has been performed at macro-scale. In this section of the doctoral thesis, PSf/Vanillin macrocapsules, with an average diameter size of 3 mm, have been successfully obtained by phase inversion precipitation technique.

Moreover, its morphology, encapsulation capacity and release behavior have been characterized. The results showed that PSf macrocapsules containing vanillin presented promising results to be used as a desirable system for perfume

encapsulation as they achieved to encapsulate more than the 50% of the total perfume added to the polymeric solution and to release perfume continuously for at least 120 h. This information has been used as a benchmark data for following investigations.

Once it was determined that PSf/Vanillin capsules showed good results concerning release behavior, encapsulation capacity, and stability, it was decided to study the mechanical properties of the PSf capsules under actual working and manufacturing conditions. In this way the optimum parameters that need to be used for the capsules formation and for the encapsulation process have been established. However, because of the shape and size of capsules, mechanical parameters cannot be measured directly with them. Thus, PSf membranes with the same chemical structure of PSf/Vanillin capsules have been used instead. Here two treatments have been performed: immersing PSf/Vanillin membranes in (a) 6000 ppm DMF aqueous solution or in (b) Milli-Q water, at different temperatures (55-90 °C). The results showed that after treating PSf/Vanillin films with both solutions at different temperatures, the porosity on the porous surface of the membranes increased. No structural changes have been detected in the dense layer. It was concluded that the presence of perfume in the structure of PSf films changed the original morphology of the films. However, after the material treatment, only the maximum strain % of PSf/Vanillin films has been modified.

After proving that capsule material has good mechanical properties, it was decided to scale down the capsule size. Thus, the third step of this thesis has been related to the production of PSf/Vanillin capsules at micro-scale in which an appropriate set-up for microcapsules production was successfully developed. Moreover, it has been verified that PSf/Vanillin microcapsules maintained the same good properties than they presented at macro-scale. The results showed that 45% of vanillin encapsulation, from the total perfume added to the polymer solution, has been reached. A treatment to increase the amount of vanillin inside of capsules has been proposed. It consisted to storage the capsules in a vanillin-saturated solution for four days. With this method the amount of vanillin in the capsules increased 100%. Concerning perfume release, it has been detected that vanillin was more rapidly released in hard water than in pure water; but in both cases, vanillin has been released continuously for more than 144 h.

In the last part of the thesis, in order to have a better understanding about the capsule performance, 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 been determined. The results corroborated that the presence of vanillin modify the physical structure of PSf/Vanillin microcapsules as it is trapped in all the capsule porosity. Moreover, it has been determined that vanillin is present in solid state in PSf/Vanillin

microcapsules. Furthermore, even heating the capsules at 50 ºC 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 ensure perfume preservation.

Therefore, PSf microcapsules prepared by phase inversion precipitation technique offer a desirable and stable system for encapsulation of vanillin that guarantee perfume protection and a long lasting fragrance release, as well as good material stability. PSf/Vanillin capsules show promising results to be used not only in detergents and softeners products, but also in other textile products. Moreover, due to the antibacterial and antimycotic properties of vanillin, these capsules may be used in fabrics that search for an antibacterial and antimycotic protection, by instant in sheets, pillowcases, mattress protectors or towels.

RESUMEN

El uso de la tecnología de encapsulación ha crecido considerablemente en los últimos años. Siendo el comienzo de su desarrollo en los años 50 con la encapsulación de pigmentos para la elaboración de papel autocopiativo sin carbón. Actualmente esta tecnología está muy bien establecida y es empleada en diversos campos industriales. Además, presenta numerosas aplicaciones en una gran variedad de productos comerciales tales como: eliminación de metales, separación de ácidos orgánicos, inmovilización de células microbianas anaerobias, protección de ingredientes alimentarios, liberación de fragancias y medicamentos, aislamiento de solventes, etc.

Principalmente, la tecnología de encapsulación se utiliza para extender la vida útil de compuestos inestables. Desde un punto de vista industrial, los compuestos encapsulados son más fáciles de manipular ya que conservan sus propiedades originales y se mantienen estables durante almacenamientos prolongados. Dicha estabilización es gracias al material que los cubre, el cual actúa como una barrera física protectora.

El producto resultante de la tecnología de encapsulación es la cápsula; la cual puede definirse como una membrana esférica que presenta un volumen vacío al interior. De acuerdo al diámetro de las cápsulas, estas pueden ser clasificadas en: nanocápsulas (con diámetros menores de 1 μm), microcápsulas (con diámetros entre 1 a 1000 μm) y macrocápsulas (con diámetros mayores que 1000 μm.

Las cápsulas pueden ser elaboradas de una amplia variedad de materiales. No obstante, los materiales poliméricos son los más utilizados debido a que sus propiedades permiten obtener cápsulas mediante una gran variedad de técnicas de encapsulación. Entre estas técnicas, la precipitación por inversión de fases es una de las más utilizadas. Esta técnica tiene sus bases en un proceso termodinámico, el cual da como resultado la separación (por precipitación) de un polímero procedente de una mezcla polímero-solvente (solución polimérica). La precipitación de la fase polimérica tiene lugar debido a un proceso de difusión, cuando la solución polimérica es sumergida en un no solvente. Esta técnica esta muy bien establecida y no es difícil de llevar a cabo; Además, ofrece la posibilidad de obtener una gran variedad de morfologías; Asimismo, la formación de cápsulas es prácticamente instantánea sin necesidad de una estabilización posterior. Adicionalmente cabe mencionar que no se producen productos tóxicos y no son necesarias altas temperaturas.

Actualmente, la liberación controlada de fragancias es un reto para las industrias que utilizan perfumes en sus productos. En general las fragancias son inestables

tienden a degradarse con el tiempo y algunas veces son necesarios algunos trucos para asegurar que en el momento en que el consumidor haga uso del producto obtenga la mejor percepción de la fragancia.

Existen muchos factores que detonan la liberación de las moléculas volátiles. Algunos detonantes pueden ser los cambios en el pH o en la temperatura, el uso de enzimas, la exposición al oxígeno o a la luz, así como también los cambios de presión. Si se fuese capaz de proteger los perfumes de las adversidades del medioambiente, la degradación o pérdida de las fragancias de estos, se podría reducir o incluso inhibir. Considerando que la tecnología de encapsulación ofrece una barrera física entre los compuestos encapsulados y el medio ambiente, entonces la encapsulación sería la solución más factible para proteger las fragancias y asegurar su calidad durante el almacenamiento y hasta su uso final.

Hoy en día, la encapsulación de perfumes esta siendo utilizada para el desarrollo de productos textiles innovadores con el objetivo de ofrecer una liberación de perfume de larga duración. Se ha demostrado que la percepción del aroma se puede mantener por varios días en telas, si estas son impregnadas con cápsulas que contienen perfume.

Debido a que la tendencia actual de los consumidores es el uso de productos que aseguren fragancias de larga duración, la industria de detergentes y suavizantes de ropas ha incorporado en sus procesos la tecnología de encapsulación de perfumes. Esta tecnología permite proteger los compuestos volátiles antes, durante y después de los procesos industriales; además, también protege las fragancias durante el ciclo de lavado; asimismo, ofrece una liberación prolongada del perfume durante el secado y almacenamiento de la ropa, haciendo que la fragancia se perciba durante tiempos prolongados. Sin embargo, algunas de las cápsulas industriales empleadas actualmente presentan una serie de desventajas tales como la baja estabilidad del material de la cápsula, la baja capacidad de encapsulación o bien la extrema dificultad de encapsular compuestos polares.

Con el propósito de resolver estos problemas, en esta investigación se han propuesto cápsulas de polisulfona (PSf) conteniendo vanilina, preparadas por la técnica de inversión de fases.

La polisulfona fue elegida como material de las cápsulas debido a que es un polímero muy bien estudiado y ampliamente utilizado por diferentes industrias; además presenta una alta estabilidad térmica y química. La vanilina fue seleccionada como perfume por que es un componente polar comúnmente utilizado en la perfumería y en cosméticos y por que posee propiedades antioxidantes y antimicrobianas contra levaduras, mohos y bacterias.

Por lo tanto, en esta investigación se han producido y analizado física y químicamente cápsulas de PSf con el objetivo de demostrar si estas pueden ofrecer un sistema estable para la encapsulación de vanilina, si pueden asegurar

una liberación prolongada de la fragancia y si pueden garantizar una buena capacidad de encapsulación.

Por lo tanto, debido a la simplicidad de la producción de macrocápsulas, las primeras cápsulas producidas fueron macrocápsulas de PSf/Vanilina. En esta sección de la tesis se obtuvieron exitosamente, por la técnica de inversión de fases, macrocápsulas de PSf/Vanilina con diámetros de alrededor de 3 mm. Además, sé caracterizó su morfología, su capacidad de encapsulación y su comportamiento de liberación del perfume. Los resultados mostraron que las macrocápsulas de PSf presentan características prometedoras para ser utilizadas como un sistema deseable en la encapsulación de perfumes, ya que estas cápsulas lograron encapsular más del 50% del total del perfume añadido a la solución polimérica; y además, lograron liberar perfume continuamente por más de 120 h. La información obtenida en esta parte de la investigación dio pie el desarrollo de esta tesis.

Una vez que se determinó que las cápsulas de PSf/Vanilina presentan buenos resultados referentes a liberación de perfume, capacidad de encapsulación y estabilidad, se decidió estudiar las propiedades mecánicas del material en condiciones extremas de fabricación. De esta manera, se establecieron los parámetros óptimos que se requieren para la formación de las cápsulas. No obstante, debido a la forma y tamaño de las cápsulas los parámetros mecánicos no se pueden determinar directamente con ellas. Por lo tanto para el desarrollo de este estudio, se utilizaron membranas con la misma estructura química que las cápsulas. De esta manera, membranas de PSf/Vanilina fueron expuestas a dos tratamientos que consintieron en sumergirlas en: (a) una solución con 6000 ppm de DMF o en (b) agua Milli-Q a diferentes temperaturas (55-90 °C). Los resultados mostraron que después de tratar las membranas con ambas soluciones a diferentes temperaturas, la porosidad de la capa porosa de las membranas se incrementó notoriamente. Mientras que en la capa densa no se detecto ningún cambio visible en su estructura. Se concluyo que la presencia de vanilina en las membranas de PSf/Vanilina cambia la morfología original de las membranas de PSf. Sin embargo, después de los tratamientos, solamente sé observo que la capacidad de elongación fue la única propiedad mecánica afectada.

Después de haberse probado que el material de las cápsulas presenta buenas propiedades mecánicas incluso al ser expuesto a condiciones extremas de trabajo, se decidió disminuir el tamaño de la cápsula. Por lo tanto, la tercera parte de la tesis se basó en la producción de cápsulas micrométricas; Así pues, se utilizó exitosamente un aparato para la producción de microcápsulas, el cual fue desarrollado en nuestro grupo de investigación especialmente para la producción de microcápsulas poliméricas. Además, se verificó que las microcápsulas mantienen las mismas buenas propiedades que las macrocápsulas. Los resultados

mostraron que las microcápsulas lograron encapsular 45% de la vanilina total añadida a la solución polimérica. Por otra parte, fue propuesto un tratamiento para incrementar la cantidad de vanilina en las cápsulas. Este consistió en depositar las cápsulas en una solución saturada de vanilina durante 4 días. Con este tratamiento se incremento en un 100% la cantidad de vanilina en las cápsulas. Respecto a la liberación de perfume, se detecto que la vanilina se libera más rápido en agua dura que en agua Milli-Q; sin embargo, en ambos casos, la vanilina se liberó continuamente por más de 144 h.

En la última parte de la tesis, y con el objetivo de entender mejor el comportamiento de las cápsulas, se determinaron diversos factores tales como la ubicación final del perfume en la matriz polimérica, el estado de agregación que éste presenta en la cápsula así como también las interacciones que éste tiene con los componentes de la cápsula. Los resultados corroboraron que la presencia de vanilina modifica la estructura física del material de la cápsula debido a que la vanilina se encuentra atrapada entre su porosidad. Además, se determinó que la vanilina está en estado sólido al interior de las cápsulas. Adicionalmente, incluso calentando las cápsulas al vacío a 50 ºC durante 12 hrs, no fue posible eliminar toda la vanilina de las cápsulas. Por lo que esto prueba que la vanilina está fuertemente atrapada en la porosidad de las cápsulas, lo que es de hecho un factor deseable que asegura la preservación del perfume.

En conclusión, las microcápsulas de PSf, preparadas por la técnica de inversión de fases, ofrecen un sistema estable y deseable para la encapsulación de vanilina; el cual garantiza una óptima protección del perfume, una liberación de perfume de larga duración y una buena estabilidad del material.

Las cápsulas de PSf/Vanilina muestran resultados prometedores para ser usadas no solamente en detergentes y suavizantes de ropa, sino también en otros productos textiles. Además, debido a las propiedades antibacterianas y antimicóticas de la vanilina, estas cápsulas podrían ser utilizadas en materiales textiles que deseen una protección antibacteriana o antimicótica; por ejemplo en sabanas, fundas de almohadas, protectores de colchones, toallas, etc.

RESUM

L'ús de la tecnologia d'encapsulació ha incrementat considerablement els últims anys. El seu desenvolupament es va iniciar als anys 50 amb l'encapsulació de pigments per a l'elaboració de paper autocopiatiu sense carbó. Actualment, aquesta tecnologia científica està molt ben establerta i s'utilitza en diversos camps industrials. A més, presenta nombroses aplicacions com ara: eliminació de metalls, separació d'àcids orgànics, immobilització de cèl·lules microbianes anaeròbies, protecció d'ingredients alimentaris, alliberament de fragàncies i medicaments, aïllament de solvents, etc.

Principalment, la tecnologia d'encapsulació s'utilitza per allargar la vida útil dels compostos inestables. A més, des d'un punt de vista industrial, els compostos encapsulats són més fàcils de manipular ja que conserven les seves propietats originals i es mantenen estables durant emmagatzematges prolongats. Aquesta estabilització es deu al material que els recobreix, que actua com una barrera física protectora.

El producte resultant de la tecnologia d'encapsulació és la càpsula, que es pot definir com una membrana esfèrica que presenta un volum buit a l'interior. D'acord amb el diàmetre de les càpsules aquestes es classifiquen en: nanocàpsules (diàmetres menors de 1 µm), microcàpsules (amb diàmetres que van des d'1 a 1000 µm) i macrocàpsules (amb diàmetre major de 1000 µm).

Les càpsules poden ser elaborades amb una àmplia varietat de materials. No obstant, els materials polimèrics són els més utilitzats degut a que les seves propietats permeten obtenir càpsules mitjançant una amplia varietat de tècniques d'encapsulació. Entre aquestes tècniques, la tècnica de precipitació per inversió de fases és una de les més utilitzades. Aquesta tècnica es basa en un procés termodinàmic que dona com a resultat la separació (per precipitació) de la fase polimèrica procedent d'una mescla polímer - solvent (solució polimèrica). La precipitació de la fase polimèrica té lloc degut a un procés de difusió que succeeix quan la solució polimèrica és submergida en un no solvent. Aquesta tècnica està molt ben establerta i no és difícil realitzar-la. A més ofereix la possibilitat d'obtenir una gran varietat de morfologies polimèriques i una formació de càpsules pràcticament instantània, sense necessitat d'estabilitzar-les posteriorment. Addicionalment, no es produeixen productes tòxics ni es requereixen altes temperatures.

Actualment, l'alliberament controlat de fragàncies és un repte per a les indústries que utilitzen perfum en els seus productes. En general les fragàncies són inestables, tenen tendència a degradar-se amb el temps i es necessari algun

enginy per assegurar que en el moment en que el consumidor farà us del producte obtindrà la millor percepció de la fragància.

Hi ha molts factor que fan que es perdin o degradin les fragàncies, alguns d'ells poden ser els canvis de pH i la temperatura, ús d'enzims, exposició a l'oxigen o a la llum, així com també els canvis de pressió. Si es fos capaç de protegir els perfums de les adversitats del medi ambient, la degradació o la pèrdua de les fragàncies es podria prevenir o reduir. Considerant que la tecnologia d'encapsulació ofereix una barrera física entre el perfum i el medi ambient, llavors aquesta tecnologia és la solució més apropiada per protegir les fragàncies durant el seu emmagatzematge i ús final.

Avui en dia l'encapsulació de perfum s'utilitza per al desenvolupament de tèxtils innovadors amb l'objectiu d'oferir un alliberament de perfum de llarga duració. Ja ha estat demostrat que la percepció de l'aroma es manté durant dies quan els teixits tèxtils han estat impregnats amb càpsules que contenen perfum.

Degut a que la tendència dels consumidor és d'utilitzar articles que asseguren una bona aroma a la roba desprès del seu rentat i emmagatzematge, la indústria de detergents i suavitzants de roba ha incorporat en els seus processos la tecnologia d'encapsulació de perfums. Aquesta tecnologia permet la protecció de les fragàncies abans i durant els processos industrials, així com també durant l'emmagatzematge del producte. A més, també aconsegueix que les fragàncies estiguin protegides durant el rentat de la roba, i que l'alliberament després del procés d'assecat i emmagatzematge sigui sostingut en el temps, fent que la fragància es percebi en un període de temps prolongat. No obstant, algunes de les càpsules industrials emprades actualment presenten una sèrie de desavantatges com ara la baixa estabilitat del material de la càpsula, la baixa capacitat d'encapsulació i, a més, amb el mètode industrial d'encapsulació és molt difícil l'encapsulació de compostos polars.

Amb el propòsit de resoldre aquests problemes, en aquesta investigació s'han proposat les càpsules de polisulfona (PSf) contenint vanilina preparades per inversió de fases.

La polisulfona va ser escollida com a material de càpsula degut a la seva alta estabilitat (tant tèrmica com química) i per que és un polímer ben estudiat i àmpliament conegut per les indústries. La vanilina va ser seleccionada com a perfum degut a que és un component polar habitualment emprat en perfumeria i cosmètics i perquè té propietats antioxidants i antimicrobianes contra llevats, fongs i bactèries. A més l'encapsulació de vanilina presenta un repte degut a les seves propietats polars.

Per tant, en aquesta investigació s'han preparat i analitzat química i físicament càpsules de PSf amb el propòsit de demostrar que poden oferir un sistema

d'encapsulació estable per a la vanilina, assegurar un alliberament de llarga duració de la fragància i obtenir una bona capacitat d'encapsulació.

El primer intent de producció de càpsules de PSf amb contingut de vanilina es va realitzar a escala macro. Això fou degut a que en aquesta escala és més fàcil la preparació de càpsules. En aquesta secció de la tesis es van obtenir exitosament, mitjançant la tècnica d'inversió de fases, macrocàpsules de PSf/Vanilina amb diàmetres de 3 mm aproximadament. A més es va caracteritzar la seva morfologia, la seva capacitat d'encapsulació i el seu comportament respecte l'alliberament de perfum. Els resultats van mostrar que les macrocàpsules de PSf/Vanilina presenten característiques prometedores per ser utilitzades com un sistema adequat en l'encapsulació de perfums. Aquestes càpsules van aconseguir encapsular més del 50% del total del perfum afegit a la solució polimèrica i van alliberar perfum contínuament durant un mínim de 120 hores. La informació obtinguda d'aquesta part de la tesis es va emprar com a base per posteriors investigacions.

Un cop determinat que les càpsules de PSf/Vanilina presenten bons resultats pel que fa a l'alliberament de perfum, capacitat d'encapsulació i estabilitat, es va decidir estudiar les propietats mecàniques del material en condicions extremes de fabricació i ús final. D'aquesta manera es van establir els paràmetres òptims que es requereixen per la formació de les càpsules. No obstant, degut a la forma i la mida de les càpsules els paràmetres mecànics no es van poder mesurar directament amb elles. Per tant, es van utilitzar membranes amb la mateixa estructura química que les càpsules. Aquestes membranes van ser exposades a dos tractaments que consistien en submergir-les en: (a) una solució amb 6000 ppm de DMF o (b) aigua Milli-Q a diferents temperatures (55-90 ºC). Els resultats van mostrar que desprès de tractar les membranes amb ambdues solucions a diferents temperatures, la porositat de la capa porosa de la membrana va incrementar. Mentre que en la capa densa no es va detectar cap canvi visible en la seva estructura. Es conclou que la presencia de vanilina a les membranes de PSf canvia la morfologia del material original. No obstant, desprès dels tractaments, s'observa que la capacitat d'estirament és l'única propietat afectada.

Desprès de demostrar que el material de les càpsules presentava bones propietats mecàniques, es va decidir disminuir la mida de les càpsules. Per tant la tercera part de la tesis es basa en la producció de càpsules a escala micro, on es va utilitzar amb èxit un sistema per la producció de les càpsules desenvolupat per aquesta utilitat en els nostres laboratoris. A més, es va verificar que les microcàpsules mantenen les mateixes bones propietats que en mida macro. Els resultats mostren que les microcàpsules van aconseguir encapsular el 45% de la vanilina total afegida a la solució polimèrica. D'altra banda es va proposar un tractament per incrementar la quantitat de vanilina a les càpsules. Aquest consistia

en guardar les càpsules en una solució saturada de vanilina durant 4 dies. Amb aquest mètode es va incrementar en un 100% la quantitat de vanilina en les càpsules. Respecte a l'alliberament de perfum es va detectar que la vanilina s'allibera més ràpid en aigua dura que en aigua Milli-Q; no obstant, en els dos casos la vanilina es va alliberar de forma continua per més de 144 hores.

En la última part de la tesis, i amb l'objectiu d'entendre millor el comportament de les càpsules, es van determinar diversos factors com la ubicació final del perfum en la matriu polimèrica, l'estat d'agregació que presenta el perfum en la càpsula i la interacció que té el perfum amb els components de la càpsula. Els resultats corroboren que la presencia de vanilina modifica l'estructura física del material de la càpsula degut a que aquesta es troba atrapada entre els porus de les càpsules. A més es va determinar que la vanilina esta en estat sòlid a l'interior de les càpsules. Addicionalment, inclús escalfant les càpsules al buit a 50ºC durant 12 hores no va ser possible eliminar tota la vanilina de les càpsules. Això demostra que aquesta esta fortament atrapada a la porositat de les càpsules, fet que es desitjable per assegurar la preservació del perfum.

En conclusió, les microcàpsules de PSf preparades per la tècnica d'inversió de fase ofereixen un sistema estable i desitjable per l'encapsulació de vanilina que garanteix una òptima protecció del perfum, un alliberament de perfum de llarga duració i una bona estabilitat del material.

Les càpsules de PSf/Vanilina mostren resultats prometedors per ser utilitzades no solament en detergents i suavitzants de roba sinó també en altres productes tèxtils. A més, degut a les propietats antibacterianes i antimicòtiques de la vanilina, aquestes càpsules podrien ser emprades en fibres tèxtils a les que es desitgi dotar d'una protecció antibacteriana o antimicòtica; per exemple en llençols, fundes de coixí, protectors de matalàs i tovalloles.

CHAPTER 1

GENERAL INTRODUCTION AND GENERAL OBJECTIVES

GENERAL INTRODUCTION

Since the beginning of the history, humans found pleasure in the aroma perception of flowers and herbs. Nowadays, fragrances are commonly used in a wide list of commercial products. However, since the introduction of perfumed articles into the market, it is often judged the quality of the fragrance perception. Perfumes present compounds that may be lost due to their highly volatility or also they can be degraded over time. If one would be able to protect the perfumes against its aggressive environment, the loss and degradation could be stopped or certainly slowed down. Encapsulation is a technique in which a physical barrier between the fragrance and the environment is made. The main objective of this investigation is to propose a well-established microcapsule system containing vanillin for the development of novel textile products. However, for a better understanding of this investigation, it is required to define and to explain certain information. The following introduction shows, in a general form, several concepts used for the developed of this thesis.

1. ENCAPSULATION TECHNOLOGY

The encapsulation technology is a scientific advance currently used by several industrial fields. It has been developed following the example of nature, in which several cases exist. Nature encloses materials to protect them from environmental influences. Some easy examples on a macroscopic scale are an egg or a seed, while on microscopic scale the best example is that of a cell along with its contents.[1] Figure 1 shows some examples of nature encapsulation.

Figure 1. Examples of nature encapsulation

Encapsulation cannot be defined as a product or as a component of a product. Rather, it is described as a process of enclosing particles in an inert shell, which isolates and protects them from the external environment.[1]

Several ways to define encapsulation can be found in the literature, however all of them agree on the mainly purpose of this technology that is the protection of a core material. Zuidam et al. describe the encapsulation as a process in which a small solid particle, liquid droplets or gas bubbles are entrapped within a thin coating material, thereby producing capsules.[2] Thies refers the encapsulation as a coating of small particles with a thin film of shell material.[3] Madene et al. explain the encapsulation as a technique by which one material or a mixture of materials are coated with or entrapped within another material or system.[4]

Encapsulation has a vast number of interesting advantages, and the main reason for its use can be summarized as follows: [1-5]

- Production of a novel product.
- Protection of the product from the surrounding environment, thus improving the storage life and the stability of the system.
- Protection of the environment from the product (where the active core material is hazardous or toxic).
- Control of the release rate of the core material.
- Masking of the undesired properties of the active component, like the odor or taste masking, or masking the chemical properties.
- Separation of components allowing control of the incompatibility of components.
- Formation of solid systems, conversion of liquid components to free-flowing powders.
- Targeting of the site of release of active material (notably for pharmaceutically active materials).

2. CAPSULES

The resultant product of the encapsulation technology is called capsule. Peña et al. defined capsule as spherical membrane with an empty volume inside.[6] Warbuton describes capsule as a small, usually spherical, body.[7] Whateley defined capsules as particles for use as carriers of several agents. [8]

Three main classifications of capsules might be distinguished:

- Nanocapsules. They have diameters smaller than 1 μm.[9-10]
- Microcapsules. They present diameters from 1 to 1000 1 μm. [6,11]
- Macrocapsules. They show diameters larger than 1000 μm.[12-13]

There are several terms to describe the substance that is encapsulated. It can be referred to as core material, active agent, fill, internal phase, nucleus or payload phase. Whereas, the substance that is encapsulating maybe called coating, membrane, shell, carrier material, wall material, external phase, or matrix.[3]

Two principal types of encapsulates exist: the reservoir type and the matrix type.[14-15] Figure 2 shows both encapsulate types. The reservoir type has a shell around the active agent. This type is also called capsule, single core, mono core or core shell type. The application of pressure to the capsule can lead to breakage of the reservoir type of encapsulates and thus to the release of its contents.[14]
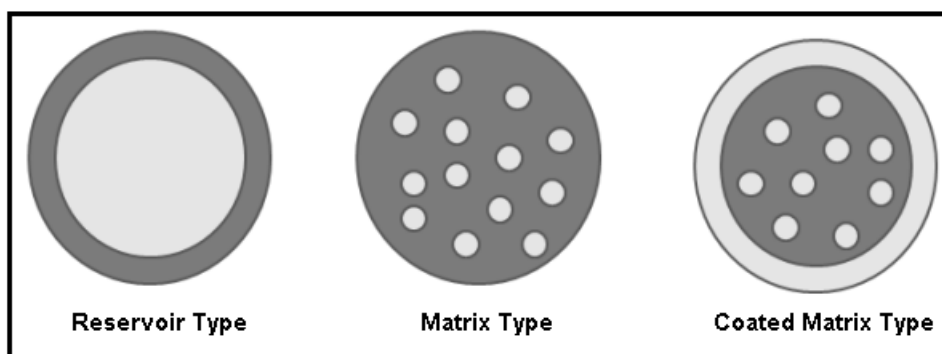
Figure 2. Schematic representation of encapsulation systems: Reservoir type (left), matrix type (middle), coated matrix type (right) encapsulates

Poly or multiple core type of encapsulates with several reservoir chambers in one particle also exist.[15] The active agent in the matrix type is much more dispersed over the shell material. It can be in the form or relatively small droplets or more homogenously distributed over the capsulate.[14] Active agents in the matrix type of encapsulates are in general also present at the surface, in contrast to those in the reservoir type, as can seen in Figure 2, where the active agent is indicated in light color and the shell in dark color. For simplification, it is only shown spherical shaped encapsulates, but they can also be cylindrical, oval or irregular shaped.

3. CAPSULES MATERIALS AND CAPSULES PRODUCTIONS

A long list of different shell-forming materials can be used to prepare capsules. However they may be classified in two main categories: [16]

- Organic materials (polymers)
- Inorganic materials

3.1 ORGANIC MATERIALS (POLYMERS)

Polymers can be described as molecules with a high molecular weight, composed from a number of basic units, the monomers. The structure of the polymers is kept due to the strong initial covalent bonds, which determine also physical properties like the flexibility of the chain or the ability to rotate around the backbone. However, not only covalent bonds are responsible of the polymer properties but also Van der Waals forces and hydrogen bonds. Physical properties of the material such as fusion, solution, vaporization, adsorption, diffusion, deformation and flow are governed by Van der Waals forces. In some systems hydrogen bonds define the properties like insolubility and thermostability.[16]

The abundance of natural and synthetic polymers provides a wider scope for the choice of shell material, which may be permeable, semi-permeable or impermeable. Permeable shells are used for release applications, while semi-permeable capsules are usually impermeable to the core material but permeable to low molecular weight liquids. Thus, the capsule can be used to absorb substances from the environmental and to release them again when brought into another medium. The impermeable shell encloses the core material and protects it from the external environment. Hence, to release the core material the shell must be broken. Release of core material through the permeable shell is mainly controlled by the thickness of the shell wall and its pore size.[1]

Therefore, the selection of the polymer is based on the final desired core release; this involves certain properties such as the structural characteristics of the polymer, its chemical and physical properties, its toxicity, its stability, the physical and chemical properties of the core, etc.[16]

Basically, all polymers can be used for the production of capsules but for this investigation, polysulfone (PSf) was selected as a polymer due to its high stability (both thermal and chemical) and because is a well-known polymer broadly used in industry.[16,18] Figure 3 shows the chemical structure of PSf.
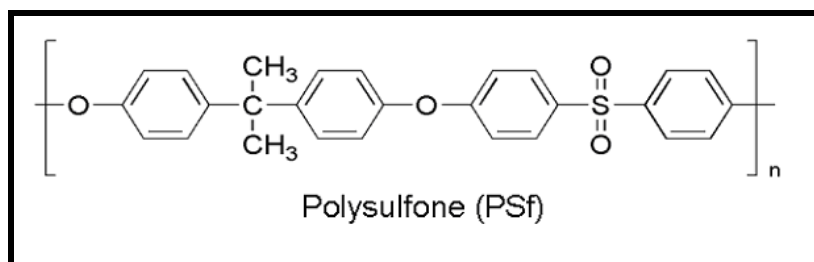
Figure 3. Chemical structure of PSf

Some relevant properties of PSf are mentioned as following:

- PSf has very good chemical and thermal stability as indicated by their T_g values (PSf: T_g 190 °C). This polymer is widely used as base material for ultrafiltration membranes.[16-18]
- It is highly resistant to mineral acid, alkali, and salt solutions as well as to detergents, oils, and alcohols.
- PSf is attacked by organic solvents such as ketones, chlorinated hydrocarbons, and aromatic hydrocarbons.[18]

For the preparation of polymeric capsules many techniques are available, but the most employed are listed following:

Spray-drying: Core particles are dispersed in a polymer solution and sprayed into a hot chamber. The shell material solidifies onto the core particles as the solvent evaporates.[19-20]

Emulsion polymerization: Many capsules are prepared through the polymerization of monomer units at the aqueous/organic interface of droplets in an emulsion. Emulsions of oil in water or water in oil are typically produced by vigorous agitation creating droplets that become the core material of the capsule. Polymerization begins in the aqueous phase by the first monomer units. These oligomeric radical species are rapidly captured by the monomer-swollen micelles leading a gradually grow until the monomer is completely consumed.[21]

Interfacial polymerization: In this process, two reactive monomers are dissolved in water and in an organic solvent respectively, while the core material is dissolved in a solvent of the dispersed phase. An oil-in water or water-in oil emulsion is formed by mixing the two immiscible solutions, with the addition of an emulsifier. The two reactive monomers in the two phases migrate to the interface of the emulsion droplets and react to form a polymer at the interface by polycondensation; this acts as wall material to encapsulate the core material in the emulsion droplets to form microcapsules.[22]

Layer-by-layer assembly: initially metal oxide particles are suspended in an aqueous solution. After that, negatively and positively charged polyelectrolytes are deposited onto these particles, forming layers of polymers held together by electrostatic interaction. When the multilayering is complete, an acid is usually employed to remove the metal oxide core, leaving behind hollow, semipermeable capsules. Because of the permeability of the shell walls, capsule cores can be readily exchanged with external media, allowing for a variety of core materials to be introduced after capsule preparation.[23-24]

Coacervation: Currently, two methods for coacervation are available: simple and complex processes. The mechanism of capsule formation for both processes is identical, except for the way in which the phase separation is carried out. In simple coacervation a desolvation agent is added for phase separation, whereas complex coacervation involves complexation between two oppositely charged polymers. The three basic steps in complex coacervation are: 1) preparation of the dispersion or emulsion; 2) encapsulation core; 3) stabilization of the encapsulated particle. First the core material is dispersed into a polymer solution. The second polymer (anionic, water soluble) solution is then added to the prepared dispersion. Deposition of the shell material on the core particles occurs when the two polymers form a complex. This process is triggered by the addition of salt or by changing the pH, temperature or by dilution of the medium. Finally capsules can be stabilized by cross-linking, desolvation or thermal treatment. [25-26]

Phase inversion: This technique started by the formation of a polymeric solution that contains a solvent, a polymer and a core material. The process of solidification takes place by the transition from one liquid state into two liquids (liquid-liquid demixing). At a certain stage during demixing the polymer will solidify, so a solid matrix surrounding the core will be formed. Phase inversion technique can be performed by different methods such as solvent evaporation, precipitation by controlled evaporation, thermal precipitation, precipitation from the vapor phase and immersion precipitation. From these methods, phase inversion technique by immersion precipitation method is the most commonly used.[6,16]

For this investigation phase inversion technique by immersion precipitation has been selected because is a very well established technique that is not difficult to perform. Moreover, it allows obtaining a large kind of different morphologies and in addition, capsule formation takes place in few seconds without necessity to stabilize the final obtained capsules. Also, not toxic products are produced and no highe temperatures are required.[16]

In a general form, in immersion precipitation method, the polymeric solution is dispersed, forming micro-droplets; after that, they are immersed in a coagulation

bath containing a non-solvent. Precipitation occurs because of the exchange of solvent and non-solvent. The capsule structure results from a combination of mass transfer and phase separation.[16] Figure 4 shows a schematic representation of microcapsule production by immersion precipitation. The solvent diffuses into the coagulation bath (J2) whereas the non-solvent will diffuse into the droplets (J1). After a given period of time, the exchange of solvent and non-solvent has preceded so far that the solution becomes thermodynamically unstable and demixing takes place. Finally solid polymeric capsules are obtained.[6]
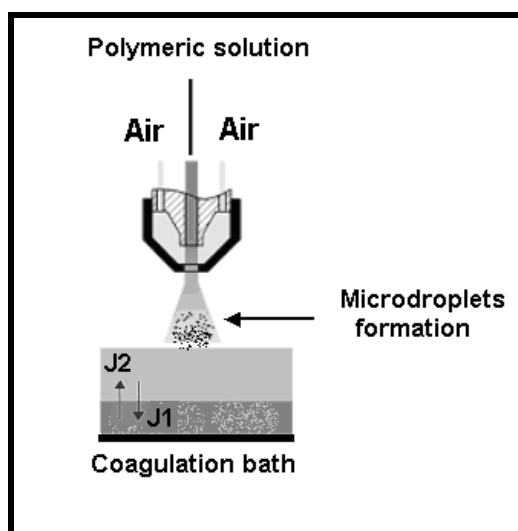
Figure 4. Schematic representation of microcapsule production

One of the principal aspects in the immersion precipitation process is the selection of the solvent/non-solvent system. For the polymer precipitation, it is necessary that the solvent of the polymer is completely miscible in the non-solvent.[16] Water is frequently uses as non-solvent. Some solvents for PSf that are miscible with water are followed listed:

- Dimethylformamide (DMF)
- Dimethlyacetamide (DMAc)
- Dimethylsulfoxide (DFP)
- Morpholine (MP)
- N-methylpyrrolidone (NMP)

The precipitation of the polymer takes place depending on the combination of solvent/non-solvent pair. This influences the morphology of capsules. Instantaneous precipitation will result in a porous capsule whereas delayed

precipitation will produce dense non-porous capsules. Table 1 shows the most important classification of some solvent/non-solvent pairs for PSf capsules precipitation

Table 1. Solvent/non-solvent pairs for PSf capsules precipitation

Solvent	non-solvent	type of capsule wall
DMF	Water	porous
DMAc	Water	porous
NMP	Water	porous
DMAc	n-propanol	non-porous
DMAc	i-propanol	non-porous
DMAc	n-butanol	non-porous

Due to the fact that we are interesting in the production of porous capsules that ensure perfume release, DMF/water system has been selected. DMF/water is a very well developed system for the production of porous PSf membranes. DMF has excellent solubility in water and many other organic solvents.[16,18] Moreover; it is a good solvent for PSf. Figure 5 shows the chemical structure of DMF.
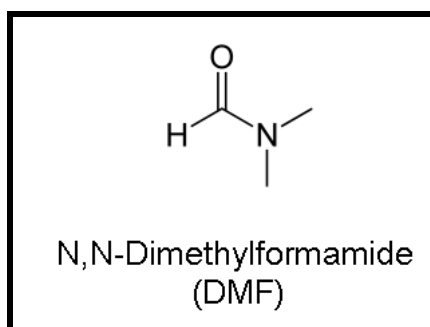
Figure 5. Chemical structure of DMF

3.2 INORGANIC MATERIALS

Inorganic materials generally offer better thermal conductivity and better chemical and mechanical stabilities than organic materials. There are different inorganic materials; however, for encapsulation, two principal types are frequently used: silicon oxide or silica (SiO_2) and zeolites. Silica matrix is thermal and photochemical stable without being hazardous to humans or environment. It is often used for slow release applications. While, zeolites are micro-porous materials that present good adsorption capacity and a crystalline structure. In both cases,

usually the fillers are added by adsorption after the capsule formation. Once the fillers are inside of the capsules they may be stabilized. In the case of zeolites, thermal treatments are commonly used while in silica microcapsules an extra shell over the capsules is required.[27-29]

4. CHARACTERIZATION TECHNIQUES FOR CAPSULES

With the aim to understand the capsule performance and therefore to improve their application, it becomes necessary to determine their physical and chemical properties. Currently, it exist a vast number of characterization techniques that can provide wide information related to capsule properties. Some of the most important capsule characterization techniques are described next. They are classified in physical and chemical characterization techniques.

4.1 PHYSICAL CHARACTERIZATION
4.1.1 SCANNING ELECTRON MICROSCOPY (SEM):

Scanning electron microscopy is a well-know technique that provides a good and easy method to characterize the capsule morphology.[6, 12] SEM is based in a narrow beam of electrons with kinetic energies in the order of 1-25 kV that hits the sample. The incident electrons are called primary electros (high-energy), and those reflected are called secondary electrons. Secondary electrons are liberated from atoms in the surface; they mainly determine the imaging. [16] To use this technique, the samples must be conductive. In the case of polymers, the sample have to be coated with a conducting layer, usually a thin gold layer.[16] Normally, the procedure consists to deposit gold atoms onto the sample under vacuum without changing its morphology.

In order to characterize the internal wall structure of capsules, some techniques have been developed such as resin inclusion or cryogenic breaking. For this investigation, cryogenic breaking was the method used to characterize the internal wall structure of PSf capsules because: it does not require a sample preparation after the formation of microcapsules; the time needed to perform the technique is shorter than in resin inclusion technique, capsule morphology is not altered during the cutting, and; in general, the process is simple to carry out;[30] However, for this procedure, a cryostat has to be employed. First of all, the capsules need to be attached over a specimen disc with a freezing medium, it may be used an embedding medium for frozen tissue specimens. Once the capsules are fixed over the specimen disc, the disc is immersed into liquid nitrogen. Then, the specimen disc is located into the cryo-chamber. After that, the sample is cut with desirable thickness intervals (usually of 1µm). Finally, the sample is ready to be analyzed by SEM.[6]

In general, the micrograph obtained allows to determine the external and internal morphological structure of the capsules as well as to offer a first estimation of the porosity and distribution of the pore size.

4.1.2 <u>ATOMIC FORCE MICROSCOPY (AFM)</u>:

AFM is a technique to determine the structure of a material surface being conductive or not. It offers topographic information and it allows to determine the pore size distribution of the material.[31-33] The advantage of this technique is that not pre-treatment is required and the measurements can be carried out under atmospheric conditions without damaging the sample. However, in our case, due to the shape and size of the capsules, AFM analyses cannot be carried out directly; thus films, with the same material composition as capsules, have to be used instead.

The technique consists in the scan of the sample surface with a cantilever that has a sharp tip with a diameter smaller than 100 Å. The scanning is performed with a constant force. The tip acts as a sensor of the surface geometry. During the scanning, it oscillates vertically according to its interactions with the sample. The oscillations, that have place due to the molecular interactions, are detected by the deflexion of a laser beam that impacts in a photo-diode (as it is showed in Figure 5).

Normally, The tip and the sample are approach to a distance between 0.1 and 100 nm. In this interval, there are different forces; the final balance of those forces would define the interaction between the sample and the tip as attractive or repulsive results. The most common force that interacts between the tip and the sample is the London-Vander-Waals.
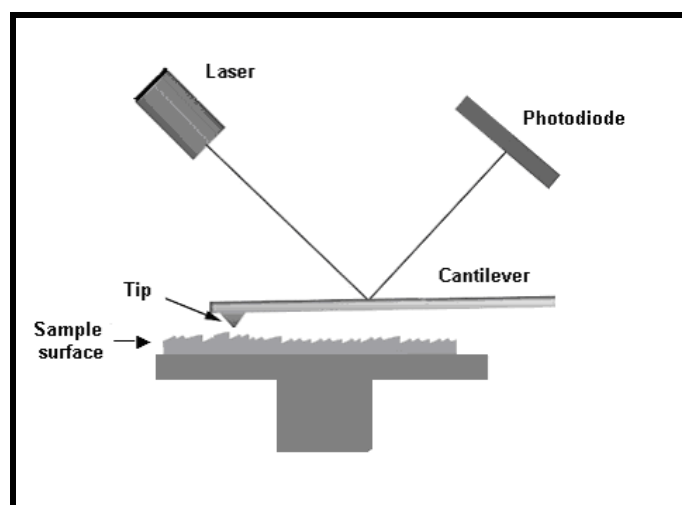
Figure 6. The principle of Atomic force microscopy

AFM analysis may be performed in three different modes: (1) Contact mode: here the distant between the tip and the sample is only of few angstroms, thus it is possible to say that the tip touches the sample. (2) Not contact mode: in this case the tip does not touch the sample; as a result, the forces that interacts are the attractive forces. (3) Intermittent mode: where the tip only touches the sample during the oscillations. From the AFM images it is possible to obtain the surface roughness, porous surface density, porosity, pore size and pore size distribution.

4.1.3 GAS ADSORPTION-DESORPTION MEASUREMENTS:

Gas adsorption measurements are broadly used for the characterization of a variety of porous solids. Of particular importance is the application of physisorption (physical adsorption) for the determination of the surface area and pore size distribution of the material.[34-40] Various procedures have been devised for determining the amount of gas adsorbed. Volumetric methods are generally employed for measuring nitrogen isotherms at temperatures of 77 K. The isotherm is created point by point by the admission and withdrawal of known amount of gas, with adequate time allowed for equilibration at each point. The majority of physisorption isotherms may be grouped into the six types shown in Figure 7.[35]

The reversible Type I isotherm is concave to the relative pressure axis and n^a approaches a limiting values as relative pressure=1. Microporous solids having relatively small external surfaces give these isotherms, the limiting uptake being governed by the accessible micropore volume rather than by the internal surface area.

Figure 7. a) Types of physisorption isotherms. b) Types of hysteresis loops

The reversible Type II isotherm is the normal form of isotherm obtained with a non-porous or macroporous adsorbent. The type II isotherm represents unrestri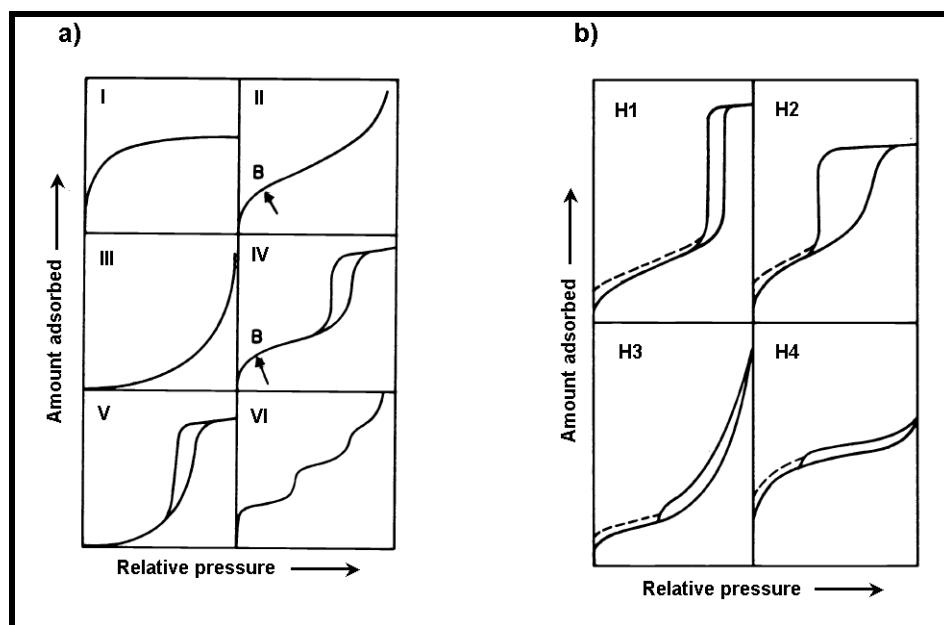cted monolayer-multilayer adsorption. Point B, the beginning of the almost linear middle section of the isotherm, is often taken to indicate the stage at which monolayer coverage is complete and multilayer adsorption is about to begin.

The reversible Type III isotherm is convex to the relative pressure axis over its entire range and therefore does not exhibit point B. Isotherms of this type are not common, but there are a number of systems that give isotherms with gradual curvature and indistinct point B. In such cases, the adsorbate-adsorbate interactions play an important role.

Type IV isotherms present characteristic features called hysteresis loop. It is associated with capillary condensation taking place in mesopores, and the limiting uptake over range of high relative pressure. The initial part of the Type IV isotherm is attributed to monolayer-multilayer adsorption since it follows the same path as the corresponding part of Type II isotherm obtained with the given adsorptive on the same surface area of the adsorbent in a non-porous form. Type IV isotherms are given by many mesoporous industrial adsorbents.

The Type V isotherm is uncommon; it is related to the Type III isotherm in that the adsorbent-adsorbate interaction is weak, but it is obtained with certain porous adsorbents.

The Type VI isotherm, in which the sharpness of the steps depends on the system and the temperature, represents stepwise multilayer adsorption on a uniform son-porous surface. The step-height now represents the monolayer capacity for each adsorbed layer and, in the simplest case, remains nearly constant for two or three adsorbed layers.

Adsorption hysteresis

Hysteresis appearing in the multilayer range of physisorption isotherms is usually associated with capillary condensation in mesopores structures. Such hysteresis loops may exhibit a wide variety of shapes. Two extreme types are shown as H1 and H4 in Figure 7.[35] In the former the two branches are almost vertical and nearly parallel over an appreciable range of gas uptake, whereas in the latter they remain nearly horizontal and parallel over a wide range of relative pressure. In certain respects Type H2 and H3 may be regarded as intermediate between these two extremes. A feature common to many hysteresis loops is that the steep region of the desorption branch leading to the lower closure point occurs at a relative pressure which is almost independent of the nature of the porous adsorbent but depends mainly on the nature of the adsorptive.

Although the effect of various factors on adsorption hysteresis is not fully understood, the shapes of hysteresis loops have often been identified with specific pore structures. Thus, Type H1 is often associated with porous materials known, from other evidence, that consist of agglomerates or compacts of approximately uniform spheres in fairly regular array, and hence to have narrow distribution of pore size. Many porous adsorbents tend to give Type H2 loops, but in such systems the distribution of pore size and shape is not well defined. Indeed, the H2 loop is especially difficult to interpret: in the past it was attributed to a difference in mechanism between condensation and evaporation processes occurring in pores with narrow necks and wide bodies, but it is now recognized that this provides an over-simplified picture and the role of the network effects must be taken into account.

The type H3 loop, which does not exhibit any limiting adsorption at high relative pressure, is observed with aggregates of plate like particles giving rise to slit-shaped pores. Similarly, the Type H4 loop is often associated with narrow slit-like pores, but in this case the Type I isotherm character is indicative of microporosity.

With many systems, especially those containing micropores, low hysteresis may be observed extending to the lowest attainable pressures. Removal of the residual absorbed material is then possible only if the absorbent is out-gassed at higher temperatures. This phenomenon may be associated with the swelling of a non-rigid porous structure or with the irreversible uptake of molecules in pores of about the same width as that of the adsorbate molecule or in some instances with an irreversible chemical interaction of the adsorbate with the adsorbent.[35]

4.1.4 THERMOGRAVIMETRIC ANALYSIS (TGA):

Thermogravimetric Analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere.[41-42] For this investigation, TGA was used to elucidate the solid content of capsules containing perfume, as it determines the lost of weight, due to the perfume release, by increasing the temperature. The method consists in adding the sample in an aluminum oxide crucible that is supported by a precision balance, in a furnace that is heated. The mass of the sample is monitored during the experiment. A sample purge gas controls the sample environment. This gas may be inert or a reactive gas that flows over the sample and exits through an exhaust.

4.1.5 TENSILE PROPERTIES:

Due to the shape and size of capsules, mechanical parameters can not be measured directly; thus membranes with the same chemical structure of the capsules have to be used instead.[43] The tensile test measures the resistance of a material to a static or slowly applied force. A test setup is shown in Figure 8. The specimen is placed in the testing machine and a force F, called the load, is applied. A strain gauge or extensometers is used to measure the amount that the specimen stretches between the gauge marks when the force is applied.[43-45]

Engineering stress and strain

Engineering stress and engineering strain are defined by the following equation:

$$\text{Engineering stress} = \sigma = F/A_0$$

$$\text{Engineering strain} = \varepsilon = l - l_0 / l_0$$

Where A_0 is the original cross-sectional area of the specimen before the test begins, l_0 is the original distance between the gauge marks, and l is the distance between the gauge marks after force F is applied.[33]

Figure 8. Tensile test setup

When tension is applied to a sample, there are two steps before the material breaks. First of all, there is an elastic region, in which the process is reversible. In this region, the stress is directly proportional to strain. Then, there is a plastic

region, in which the process is irreversible. In the latest case, the response to the load is no longer linear and the sample ends up by breaking. In the elastic region, two properties are determined: the yield strength and Young's modulus (E), which is the ration of the stress change during the elastic deformation and, consequently, its value corresponds to the slope of the curve detected until the material reaches the plastic region.[44-45] This relationship is Hooke's law:

$$E = \sigma/\varepsilon$$

The Yield strength is the stress at which plastic deformation becomes noticeable. Therefore it is the strength that divides the elastic and plastic behavior of the material.[44] In the plastic region, two points are characterized. They are the maximum stress and the stress when the sample breaks. At these two points, stress and elongation are evaluated. Young's modulus is related to the rigidity of the material, yield strength to resistance and elongation to fragility.[45]

4.1.6 **PROTRUSION PUNCTURE TEST:**

Protrusion puncture test method determines the resistances of a stretch wrap film to the penetration of a probe at a standard low rate, a single test velocity.[43, 46] It is a measure of the energy-absorbing ability of a stretch wrap film in resisting a protrusion. The test method imparts a biaxial stress that is representative of the type of stress encountered in many products end-use application.[46] The maximum force, force at break, penetration distance and energy to break are determined. A test setup is shown in Figure 9.
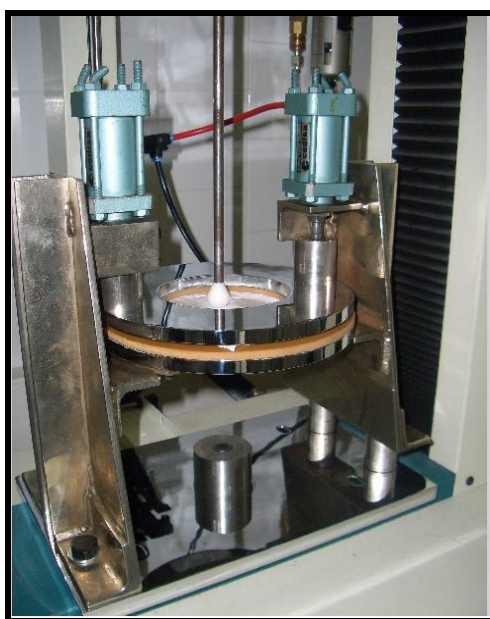
Figure 9. Protrusion puncture test setup

With this method it is easier to perform a measure of the maximum elongation because membranes can be produced with a desirable area for the test, avoiding in this way defects created by the sample cut. Additionally, excluding the Young's module, it is possible to obtain the same parameter results with more reliability with protrusion puncture method than with tensile properties test.[43]

4.2 CHEMICAL CHARACTERIZATION

4.2.1 NUCLEAR MAGNETIC RESONANCE (NMR):

NMR is the most widely applied magnetic spectroscopy method. It is an important tool for studying molecular structures and molecular dynamics of booth organic and inorganic compounds. It offers a great tool for identifying molecules.[47-54] The NMR is a phenomenon that occurs when the nuclei of certain atoms are immersed in a static magnetic field and exposed to a second oscillating magnetic field. Some nuclei experience this phenomenon depends upon whether they possess a property called spin, which is a small magnetic field, and will cause the nucleus to produce a NMR signal. When an atom is placed in a magnetic field, its electrons circulate with the direction of the applied magnetic field. This circulation causes a small magnetic field at the nucleus, which opposes the externally applied field. The electron density around each nucleus in a molecule varies according to the types of nuclei and bonds in the molecule.[53] The opposing field and therefore the effective field at each nucleus will vary resulting in the chemical shift phenomenon. Figure 10 shows the schematic diagram of NMR.

Figure 10. Schematic diagram of NMR

The abscissa of the NMR spectra represents the chemical shift, which is a dimensionless number equal to the ratio of the difference in the frequencies of the signal of the 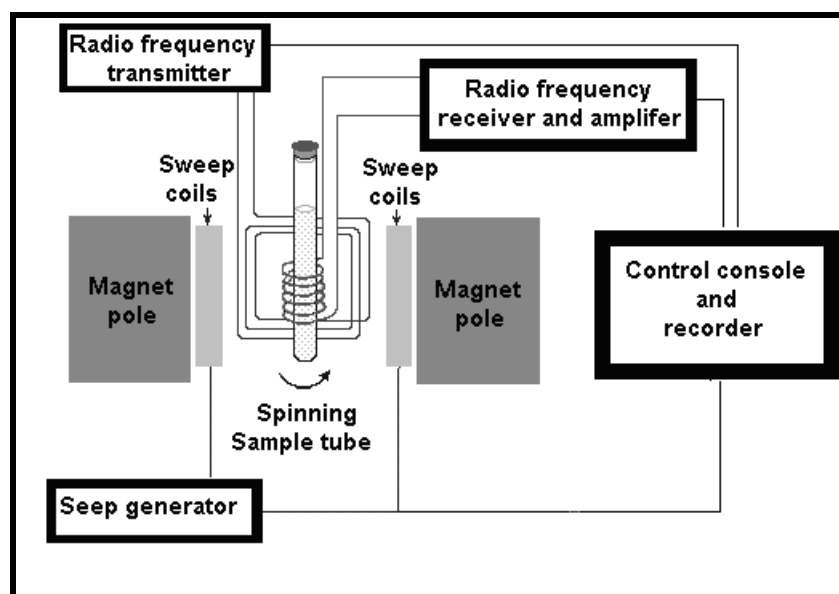nucleus and the reference to the operating frequency. The chemical shift is expressed in parts per million (ppm) and the frequency scale from left (upfield) to right (downfield). [49]

4.2.2 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC):

High performance liquid chromatography is the most versatile and widely used type of elution chromatography. The technique is used to separate and determine species in a variety of organic, inorganic and biological compounds.[55] In liquid chromatography; the mobile phase is a liquid solvent containing the sample as a mixture of solutes. The basic components of HPLC are the column that has the chromatographic packing material (stationary phase), the pump that moves the mobile phase through the column, and the detector that shows the retention times of the molecules. The retention time is the time in which an analyte elutes. This time will be unique for each compound depending on the interactions between the stationary phase, the molecules properties, and the solvent used.[55]

In a general form, an adsorbent, for instance alumina or silica, is packed into a column and is eluted with a suitable mobile phase. A mixture to be separated is introduced at the top of the column and is washed through the column by the eluting liquid. If a component of the mixture is adsorbed weakly on to the surface of the solid stationary phase, it will travel down the column faster than another solute that is more strongly adsorbed. Thus, the separation of solutes is possible if there are differences in their adsorption interactions with the solid.[55]

4.2.3 ATTENUATED TOTAL REFLECTANCE INFRARED (ATR-IR) SPECTROMETRY:

IR spectrometers are useful to analyze solids, liquids and gases providing a characteristic infrared spectrum for each chemical compound.[55-58] In our case, the technique was used to identify the functional groups of the capsules liquid core, and therefore determine the compounds that were encapsulated. Liquid samples, are analyzed as thin films in cells; a cell consists of two IR transparent windows. The attenuated total reflection (ATR) technique operates by measuring the changes in molecular vibration that occur in a totally internally reflected infrared beam when the beam comes into contact with a sample. An infrared beam is directed onto an optically dense crystal with a high refractive index at a certain angle. This internal reflectance creates an evanescent wave that extends beyond the surface of the crystal into the sample held in contact with the crystal. This evanescent wave protrudes only a few microns (0.5 μm - 5 μm) beyond the crystal surface and into the sample. In regions of the infrared spectrum where the sample

absorbs energy, the evanescent wave will be attenuated or altered. The attenuated energy from each evanescent wave is passed back to the IR beam, which then exits the opposite end of the crystal and is passed to the detector in the IR spectrometer. The system then generates an infrared spectrum. The infrared domain that shows the energy states of vibration and rotational of molecules are the mid infrared, which cover a range of 4000-200 cm^{-1}.[55]

4.2.4 X-RAY DIFFRACTION (XRD):

X-ray diffraction (XRD) is a versatile, non-destructive technique that offers detailed information about the chemical composition and crystallographic structure of solid matters.[55, 49-60] Solid matters can be described as:

- Amorphous: The atoms are arranged in a random way similar to the disorder we find in a liquid. Glasses are amorphous materials.
- Crystalline: The atoms are arranged in a regular pattern, and there is a smallest volume element that by repetition in three dimensions describes the crystal. It is possible to describe a brick wall by the shape and orientation of a single brick. This smallest volume element is called a unit cell. Three axes describe the dimensions of the unit cell: a, b, c and the angles between them alpha, beta and gamma.[59]

An electron in an alternating electromagnetic field will oscillate with the same frequency as the field. When an X-ray beam hits an atom, the electrons around the atom start to oscillate with the same frequency as the incoming beam. In almost all directions it will have destructive interference, that is, the combining waves are out of phase and there is no resultant energy leaving the solid sample. However the atoms in a crystal are arranged in a regular pattern, and in a very few directions it will have constructive interference. The waves will be in phase and there will be well-defined X-ray beams leaving the sample at various directions. Hence, a diffracted beam may be described as a beam composed of a large number of scattered rays mutually reinforcing one another.[60]

5. APPLICATIONS OF ENCAPSULATION TECHNOLOGY

Encapsulation technology presents numerous applications to improve several industrial commercial products. The beginning of the encapsulation technology started in 1950s with the preparation of capsules containing dyes. These were incorporated into pressure sensitive coatings for the manufacture of carbonless copy paper.[61] Nowadays, encapsulation technology is well developed and

accepted within a vast number of industries such as the pharmaceutical,[62-71] chemical,[72-75] cosmetic,[76-77] food,[78-79] perfumery,[80-81] textile,[82] etc.

As the main object of this thesis is the encapsulation of hydrophilic perfumes for textile applications, the following introduction will be focused in the encapsulation technology for textile products, more exactly for fragrance encapsulation.

5.1 APPLICATION OF ENCAPSULATION TECHNOLOGY ON TEXTILE PRODUCTS

The process of encapsulation technology has wide current and potential applications in textiles, providing them extra added value and extra functionality. Its application have proliferated greatly, and today the technology is used on textiles to impart smart finishes and desirable properties that are simply not possible using other technologies, or are not cost-effective.[83]

Microcapsules can be applied on any fabric (woven, knitted, no woven or garments). The substrate may be wool, silk, cotton, flax or synthetic fibers such as polyamide or polyester, or mixtures.[83] Most of the microcapsules can be applied using conventional finishing techniques without altering the feel and color of colored fabrics or printed patterns. Microcapsules can also be applied during the rinse cycle of a washing machine.

Some examples of microencapsulation technology in textiles are perfume encapsulation for a long lasting fragrance release [84-86], encapsulation of phase change materials to create a thermo-regulating fabrics [87-94], encapsulation of flame retardants,[95-96] vitamin encapsulation for skin treatment[27], repellent encapsulation for textiles[97], microencapsulation of pigments[98], etc.

5.2 FRAGRANCES ENCAPSULATION

Fragrances are often described as a compound or sets of compounds that offer grateful aroma perception.[99] Natural products are usually used for the fabrication of fragrance; however, synthetic compounds are used as well. Fragrance ingredients suppliers deal with the same issues as flavor ingredients suppliers, although their molecules need to be able to withstand more severe conditions. The stability of the fragrances itself is mainly determined by chemical parameters.[99] In general fragrance ingredients are instable, they tend to degrade over time and it is need to have tricks to make sure that the best fragrance perception is obtained at the moment the consumer use the product.

There are several factors that release the desirable volatile molecules. Triggers can be pH and temperature but also enzymes, oxygen, light or even pressure

change could be used to release the fragrance. If one would be able to protect the perfume against its hostile environmental, the degradation could be stopped or certainly slowed down. Encapsulation technology is a technique in which a physical barrier between the perfume and its environment is made.

There are five principal reasons for encapsulation of perfumes[99]:

- To prevent perfume oxidation by air oxygen
- To prevent hydrolysis by water
- To prevent reactions of flavor ingredients with each other
- To prevent evaporation
- To change liquids into powders, making the perfumes more easily to handle.

Encapsulation traditionally has been used to protect fragrances but current research is focusing on delivery systems. In the past it was wanted to store the powder until its final use; nowadays encapsulation helps to deliver the fragrance at the right time, at the right quantity and at the right rate. In fact it is often mentioned the slow release mechanisms.

Currently, microcapsules containing fragrances are used in many areas, including air fresheners, cosmetics, textiles and laundry detergents. As most perfumes are volatile substances, their effect is lost very rapidly from the application site. Perfumes added to detergents and softeners are lost during the laundering operation due to the relative warm temperature of the water, as well as during the washing and drying processes, and consequently laundered fabric will have only a very faint desired odor. On the other hand, when perfume is added in the form of microcapsule, the microcapsules may penetrate the fabric during laundering and release the perfume during drying, and/or when laundered fabric is being used afterwards. However, certain current industrial microcapsules present a number of drawbacks such as low material stability, low perfume encapsulation capacity and, in addition, with the industrial encapsulation method presently used it is extremely complicated to encapsulate hydrophilic perfumes. With the aim to solve these problems, polysulfone capsules are proposed in this work for the encapsulation of vanillin, a hydrophilic component commonly used in perfume and cosmetic formulations and that it represents a challenge for encapsulation due to its chemical properties. Moreover, it is important to mention that vanillin has been chosen not only for their sweet and delicate aroma, but also because of some important properties that this compound possess and therefore they can be used for further applications. Some interesting aspects of vanillin are mentioned next.

5.2.1 VANILLIN

Vanillin is one of the most important aromatic aldehyde. It is the single most important component of vanilla.[99] The synthesis of vanillin by many routes has been reported, including carbonylation of guaiacol, and by the degradation of lignin obtained as waste from paper production. Vanillin is widely used in both flavors and fragrances; in general, it is stable, but there can be a problem with discoloration. As a phenol, it reacts with traces of iron to give purple coloration, and indeed this could be used as a test for the metal.[100-101] Figure 11 shows the chemical structure of vanillin and Table 2 collects some physical properties of vanillin
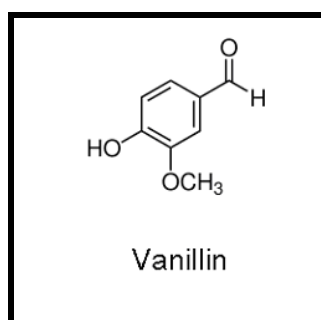
Figure 11. Chemical structure of vanillin

Table 3. Physical properties of vanillin[18]

Vanillin properties	
Boiling point:	170°C
Molar mass:	152.15g/mol
Water solubility:	1g/100 mL
Vapor pressure:	0.01 mmHg a 25°C
Melting point:	81°C
Flash point	147 °C

Furthermore, vanillin exhibits several bioactive properties such as; antioxidant and antimicrobial activities against yeasts, moulds and bacteria. In the antimicrobial packaging area, vanillin has been used to develop antimicrobial film. The antimicrobial property of vanillin is the effect of phenolic compound in chemical structure that makes vanillin effective in inhibiting bacteria, yeasts and moulds. It is structurally similar to eugenol (2-methoxy-4-(2-propenyl) phenol) from cloves and is known to be antimycotic and bacteriostatic. At low concentrations, phenols affect

enzyme activity, especially those enzymes associated with energy production, while at greater concentrations they cause proteins to denature.

Vanillin has also been reported to possess anticlastogenic, antimutagenic and antitumor properties and, therefore, it can be considered as a nutraceutical molecule. That is why vanillin is also useful in the synthesis of drugs. Up to 40% of the vanillin is consumed in manufacturing drugs such as Aldomet (antihypertensive drug), L-dopa (treatment of Parkinson's disease) and Trimethoprim (treatment of upper respiratory tract infections and some strains of venereal disease).[102]

Other uses for vanillin include prevention of foaming in lubrication oils, as a brightener in zinc coating baths, as an activator for electroless plating of zinc, as an aid to the oxidation of linseed oil, as an attractant in insecticides, as an agent to prevent mouth roughness caused by smoking tobacco, in the preparation of syntans for tanning, as a solubilizing agent for riboflavin and as a catalyst to polymerize methyl methacrylate.[103]

Therefore, the encapsulation of vanillin and consequently its controlled release offers potential applications for textile products. The antibacterial and antimycotic properties of vanillin together with its pleasant aroma could be used not only in detergents and softeners, but also in several fabric products; For example, it may be possible to stick capsules containing vanillin in sheets, pillowcases and mattress protectors.

GENERAL OBJECTIVES

The main goal of this work is to offer a well-established encapsulated system of vanillin for the development of innovative textile products. Capsules have to offer a long-lasting fragrance release, guarantee a high encapsulation capacity, ensure the preservation of the fragrance, and have a good physical and chemical stability. With this purpose, PSf/Vanillin capsules have been proposed.

Therefore, in this investigation PSf/Vanillin capsules were analyzed with the aim to prove that PSf capsules may offer a stable system for vanillin encapsulation, a long lasting fragrance release, a good encapsulation capacity and a desirable physical and chemical stability.

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CHAPTER 2

VANILLIN RELEASE FROM POLYSULFONE MACROCAPSULES

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ABSTRACT

Microencapsulation has been successfully implemented in various fields of science. It can be used to remove, protect, preserve and disseminate many substances. The objective of this work is to investigate the vanillin release from polysulfone macrocapsules as a first approach to characterize microcapsules afterward. The capsules were synthesized from polysulfone as polymer, dimethyl formamide as solvent, and vanillin as active agent, by phase inversion precipitation. Morphological characterization was made by scanning electron microscopy. Vanillin release from the capsules was monitored by withdrawing samples, from the release medium, at different time intervals. The vanillin concentration was determined by high performance liquid chromatography. Vanillin release from capsules was encountered to increase when increasing the stirring rate or when increasing the temperature of the release medium. Total amount of vanillin encapsulated was estimated by sequentially refreshing the release medium and corresponded to ca. 50% of the perfume initially incorporated in the polymeric solution.

Keywords: Macrocapsule, phase inversion (immersion) precipitation, Polysulfone, Vanillin, Release.

1. INTRODUCTION

The microencapsulation is defined as a process in which tiny particles are surrounded by a coating. Microcapsule is a circular cross-section shape particle with certain nonsolid volume inside. The material that is encapsulated inside can be referred to as the active agent, core, internal phase, or fill, whereas the wall is sometimes called shell, coating, wall material, or membrane.[1] The diameter of the microcapsules is usually in the range of 1-1000 μm.[2] Below 1 μm, they are called nanocapsules, and over 1000 μm they are referred to as macrocapsules.[3] The capsules can be prepared from a wide range of different materials. Among them, polymeric materials are the most used ones.[4] In this case, phase inversion precipitation is the synthesis technique mostly employed.[5] Phase inversion precipitation may be induced by different methods, the most common being the immersion precipitation.[6]

Numerous applications have been found for microcapsules. They can be used to remove, protect, preserve, and disseminate many substances like metals, acids, nutrients, fertilizers, perfumes, etc., and they may be used in various fields, such as; cosmetic, pharmaceutical, textile, chemical, biomedical, petroleum, and pesticide industries.[7-10] The pore microstructure of the capsule is fundamentally used to control the core release. Scanning electron microscopy provides a very convenient and simple method for characterizing and investigating the porous structure of polymeric capsules. In this work, the behavior of polysulfone macrocapsules containing perfume was analyzed as a first approach to characterize microcapsules of the same kind afterward.

The capsules were synthesized by phase inversion (immersion) precipitation technique,[6] using polysulfone as polymer, dimethyl formamide (DMF) as solvent, and vanillin as the active core. This approach allows encapsulation of vanillin perfume, which is not possible with other encapsulations methods, such as common polymerization because of its hydrophilic properties. The morphological characterization of the external surfaces and of the internal porous structures of macrocrocapsules was carried out using the scanning electron microscopy (SEM). For characterizing the internal porous structure, macrocapsule samples were cryogenically cut, in order to obtain a cross-section without deforming the structure.[11] The release of the vanillin, under different working conditions (temperature, stirring rates, etc.) was monitored by high performance liquid chromatography (HPLC).

2. MATERIALS AND METHODS

2.1 MATERIALS

Polysulfone (PSf) ($[C_6H_4$-4-$C(CH_3)_2C_6H_4$-4-OC_6H_4- $4SO_2C_6H_4$-4-$O]_n$), in a transparent pellet form, and vanillin (4- $(OH)C_6H_3$-3$(OCH_3)CHO$), in a white powder form, were purchased from Sigma-Aldrich (Spain). *N,N*-dimethylformamide (DMF) reagent grade, ACS, ISO, C_6H_{12}, and acetonitrile, multisolvent HPLC grade, ACS, UV-vis, CH_3CN were obtained from Scharlau (Spain). MilliQ water was used for all release experiments.

2.2 PREPARATION OF MACROCAPSULES

Capsules were synthesized from polysulfone as polymer, dimethyl formamide (DMF) as solvent, and vanillin as active agent. For the preparation of the polymeric solution, 15% w/w PSf and 10% w/w vanillin were mixed and dissolved in DMF. The mixture was stirred during 24 h at room temperature. The macrocapsules were obtained by phase inversion (immersion) precipitation technique by dropping the polymeric solution into a bath containing 3 L of MilliQ water. In a second step the capsules were separated from the coagulation bath by filtration and stored in an amber glass bottle.

2.3 CHARACTERIZATION OF MACROCAPSULES

The morphological characterization, of the external surfaces and of the internal porous structures of macrocapsules was investigated by scanning electron microscopy (SEM). The SEM used was JEOL JSM- 6400 scanning microscopy series, with a working voltage of 15kV. To obtain micrographs of the internal porous structure, capsule samples were cryogenically cut, in order to have a crosssection cut without modifying the polymeric structure.[11] The samples were gold coated. The diameters of the capsules were measured on the SEM micrographs. On the other hand, to verify the chemical composition of the encapsulated core, an ATR-IR was used. The infrared spectrum of the liquid encapsulated was measured using the spectrometer Jasco FR/IR 680 Plus with a diamond cell.

2.4 RELEASE EXPERIMENTS

Several experiments were made in order to analyze the vanillin release. Table 1 shows the conditions for all the experiments. In general, 1 g of capsules were added into 100 mL of a water solution and stirred, using an SBS multipoint magnetic stirrer, during 120 h. With the purpose to measure the vanillin concentration in the release medium, samples were withdrawn from the aqueous solution at different times, according to Table 1, and analyzed by HPLC.

Table 1. Experimental working conditions

Experiment	Release medium (100 ml)	Capsules Weight (g)	Stirring rate (rpm)	Temperature (°C)	Time (h)
Stirring					
1	MiliQ water	1	0	20	120
2	MiliQ water	1	300	20	120
4	MiliQ water	1	700	20	120
Temperature					
5	MiliQ water	1	700	25	120
6	MiliQ water	1	700	35	120
7	MiliQ water	1	700	45	120
8	MiliQ water	1	700	55	120
Medium renewals					
9	MiliQ water	1	700	20	48
10	MiliQ water	0.92 ± 0.02	700	20	48
11	MiliQ water	0.84 ± 0.004	700	20	24
Vanillin saturated solution					
12	MiliQ water	1	700	20	96
13	Vanillin solution	1	700	20	96
14	MiliQ water	0.96 ± 0.017	700	20	96

2.6 ANALYTICAL TECHNIQUES

The vanillin concentration of the aqueous samples was measured using an HPLC Agilent 1100 series autosamplers with a Supelcosil LC-8 (SUPELCO) column and a diode array detector. The mobile phase used was MilliQ water:acetonitrile 80:20. For all analysis, the flow rate was set at 1 mL/min, the column temperature at 40 °C, the análisis time was 8 min and the injection volume was 4 μL. Vanillin concentration was determined at 229 nm, showing a typical retention time of 4.2-4.5 min.[12]

3. RESULTS AND DISCUSSIONS

3.1 STIRRING EFFECT ON VANILLIN RELEASE

Three experiments were made with different stirring rates (0, 300, and 700 rpm) of the release medium, with the aim to study its effect on the vanillin release. Other experimental conditions were fixed according to Table 1. Figure 1 shows the results obtained.

As expected, higher stirring rates favor the vanillin release. As can be seen in Figure 1, at 700 and 300 rpm the equilibrium is sooner achieved. Though, without stirring, the equilibrium step was also reached, as the polymer matrix is very porous, but it took longer time. Stirring of the release medium favors the release because it acts to remove the perfume molecules from the capsule outer surface. Therefore, all the following experiments were performed at 700 rpm.
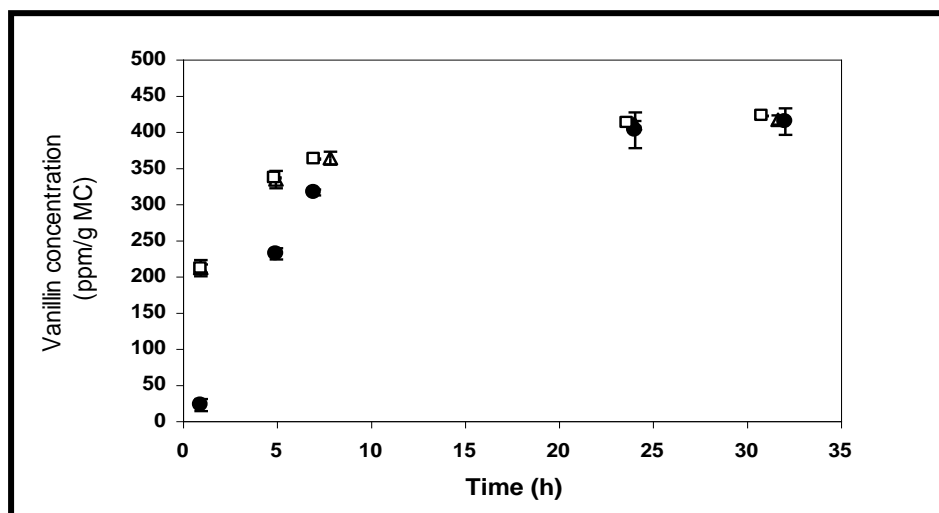
Figure 1. Vanillin release at different release medium stirring rates (●, □, Δ correspond to 0, 300, and 700 rpm, respectively)

3.2 TEMPERATURE EFFECT ON VANILLIN RELEASE

Figure 2 shows vanillin release at different release medium temperatures. The working conditions for the experiments are collected in Table 1.

As can be seen, all experiments show the same release tendency. As may be seen, the vanillin release progressively increases when increasing the temperature of the release medium from 25 to 55 °C, as could be expected. It occurs because higher temperatures increase vanillin solubility in water phases,[13,14] thus the partition equilibrium of vanillin between the capsule and the release medium is switched to the outer phase.
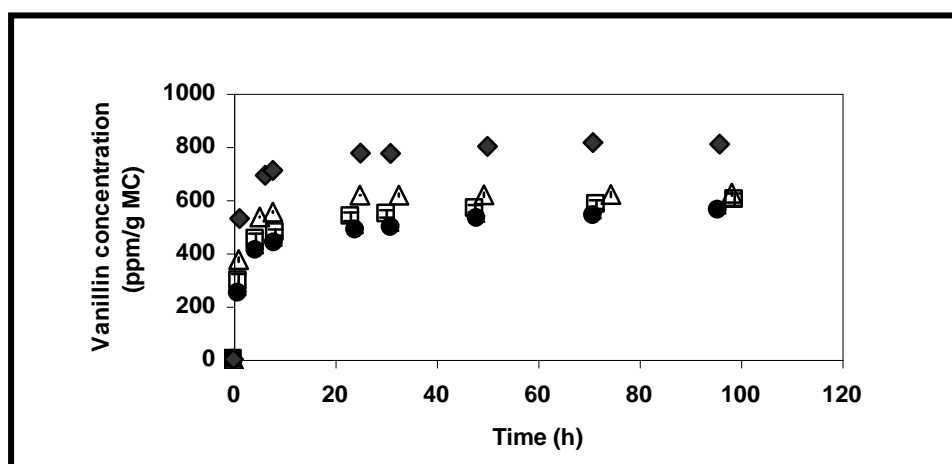

Figure 2. Vanillin release at different release medium temperatures (●, □, Δ, ♦ correspond to 25, 35, 45 and 55 °C, respectively)

3.3 RELEASE MEDIUM RENEWAL

With the objective to determine the maximum vanillin release capacity of the capsules, certain experiments involving release medium renewal were carried out. The experimental conditions can be seen in Table 1. Figure 3 shows the results of these experiments.
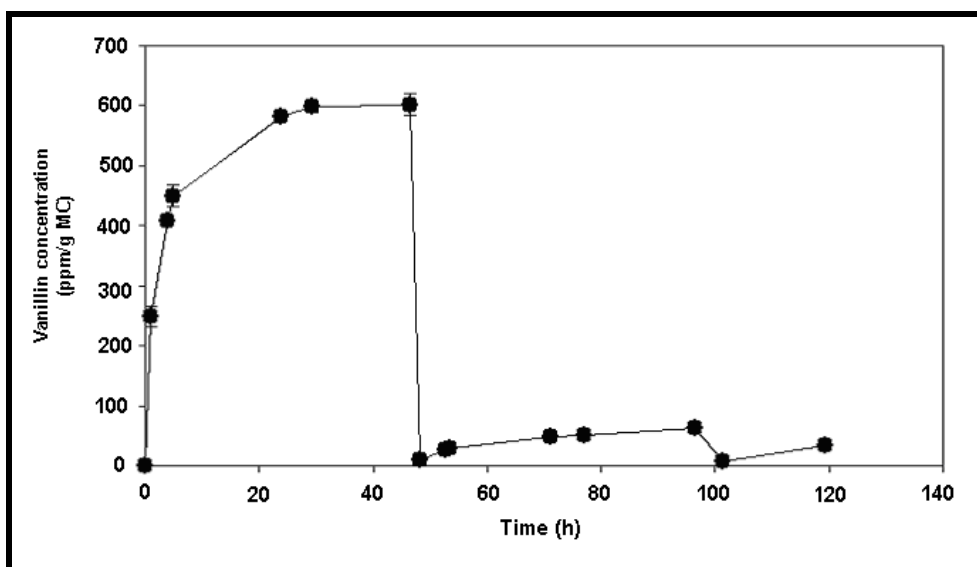

Figure 3. Vanillin release with release medium refreshing

Although the 75% of vanillin release takes place within the first 48 h, it may be seen that, when renewing the release medium, the release of the perfume continued, during at least 120 h. Therefore, polysulfone polymeric capsules present promising features for applications where long release times may be desirable.

3.4 ENCAPSULATION CAPACITY

The maximum vanillin encapsulation capacity of polysulfone capsules was estimated from experiment 8, as it was the one leading to a highest amount of perfume released. It was found that, the maximum vanillin quantity encapsulated was around 50% from the total perfume added in the polymeric solution. The encapsulation capacity of these capsules is far more larger than that usually encountered in current industrial processes. Thus, it may be stated that the polysulfone capsules here developed show promising potential as encapsulation media. According to that, the mean vanillin release in all the experiments presented in this work corresponds approximately to 88% of the total encapsulated.

3.5 REMOVING DMF FROM CAPSULES

As stated up to now, the capsules prepared here show very promising characteristics in terms of vanillin encapsulation capacity, or vanillin release time; however we have to face up the fact that not only vanillin is being released but also DMF.

Results show that, in the capsules production process, part of the polymer solvent and non-solvent are also encapsulated together with the perfume. To corroborate this statement, the liquid encapsulated into the capsules was analyzed by IR. To get a representative amount of encapsulated liquid from the capsules, five capsules were conveniently pressed in a dry bottle, obtaining a few drops. The IR spectra corresponding to water, DMF, and encapsulated solution are shown in Figure 4. The spectrum, of the encapsulated liquid, confirms the presence of both polymer solvent and non-solvent inside the capsules.

The encapsulation and release of DMF from capsules might be a problem as it is harmful and toxic. Therefore applications of the capsules are limited if the DMF is not significantly removed from the capsule.

A solution saturated with vanillin, as release medium, was proposed with the purpose to remove the DMF and retain the vanillin inside the capsule. Therefore, two different experiments were performed. In one of them (experiment 13) certain capsules were added in a vanillin-saturated solution for several days. In the second one (experiment 14) the capsules recovered from the previous experiment (13) were added in a usual release medium (MilliQ water). For comparison, a common experiment (without previous storing the capsules in a vanillin saturated solution, expt12) also was done. Results are collected in Figures 5 and 6.

As can been see in Figure 5, previously storing the capsules in an aqueous solution saturated with vanillin provides a very significant removal of DMF from the capsules, of nearly 99%. However, also around 30% of vanillin was lost (see Figure 6). The lost of vanillin may be because the vanillin inside the capsules can be partly dissolved in DMF and partly dissolved in water. Hence, when DMF was released the vanillin dissolved in DMF was also released. Capsules could be stored in this media before their application and still be optimal for their application.
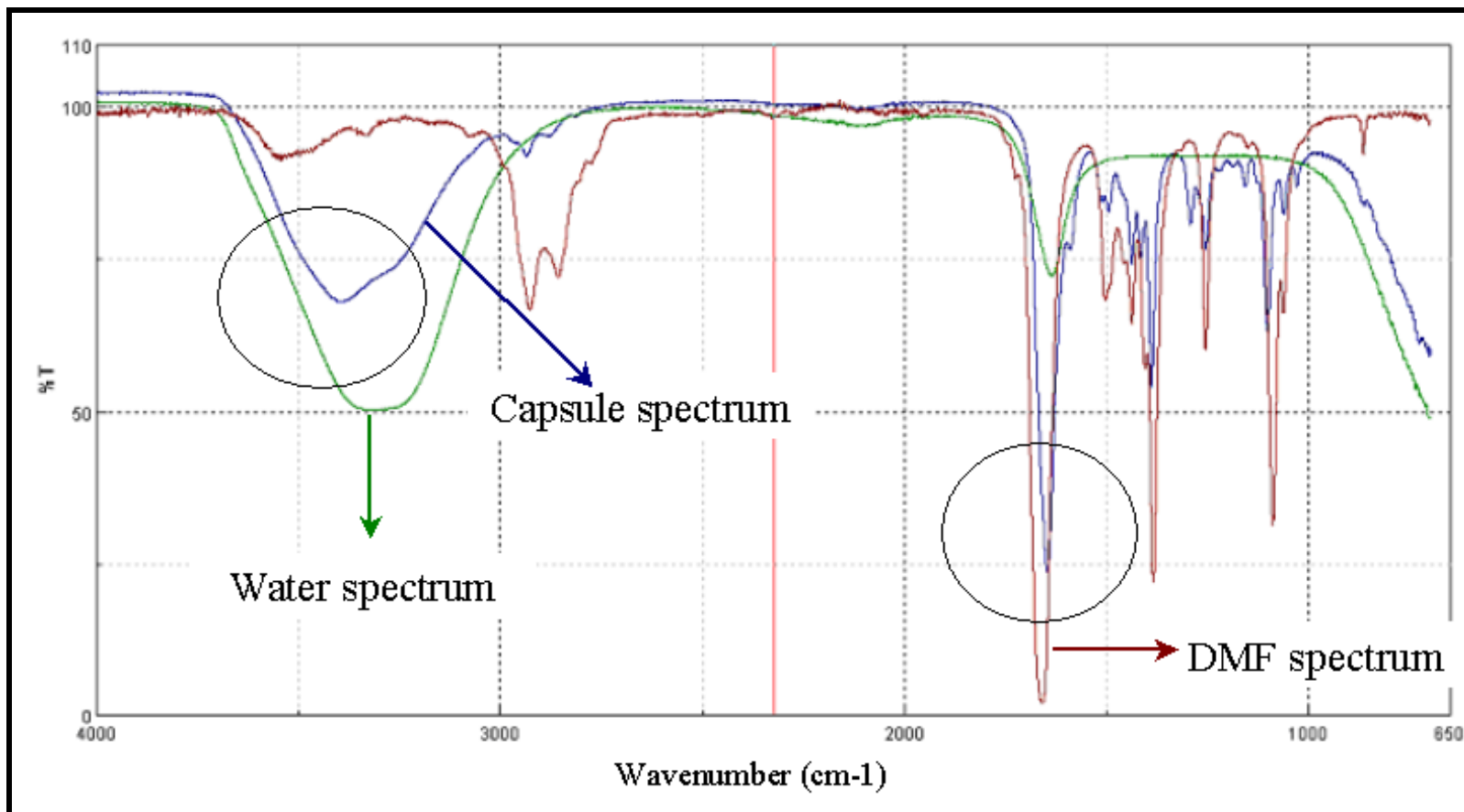
Figure 4. Infrared spectrum of encapsulated liquid

Figure 5. DMF release in a solution saturated with vanillin: (●) normal experiment; (□) experiment performed after storing the capsules in a vanillin saturated solution. (Δ) DMF release during the storing period in a vanillin saturated solution

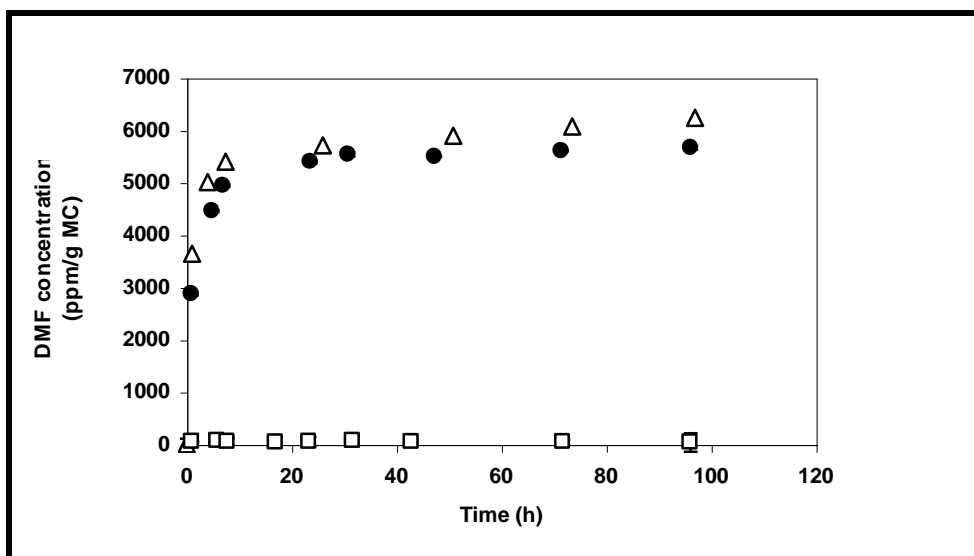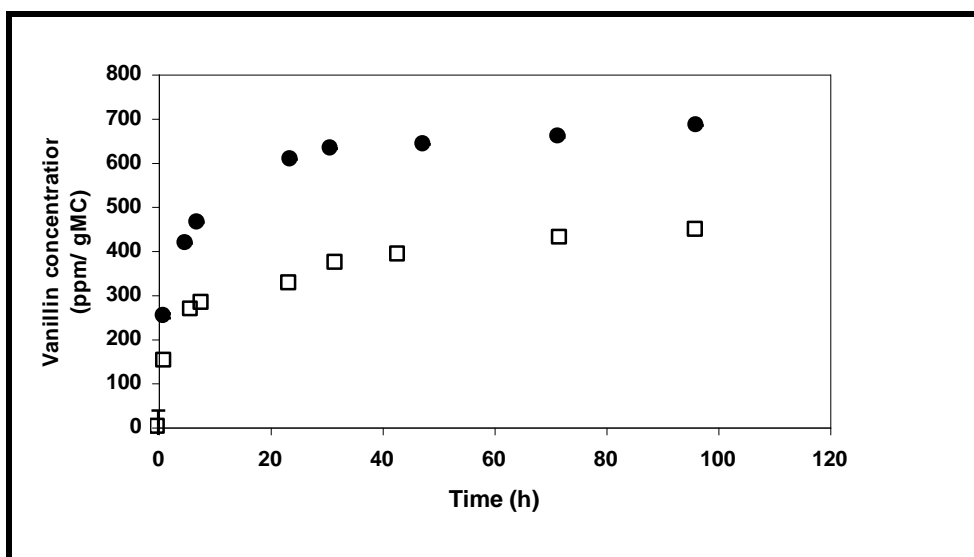Figure 6. Vanillin release in a solution saturated with vanillin: (●) normal experiment; (□) experiment performed after storing the capsules in a vanillin saturated solution

3.6 MORPHOLOGICAL CHARACTERIZATION OF CAPSULES

Finally, morphological characterization of capsules was also carried out. Typical SEM micrographs of macrocapsules can be found shown in Figure 7. Capsules show a diameter size between 3 and 4 mm with a mean value of 3.48 $\pm$ 0.53 mm. As can been observed, capsules have a highly porous configuration, which ensures a notorious volume for perfume encapsulation, as encountered. At the same time, the presence of the polymer matrix throughout the whole capsule volume provides good mechanical properties to the capsules. Further work is now being done to quantify the aforementioned mechanical properties.
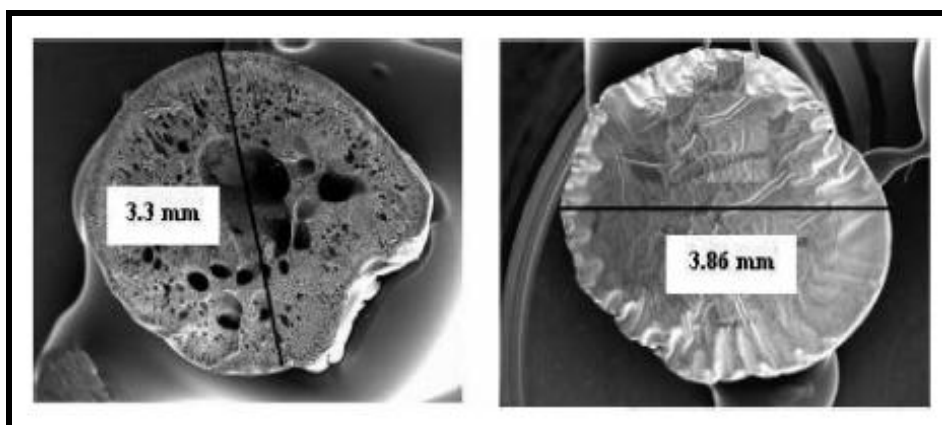
Figure 7. SEM micrographs of the capsules

4. CONCLUSIONS

Polysulfone macrocapsules, of certain millimeters of diameter size, and containing vanillin, have been produced by phase inversion precipitation, showing promising release results in terms of time and mechanical resistance. Several working parameters, such as temperature and stirring rate of the release medium, have been studied and optimized, in order to characterize vanillin release from capsules. The maximum amount of vanillin encapsulated has been estimated to be 800 ppm (ca. 1 mg vanillin par capsule). This quantity corresponds almost to the 50% of the total perfume added to the polymer solution. The total release time encountered has been 120 h. In that time, vanillin was released almost entirely; 75% of the total encapsulated was in the first 48 h. A good solution to avoid DMF release was also proposed, consisting of storing the capsules in a saturated vanillin solution for 96 h. With this, nearly 98% of DMF was removed. Moreover the capsules characterization shows a high volume for perfume encapsulation and good mechanical properties.

5. ACKNOWLEDGMENT

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CHAPTER 3

STUDY OF THE MECHANICAL PROPERTIES OF PSF/VANILLIN FILMS.
INFLUENCE OF TEMPERATURE TREATMENTS

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STUDY OF THE MECHANICAL PROPERTIES OF PSF/VANILLIN FILMS.
INFLUENCE OF TEMPERATURE TREATMENTS

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ABSTRACT

The encapsulation method is used in the textile detergents and softeners industry to provide a long-lasting fragrance. Capsules currently employed show low encapsulation capacity and stability. However, polysulfone (PSf) microcapsules were proposed, as they show promising results. To characterize PSf capsule morphological and mechanical properties, flat sheet PSf/Vanillin membranes have been prepared simulating capsules obtainment procedure. Two treatments were performed: immersing PSf/Vanillin membranes in (a) 6000 ppm DMF aqueous solution or in (b) Milli-Q water, at different temperatures (55-90 °C). Membrane samples were analyzed by SEM, IFME software, and the test methods of the ASTM (puncture resistance and tensile methods). Morphological analysis showed that temperatures above 55 °C and DMF aqueous solution caused an increment of the pore number and size of the PSf/Vanillin films porous layer. No structural changes were detected in the dense layer. After material treatment, only the maximum strain % of PSf/Vanillin films was modified.

Keywords: Tensile properties, Protrusion puncture, Polysulfone membranes, Dimethylformamide, Porous layer reduction.

1. INTRODUCTION

The encapsulation process has been employed in several fields of industry and science, to eliminate, disseminate, and preserve many substances of interest like nutrients, cells, tissues, perfumes, etc.[1-7]

Currently, perfume encapsulation is used in industrial production of clothes softeners and detergents, with the aim to provide a long-lasting fragrance.[1] However, the capsules used in this industry present some problems related to low encapsulation capacity of hydrophilic perfumes and low material stability. To solve these problems, polysulfone (PSf) microcapsules were proposed.[5] PSf capsules have been already investigated and showed promising results concerning release behavior, encapsulation capacity, and stability.[5-7]

In a previous work[5] dealing with PSf macrocapsules containing vanillin, it was observed that vanillin release from PSf capsules increased when increasing the temperature of the release medium. To confirm that temperature does not cause any degradation of the capsule material, it is fundamental to determine the mechanical properties of the PSf capsules under actual working and manufacturing conditions to establish the optimum parameters to be used for capsules formation and the encapsulation process. However, due to the shape and size of capsules, mechanical parameters cannot be measured directly; therefore, PSf membranes with the same chemical structure of the abovementioned capsules have to be used instead. The morphology of the pore microstructure and the pore distribution of porous membranes are key factors as they determine both membrane stability and transport properties.[5,8] Scanning electron microscopy (SEM) offers an appropriate method to characterize the morphological structure of porous polymeric films;[9,10] in addition, when analyzing SEM micrograph of polymeric membranes with Interpretació de Fotografies de Microscòpia Electrònica IFME software, it is possible to provide quantitative information related to the number of pores.[11] American Society for Testing and Materials (ASTM) methods are robust and well-established techniques for physical characterization of a wide range of materials, including polymeric membrane materials.[12-18]

With the purpose to characterize the mechanical properties of PSf capsules, two standard test methods of the ASTM were compared: (1) the tensile test method,[12] which has been employed in several investigations to establish the mechanical characterization of membrane materials;[13-17] and (2) the puncture resistance test method,[18] which can provide important results regarding the mechanical properties. In this work, the influence of working media temperature in the mechanical properties of PSf/Vanillin films has been investigated. In addition, an easy and

suitable test method to characterize the mechanical properties of those films has been proposed.

2. MATERIALS AND METHODS

2.1 MATERIALS

Polysulfone (PSf) and vanillin reagent higher than 99% were purchased from Sigma-Aldrich (Spain). N,Ndimethylformamide (DMF) reagent grade ACS ISO was obtained from Scharlau (Spain). Milli-Q water was used for all experiments.

2.2 MEMBRANE PREPARATION

Membranes were prepared by phase inversion (immersion) precipitation technique[10] from a polymeric solution containing 15% w/w of PSf, 10% w/w of vanillin, and 75% of DMF. The polymeric solution was prepared by dissolving PSf and vanillin in DMF 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 x 20 cm^2) using a casting knife, providing films 150 µm thick, which was pushed by an applicator (K-Paint applicator, United Kingdom) at a constant velocity of 3 m/min. Afterward, the glass with the wet 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 x 20 cm^2.

2.3 MEMBRANE DEGRADATION

With the purpose to simulate the degradation of the microcapsules both during manufacturing and cleaning washing cycles, two different treatments were developed. These consisted of immersing PSf/Vanillin membranes either in (a) 6000 ppm DMF aqueous solution, which was the DMF quantity encountered in PSf/Vanillin macrocapsules in our previous work,[5] or in (b) Milli-Q water. Both treatments were carried out at different temperatures (55, 70, and 90 °C), to cover working temperature ranges of cloth washing machines, and using a stirring rate of 700 rpm. Membrane samples where withdrawn periodically and afterward analyzed by SEM, IFME software, and the test methods of the ASTM. Experimental parameters of all membrane degradation treatments are collected in Table 1.

Table 1. Experimental Parameters of Treatments

Experiment	Solution medium	PSf/Vanillin films used	Withdrawn time	Solution medium temperature (°C)
1	Solution with 6000 ppm of DMF	10 for each experiment	5 days	55
2				70
3				90
4	MilliQ Water			55
5				70
6				90
7	Solution with 6000 ppm of DMF	5 for each experiment	one sample per day during 5 days	55
8				70
9				90
10			at 1, 2, 4, 5, 6 and 24 hours	70
11				90
12			at 10, 20, 30, 45 and 60min.	90

Samples per PSf/Vanillin film used in tensile properties' probes $= 14 \pm 4$
Samples of PSf/Vanillin films used in protrusion puncture probes $= 10$
Stirring rate of the solution media $= 700$ rpm

2.4 MORPHOLOGICAL CHARACTERIZATION

Membrane morphology was determined by scanning electron microscopy (SEM) (JEOL JSM-6400 Scanning Microscopy Series), with an acceleration voltage of 15-20 kV. Three different membrane parts (top layer, bottom layer, and cross-section) were examined. To obtain cross-section images, the membranes were cryogenically cut, ensuring in this way no deformation of the polymeric structure.[9,16] Hence, membranes were first immersed into pure ethanol, then in liquid nitrogen, and finally cut using a bistoury. With the purpose of determining the number and the mean size of the PSf/Vanillin membrane pores from SEM micrographs, the IFME software was used.[11]

2.5 MECHANICAL AND PHYSICAL CHARACTERIZATION

The mechanical properties of PSf/Vanillin films were determined using two ASTM methods: (1) ASTM-D5748-95[18] (protrusion puncture resistance of stretch wrap film) and (2) ASTM-D882-09[12] (standard test method for tensile properties of thin plastic sheeting). The ASTM-D5748-95 was carried out with a speed of 4.16 mm/s and analyzing five different films per test. Membranes formed with an area of

20x20 cm^2 were used as samples, avoiding in this form defects created by the sample cut. The ASTM-D882-09 was performed with a test speed of 0.16 mm/s and 10 tests per sample. In this case, membranes with an area of 15 x 1 cm^2 were used. Membrane samples were obtained cutting strips from an entire PSf/Vanillin film according to the ASTM standard. The cutting process had to be made very carefully to avoid defects in the membranes borders. Both tests were carried out using a Universal Testing Machine (Houndsfiel H10KSks). The apparatus was adjusted, specifically for this work, according to the ASTM standards. Figure 1 shows the adaptation of the device for each test. The films tested were PSf/Vanillin membranes treated according to Table 1. The thickness of the membranes was measured using a micrometer (Mitutoyo 547-401).
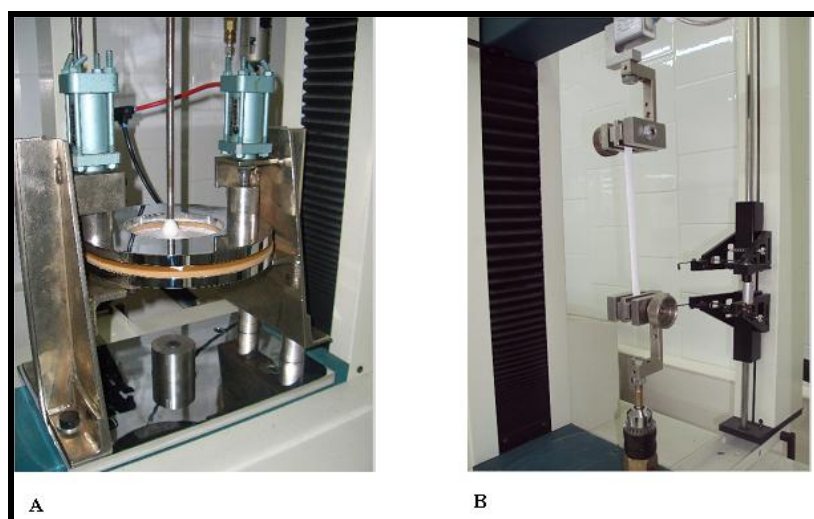

Figure 1. Testing machines used to determine the mechanical properties of PSf/Vanillin films. A) Adaptation of the apparatus for the standard ASTM D5748-95 (Protrusion puncture resistance of stretch wrap films. B) Adjustment made to employ the standard ASTM D882-09 (Standard test method for tensile properties of thin plastic sheeting)

3. RESULTS AND DISCUSSION

All the PSf/Vanillin membranes obtained were physically characterized in terms of morphologic and mechanical resistance.

3.1 MORPHOLOGICAL CHARACTERIZATION

The PSf/Vanillin films SEM micrographs were carried out using scanning electron microscopy (SEM). Figures 2 and 3 show SEM micrograph sections of PSf/Vanillin membranes immersed in Milli-Q water and into solutions with 6000 ppm of DMF respectively, both of them at different media temperature. PSf/Vanillin membranes, shown in Figures 2 and 3, present an asymmetric shape with two regions, a dense

layer and a porous layer, which presents macrovoids in its structure. This morphology was also observed in PSf capsules.[5,16,19] In the Figure 2 micrographs, it is possible to observe the formation of new pores, when the temperature of the solution media was fixed at 55 and 70 °C, in the porous layer. Besides, at 90 °C, not only an increment of the pores number was observed, but also a damage of the porous surface was detected as well. The analysis of the micrographs by IFME software corroborated the increment in the number of pores in the porous layer with high temperatures, as can be seen in Table 2. Conversely, no degradation (pore formation) was detected on the dense surface layer after any treatment.

Table 2. IFME Analysis of the number of pores in PSf/Vanillin membranes after treatments using water as a solution media

Membrane	Number of pores
Without treatment	141
With water solution at 55 °C	216
With water solution at 70 °C	431
With water solution at 90 °C	725

Previous studies concerning the thermal effect on polymeric membranes have been reported.[20-23] It was observed that polyacrylonitrile (PAN) membranes become denser after heat treatments with temperatures over 120 °C.[20] In another case, it was reported that temperatures around 150 °C shrank composite polyamid (polyamide/polyetherimide blend support) membrane fibers, which could cause damage to the membranes if constrained inside a module.[21] Also, it was investigated that temperatures over 120 °C shrank polyethersulfone (PES) hollow fiber membranes.[22] In the case of PSf membranes, it is well know that they possess remarkable high thermal[8,23-30] and chemical stability;[30] however, the presence of other compounds in the PSf structure can modify their morphology and therefore their physical properties.[8-30] Vanillin is an organic compound[31-33] that is added in the preparation of the polymeric solution, and it is present in the porous structure of PSf films. When the precipitation takes place, vanillin is trapped into the membrane pores, affecting in this way the shape and the size of the pores. Hence, its presence could cause a structural change in the films morphology affecting their stability.

Figure 3 micrographs show characteristics similar to those in Figure 2. A growth of the pores, in the porous layer, when the experimental temperatures were above 55 °C was also observed; IFME analysis elucidated an increment in the number of pores directly related to DMF solution temperature. Table 3 shows the results of the number of pores in PSf/Vanillin membranes after treatments with DMF aqueous solution (6000 ppm) as a solution media.

Table 3. IFME ® Analysis of the number of pores in PSf/Vanillin membranes after treatments using DMF as a solution media

Membrane	Number of pores
Without treatment	141
With DMF solution at 55 °C	653
With DMF solution at 70 °C	1235
With DMF solution at 90 °C	1794

Again, as can be observed in Figure 3, the presence of pores was not detected in the dense surface. Therefore, we may conclude that neither the temperature nor the DMF aqueous solution (6000 ppm) caused any damage on the dense layer. When comparing, the number of pores increase between water and the DMF treatment, it is possible to see that the formation of new pores is higher in the DMF treatments than in those with water.

The hard degradation of the porous layer in DMF solutions can be associated with an easier penetrability of the DMF into the porous layer, which can cause a partial dissolution of the films, as DMF is a solvent of PSf.[10]
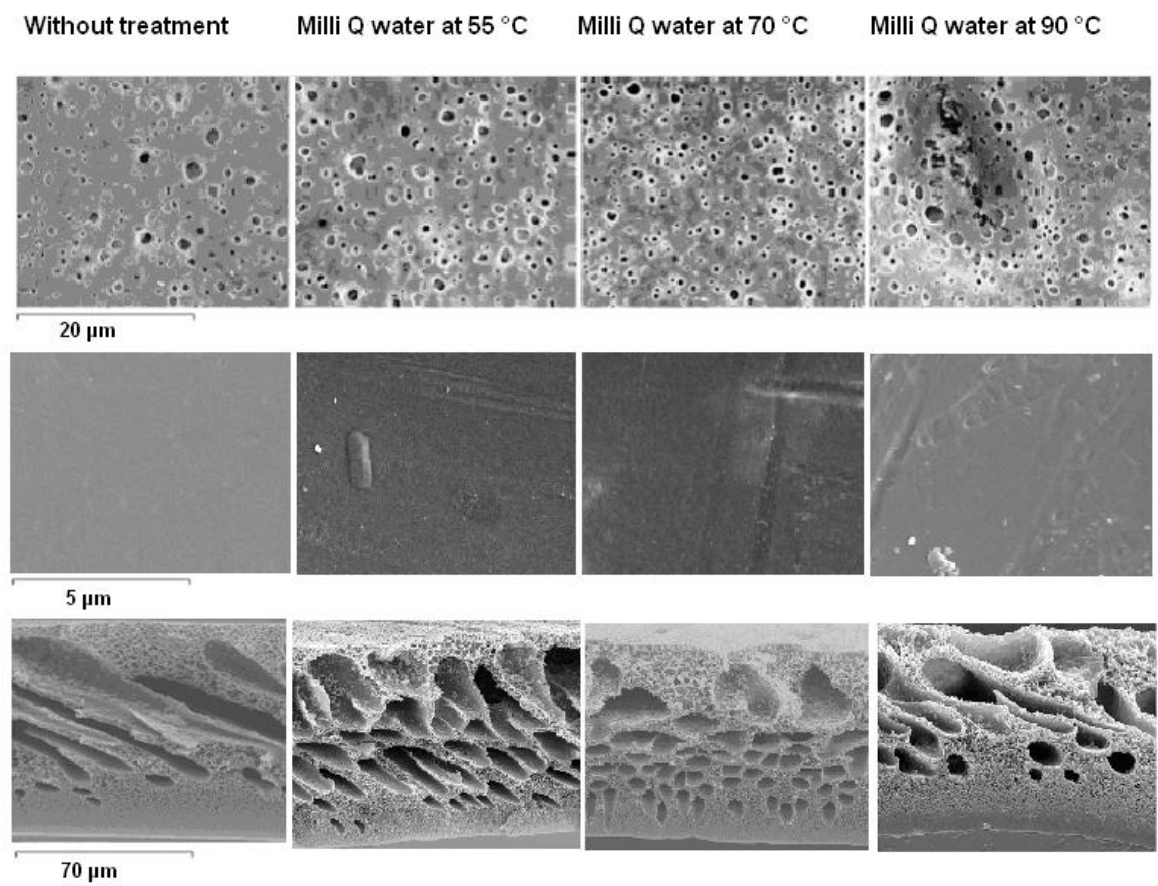
Figure 2. SEM micrographs of PSf/Vanillin film treated with MilliQ water at different temperatures. (Top images: surface top views of porous layers. Middle images: surface top view of dense layers. Bottom images: cross section)
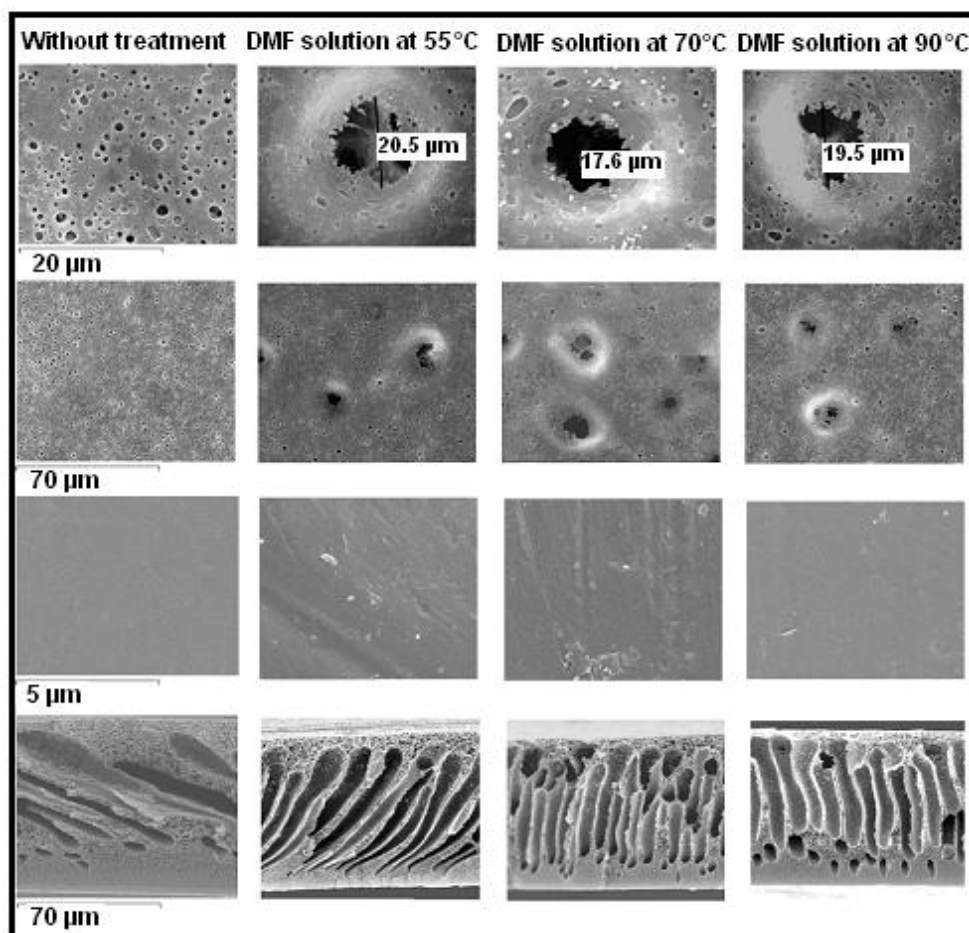
Figure 3. SEM micrographs of PSf/Vanillin film treated with 6000 ppm of DMF at different temperatures. (Two first top images: porous layers. Middle images: dense layers. Bottom image: cross section)

3.2 LOSS OF THICKNESS ANALYSIS IN PSF/VANILLIN MEMBRANES

A thickness analysis was determined in PSf/Vanillin membranes after water and DMF treatments with the purpose of knowing if the material degradation takes place. Experimental parameters are also collected in Table 1 (experiments 1-6). Figure 4 shows the obtained results.

It may be observed that a reduction of the membrane thickness occurred. In both cases, the loss of thickness was favored by high temperatures, the DMF treatments being those that presented the highest value of thickness reduction.

As we mentioned before, DMF is a good solvent for PSf, which can cause partial material dissolution.

According to the SEM micrograph, we believe that the loss of thickness occurs principally on the porous layer, because the dense layer was not visibly affected by any treatment.

This observation comes out to be very relevant as in most cases membrane performance is determined by the dense layer. Therefore, in this case, it appears that the reduction of the porous layer is a drawback, but it could be, in fact, a desirable factor for achieving a faster perfume release. Therefore, considering that the main reduction of the material was produced by the DMF solutions, a detailed loss of thickness analysis of PSf/Vanillin membranes treated with DMF was performed with membrane samples corresponding to experiments 7-12 (Table 1).
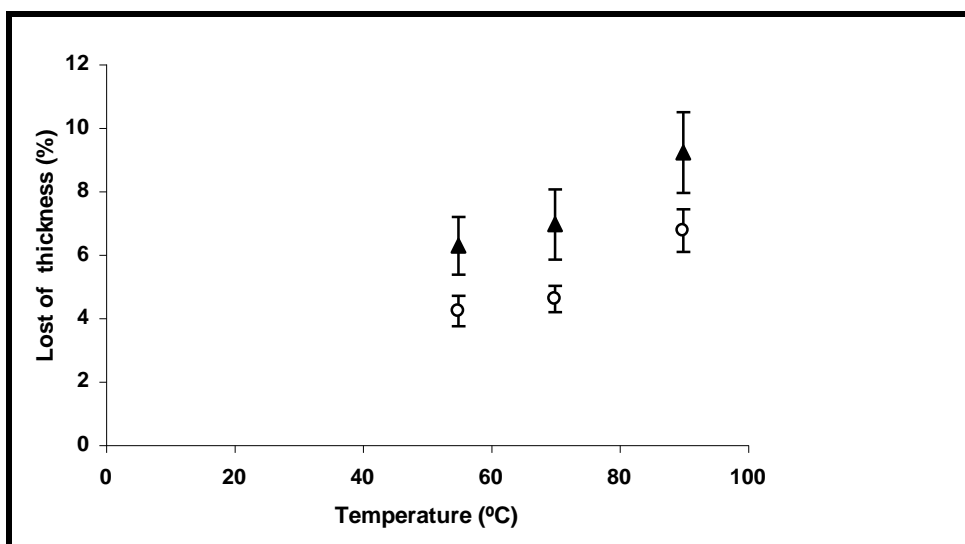
Figure 4. Loos of thickness of PSf/Vanillin membranes exposed to DMF and water treatments at different temperatures during 5 days (▲, DMF treatment; ○, water treatment).

As seen in Figure 5, the lost of thickness of PSf/Vanillin membranes, treated with the DMF solution at 55 °C, occurred in a gradual form, reaching its maximum degradation in the fourth day of treatment. However, in the case of the films immersed into DMF solutions at 70 and 90 °C, a faster reduction of the material thickness takes place during the fist day of treatment.

A significant degradation of the films immersed into DMF solutions at 70 and 90 °C occurred already after 4 and 1 h, respectively.

Figure 5. Lost of thickness analysis of PSf/Vanillin membranes exposed to DMF treatments at 55, 70 and 90 ºC

In Figure 5, it is also possible to observe the reduction of the thickness of PSf/vanillin membranes of experiment 12 (Table 1). During the first 10 min of treatment, a reduction of the material was already observed, but the total material lost after 1 h of treatment represented only 7% of the total thickness.
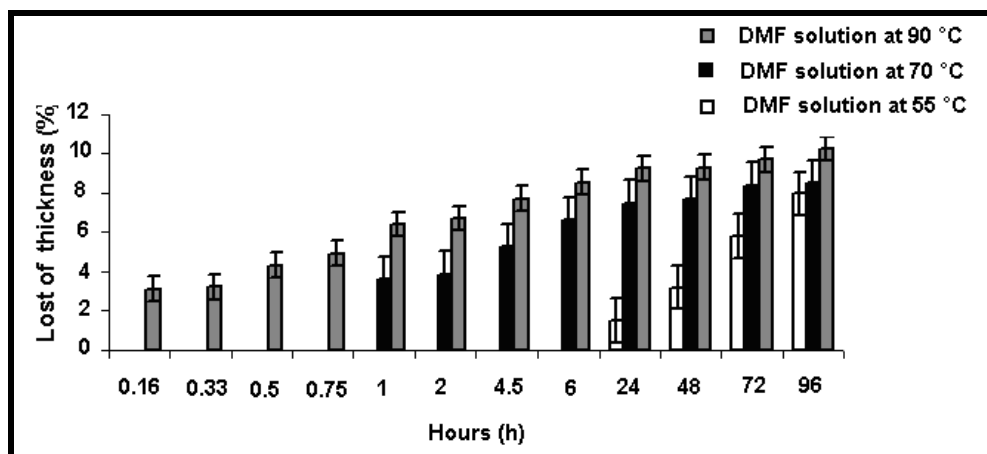
3.3 MECHANICAL CHARACTERIZATION

Two standard methods of the ASTM were considered with two objectives: (1) to verify the mechanical properties of the material after the degradation treatment and (2) to determine the best test method for the mechanical characterization of PSf capsules.

3.3.1 PROTRUSION PUNCTURES ANALYSIS

Membranes treated according to the three first experiments of Table 1 and membranes without treatments were analyzed by the standard ASTMD5748- 95 (protrusion puncture resistance of stretch wrap film). Figures 6 and 7 show the results obtained related to the energy to break and the break force.

As can be seen in Figure 6, no significant differences of the break force were observed between the membranes treatments. The increment of the temperature in the treatments did not affect the break force. It seems that the dense layer of the membrane, which did not present any damage during the treatments, is responsible for this property.
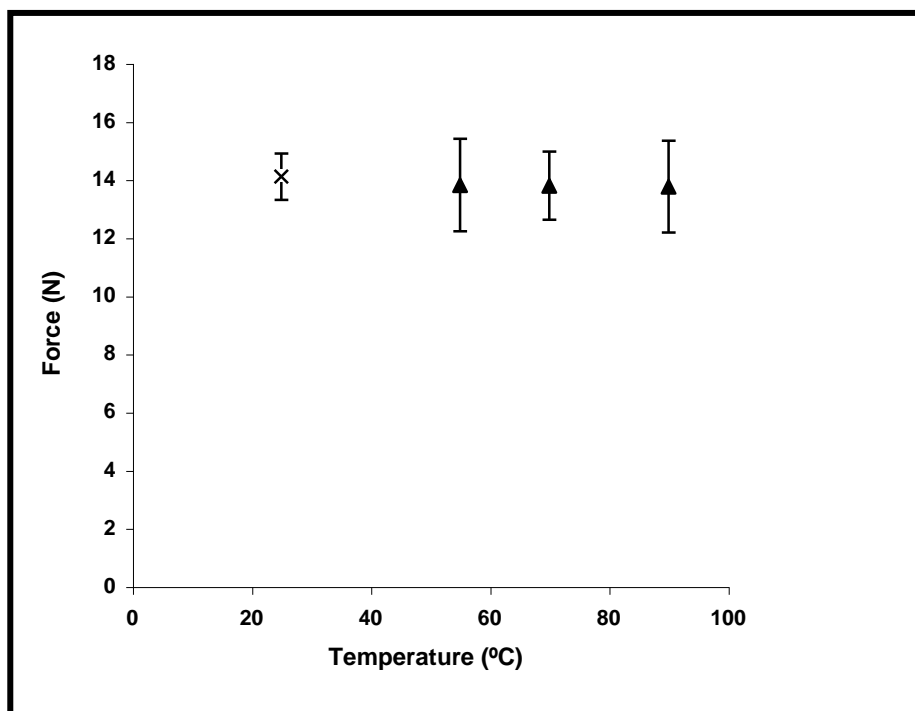
Figure 6. Break force of PSf/Vanillin membranes immersed in DMF solutions at different temperatures and analyzed by Protrusion puncture. (X, without treatment; ▲, DMF treatment)
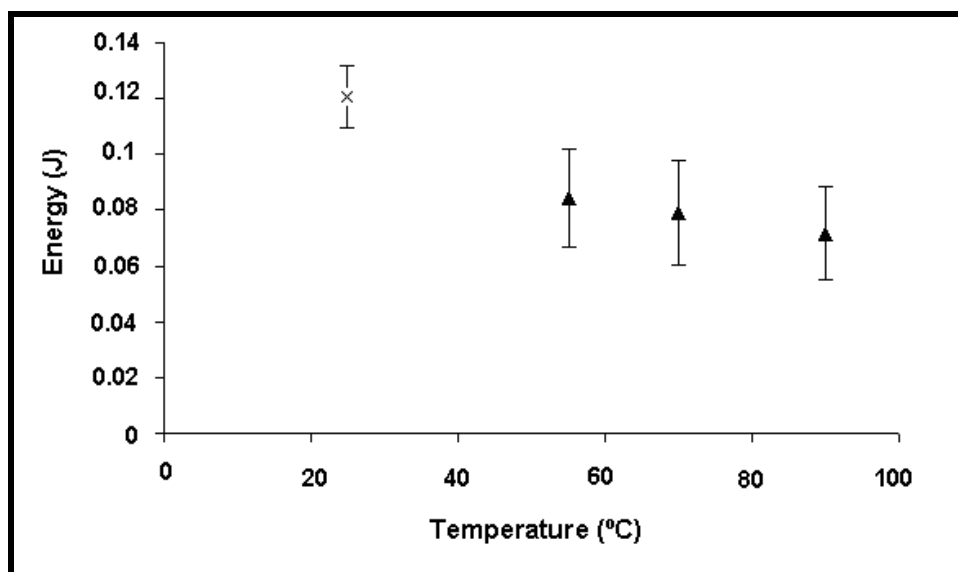

Figure 7. Energy to break of PSf/Vanillin membranes treated with DMF solutions at different temperatures and analyzed by Protrusion puncture. (X, without treatment; ▲, DMF treatment)

Figure 7 shows a reduction of the energy to break (required energy to break the film by elongation), which was favored by a temperature increment of the solution media. Knowing that the force is constant, this parameter is correlated to the membrane elongation. Therefore, higher temperature of DMF solutions decreases the elongation capacity of the PSf/Vanillin films. This is due to the increment in the pore size and the formation of new pores, which favor the membrane break, with low energy requirements.

3.3.2 TENSILE PROPERTIES.

The standard ASTM-D882-09 (standard test method for tensile properties of thin plastic sheeting) was employed to determine the tensile properties of PSf/Vanillin films treated with DMF and water solutions, according to the six first experiments of Table 1, and for PSf/Vanillin membranes without treatment.

Figures 8 and 9 and Table 4 show the results obtained. Figure 8 shows the Young's modulus of the PSf/Vanillin membranes after the experiments. As can be observed in Figure 8, no significant differences were encountered between the values of the Young's modules of the PSf/Vanillin films treated and the PSf/Vanillin films without treatment.

Table 4 collects some tensile properties of PSf/Vanillin films after the treatments and PSf/Vanillin films without treatment. In summary, the treatments did not affect these tensile properties of the membranes. However, the results related to the maximum strain (%) of the PSf/Vanillin membranes show that it was clearly affected by the treatments as shown in Figure 9.
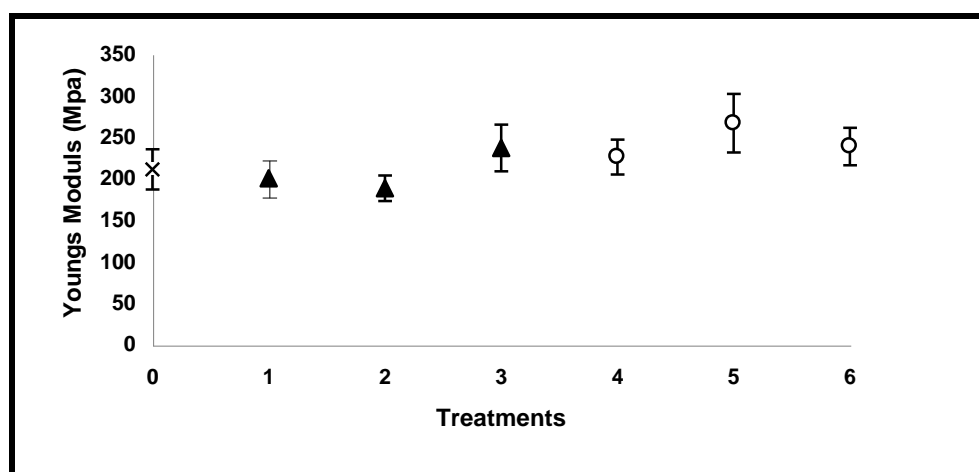
Figure 8. Young's Modules of PSf/Vanillin membranes (▲, DMF treatment; ○, Water treatment; X, membrane without treatment). The value of treatment 0 corresponds to membranes without treatment.

Table 4. Tensile Properties of PSf/Vanillin Films

Experiment	Strength at break MPa	Maximum strength N/mm	Maximum strength MPa
1	4.52 ± 0.3	0.5 ± 0.03	5.55 ± 0.5
2	4.84 ± 0.2	0.52 ± 0.04	5.82 ± 0.4
3	4.93 ± 0.2	0.5 ± 0.02	5.91 ± 0.2
4	4.51 ± 0.3	0.53 ± 0.02	5.91 ± 0.1
5	4.82 ± 0.2	0.56 ± 0.03	6.05 ± 0.2
6	4.35 ± 0.2	0.48 ± 0.04	5.46 ± 0.3
Without treatment	3.78 ± 0.1	0.47 ± 0.04	5.12 ± 0.4

The maximum strain (%) of PSf/Vanillin membranes, treated with water solution at different temperatures, is shown in Figure 9. According to the results previously described, the temperature of the medium leads to an increase of the number of pores and, therefore, to a degradation of the film material. This degradation reduced the maximum strain (%) of the PSf/Vanillin films, as the increment of the size and number of pores favored the breaking of the membrane.

Figure 9 Maximum strain % of PSf/Vanillin membranes exposed to DMF and water treatments at different temperatures. (X, without treatment; ○, Water treatment; ▲, DMF treatment)

Figure 9 also shows the maximum strain (%) of PSf/Vanillin films treated with DMF solutions, as it can be seen the maximum strain (%) of these membranes decreased when the temperature of the DMF solution was increased.

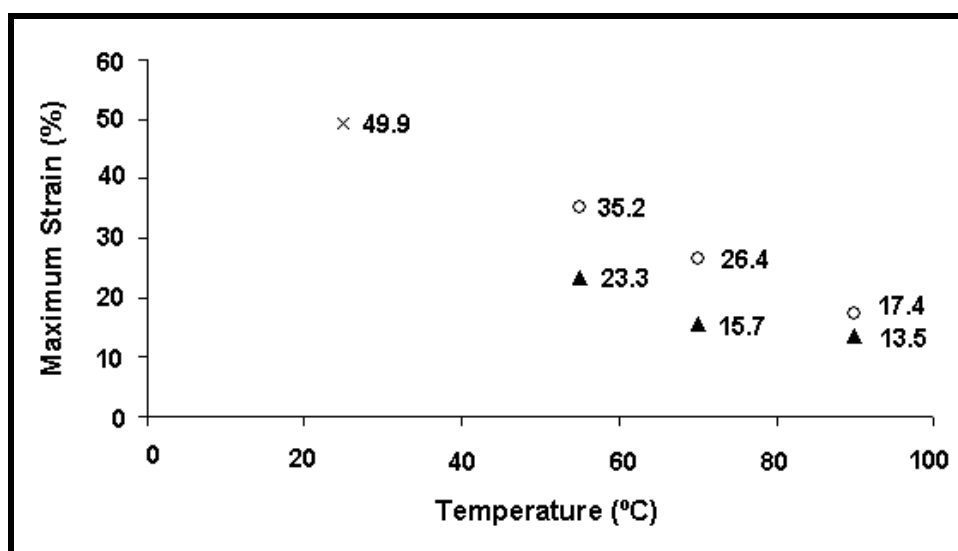This occurred because higher temperatures deteriorated the porous layer, and by combining the effect of the temperature with the solvent of the polymer, the damage is more visible, presenting an outstanding increment of the pores size and also an increment of the number of pores. The increment of the pore size and the number of pores reduced greatly the elongation capacity of the membrane, making the membrane easier to break than after water treatments.

The degradation of the porous layer and the loss of thickness in PSf/Vanillin films only affected the elongation of the material. Considering the fact that the principal reduction of the thickness takes place in the porous layer and no other properties were modified, it is possible to conclude that what is responsible for almost all mechanical properties (Young's module, maximum strength, and strength at break) is the dense layer. Therefore, the loss of thickness does not affect the material mechanical properties. Consequently, it has no negative implication on the membrane material stability.

Because of the fact that the Young's module and the maximum force are constant, we strongly recommend the protrusion puncture method to characterize the mechanical degradation of the films. With this method it is easier to perform a measure of the maximum elongation because membranes can be produced with a desirable area for the test, avoiding in this way defects created by the sample cut. Additionally, excluding the Young's module, it is possible to obtain the same parameter results with more reliability with the protrusion puncture method than with the tensile properties test.

4. CONCLUSIONS

Flat sheet PSf/Vanillin membranes have been successfully prepared and morphologically, physically, and mechanically characterized, after being exposed to various degradation treatments. The membrane obtention procedure has been designed to simulate capsules containing vanillin preparation method.

According to the mechanical characterization of the membrane, two different approaches have been considered. Among them, the most appropriate characterization method, which is the protrusion puncture method, has been proposed.

In view of the results obtained, both temperature and dissolving media (DMF) degraded the PSf material. Degradation becomes more important when combining both effects. The degradation was observed in terms of an increment of pore number and size in the porous layer and also as a decrease of the membrane thickness.

The main reduction of the membrane thickness took place in the porous layer because it showed a significant degradation in its surface. Far away from being a drawback, it could be, in fact, a desirable factor for a faster perfume release from PSf capsules.

Performing the mechanical tests, we saw that the thickness reduction of the films and the degradation of the porous membranes only affected the maximum strain (%); however, most of the mechanical properties of the material were kept constant, as the dense layer is the principal layer responsible for providing the mechanical properties of PSf/Vanillin membranes.

We strongly recommend the protrusion puncture method to characterize the mechanical properties of PSf films.

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CHAPTER 4

PREPARATION AND CHARACTERIZATION OF POLYSULFONE MICROCAPSULES FOR PERFUME RELEASE

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ABSTRACT

Textile detergent and softener industries, among others, have been incorporating the recent scientific advances; such as microencapsulation technology, to successfully improve their final products. Perfume encapsulation allows perfume protection until use and provides a long-lasting fragrance release. However, certain current industrial microcapsules show low encapsulation capacity and lack of mechanical stability. Polysulfone (PSf) microcapsules are an emerging promising alternative as they have both high mechanical stability and notorious encapsulation capacity. In the present investigation, PSf/Vanillin microcapsules have been prepared by phase inversion precipitation technique and characterized by Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) and thermogravimetric analysis (TGA). Vanillin release has been monitored by High Performance Liquid Chromatography (HPLC). 45% of vanillin encapsulation, from the total perfume added to the polymer solution, has been reached. A treatment to increase the amount of vanillin inside of capsules has also been proposed. Concerning perfume release, it has been detected that vanillin is more rapidly released in hard water than in pure water; but in both cases, vanillin was released continuously for more than 144 h (6 days).

Keywords: Microcapsule, Phase inversion precipitation, Polysulfone, Controlled Release, Vanillin.

1. INTRODUCTION

Encapsulation process is described as the capture of a compound into a coating material.[1] It is a scientific advance currently used by several industrial fields. It presents numerous applications to improve industrial commercial products, such as; to immobilize, isolate, protect and control the rate of transfer of many substances like metals, acids, drugs, nutrients, pesticides and herbicides, perfumes, etc. [1-15]

Mainly, encapsulation is used to extend the shelf life of labile compounds. From an industrial point of view, the encapsulated compounds are easy to handle as they preserve their properties and stay safety in case of prolonged storage. This stabilization is due to the coating material, which acts as a protective physical barrier. [15-20] Capsules can be defined as spherical membranes with an empty volume inside. [1, 3, 9] They can be classified, according to their diameter size, in nanocapsules (with diameter smaller than 1 µm), microcapsules (with diameter between 1 to 1000 µm) and macrocapsules (with diameter larger than 1000 µm). [3, 9] A long list of different materials can be used to prepare capsules. Among them, polymeric materials are frequently used. [2-14] In the latest case, phase inversion precipitation is one of the most commonly employed techniques for their preparation. [3-13] It is based on the separation (by precipitation) of the polymeric phase from a mixture that contains a solvent and a polymer, by means of thermodynamic processes. The precipitation of the polymeric phase occurs by a diffusion process in which the polymeric solution is immersed into a non-solvent (immersion precipitation). [13]

The controlled release of fragrances is a challenge for the industries, which use perfumes in their products, due to the fact that the consumers are attracted by articles with a long-lasting fragrance perception. Perfumes present compounds that may be lost due to their highly volatility; [21-23] but, by encapsulation, they can be protected during storage and until the final use of the product. [2-4,15, 23-24]

Nowadays, the perfume encapsulation technology is being used for the development of innovative textile products in order to offer a long-lasting fragrance release. It has been proved that the aroma perception is maintained for several days in fabrics if these are impregnated with capsules containing perfume. [2, 25-26] A previous investigation confirmed that fabrics impregnated with microcapsules released aroma up to five washing cycles.[2] Another study demonstrated a long lasting fragrance release in cotton towels where it was applied a fabric softener containing fragrance in microencapsulated form.[26]

As the current tendency of consumers is the use of articles that ensure the preservation of the fragrance in the fabrics during drying and storage, textile detergent and softener industries have been incorporating in their processes the perfume microencapsulation technology. [4] This technology allows the protection of the fragrance before and during industrial processes, as well as in the product storage. Moreover, it protects the perfume during the laundry and it provides a long-lasting fragrance release after the drying and storage of fabrics. However, certain current industrial microcapsules present a number of drawbacks such as low material stability, low perfume encapsulation capacity and, in addition, with the industrial encapsulation method presently used it is extremely complicated to encapsulate hydrophilic perfumes.[4] With the aim to solve these problems, polysulfone (PSf) capsules were proposed. [3, 4, 9]

PSf macrocapsules containing vanillin, a hydrophilic component commonly used in perfume and cosmetic formulations, [27-28] have been formerly investigated and showed promising results related to material stability, high encapsulation capacity and release behavior.[3] However, in order to fulfill with commercial applications, capsules need to be obtained at micro-scale rather than at macro-scale. In a previous investigation, a first attempt of PSf/Vanillin microcapsules production was performed.[4] In that case, a set-up containing two micro-devices was used for the microcapsules manufacturing. However, it presented several problems, which strongly limited the use of the set-up in microcapsules production. The principal problems were: 1) the polymeric solution often precipitated into the micro-channels impeding the continuous production. 2) Trying to avoid the polymer precipitation, the PSf concentration into the polymeric solution was lowered; thus this affected the physical stability of the capsules. 3) Even under the best conditions, the microcapsules production was not significant. Therefore, not only is fundamental to determine if PSf macrocapsules may be scaled down, but also to develop an appropriate set-up for its production. Moreover, it is necessary to verify if PSf microcapsules maintain the same properties than they presented at macro-scale and, hence confirm, their suitability for detergent and softener products.

In this investigation, PSf/Vanillin microcapsules containing vanillin as perfume, and prepared by phase inversion precipitation technique, were obtained and analyzed with the following purposes: to prove the capability to incorporate hydrophilic perfumes, to investigate their encapsulation capacity, to determine their suitability for a long lasting perfume release and to examine the effect of the water quality in their release behavior. In addition, a comparison between PSf/Vanillin macro and microcapsules was also included.

2. EXPERIMENTAL

2.1 MATERIALS

Polysulfone (PSf) and vanillin reagentPlus® 99% were purchased from Sigma-Aldrich (Spain). N,N-Dimethylformamide (DMF) reagent grade ACS ISO and Acetonitrile multisolvent® HPLC grade ACS UV-VIS were obtained from Scharlau (Spain). Ultra pure water (MilliQ water) was used during the experiments and capsules preparation.

2.2 MICROCAPSULES PREPARATION (STANDARD PROCEDURE)

Polymeric solution was prepared by dissolving 15% w/w of PSf (Figure 1) and 10% w/w of vanillin (Figure 1) in DMF (Figure 1). The mixture was stirred at 500 rpm during 24 h at room temperature. Afterwards, PSf/Vanillin microcapsules were obtained by dispersing the polymeric solution, forming micro-droplets, into a coagulation bath containing 200 mL of milliQ water. Micro-droplets precipitation took place, because of an exchange between water and DMF, which led to vanillin encapsulation. Finally, PSf/Vanillin microcapsules were collected by filtration.

For the comparison of XRD results, microcapsules without vanillin were prepared by the same procedure from a polymeric solution containing 15% w/w of PSf and 85% w/w of DMF.
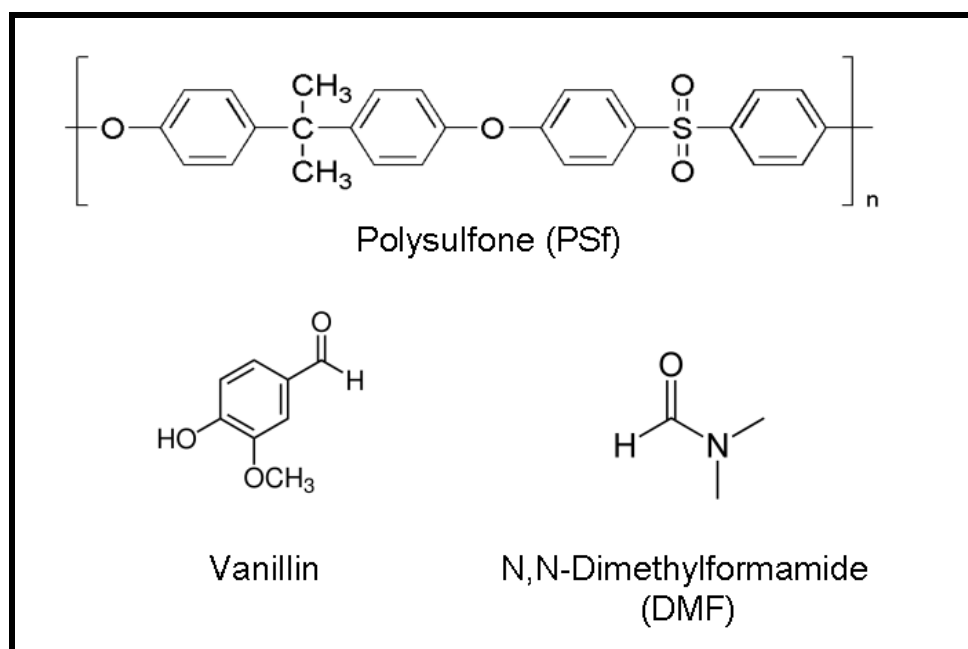

Figure 1. Chemical structures of the capsule components

2.3 MICROCAPSULES PREPARATION WITH DIFFERENT VANILLIN CONCENTRATION

The composition of the polymeric solution used in this investigation has been widely studied in previous investigations where different PSf concentrations in the polymeric solution were tested in order to determine the more adequate one for the capsule formation.[3, 9] However, as one of the principal aims of this study is the production of capsules with high perfume encapsulation, several PSf/Vanillin microcapsules were prepared by increasing the concentration of vanillin. In this case, the composition of PSf remained constant and the DMF was decreased until the minimum quantity that allowed capsule formation. In this way, and with the purpose to determine the maximum encapsulation capacity of PSf/Vanillin microcapsules, five polymeric solutions, with different vanillin concentration (w/w), were prepared by dissolving (a) 15% w/w of PSf and 15 % w/w of vanillin in 70% w/w of DMF, (b) 15% w/w of PSf and 20 % w/w of vanillin in 65% w/w of DMF, (c) 15% w/w of PSf and 25 % w/w of vanillin in 60% w/w of DMF (d) 15% w/w of PSf and 30 % w/w of vanillin in 55% w/w of DMF and (e) 15% w/w of PSf and 35 % w/w of vanillin in 50% 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 it has been mentioned above.

2.4 MORPHOLOGICAL CHARACTERIZATION OF MICROCAPSULES

Both internal and external morphology of PSf/Vanillin microcapsules were analysed by Scanning Electron Microscopy SEM (JEOL JSM-6400 Scanning Microscopy Series), with an acceleration voltage of 15 – 20 KV. Particle size distribution was determined by SEM micrographs analysis using the Image processing and analysis in Java program (IMAGE J). The particle population was at least of 350 counts.

With the objective to obtain cross-section images without modifying the polymeric structure of microcapsules, they were cryogenically broken.[29] For this procedure, a cryostat (Leica CM 1850) was employed. First of all, the capsules were attached over a specimen disc with a freezing medium. It was used an embedding medium for frozen tissue specimens (Sakura Tissue). Once the capsules were fixed over the specimen disc, the disc was immersed into liquid nitrogen. Then, the specimen disc was located in the cryo-chamber. After that, the sample was cut with thickness intervals of 1μm. Finally the capsules were analysed by SEM.

The porosity characterization of PSf/Vanillin microcapsules was determined by N2 gas adsorption-desorption at 77 K with a Micrometrics ASAP-2020 device. Prior to the analysis, samples were vacuum degassed for 12 h at 50 °C.

2.5 RELEASE EXPERIMENTS

Release experiments were performed in order to determine the effect of water nature on the perfume release from PSf/Vanillin microcapsules. With that purpose, 1g of PSf/Vanillin microcapsules were added into 80 ml of either hard water or pure milliQ water and stirred at 700 rpm during at least 96 h. Table 1 shows the experiment working conditions. Release medium samples of 1 ml were periodically withdrawn and hermetically stored until the quantitative analysis was performed.

Table 1 Experimental parameters.

Experiment	Release medium (100 ml)	Capsules Weight (g)	Stirring rate (rpm)	Temperature (°C)	Time (h)
Release experiment 1	MiliQ water				
		1 ± 0.01	700	25	
2	Sink water				
					96
Vanillin solution treatment 3	Vanillin saturated solution	1 ± 0.01	700	25	
Release experiment after vanillin treatment 4	MiliQ water				
		1 ± 0.05	700	25	
5	Sink water				
Medium renewals after vanillin treatment 6 7 8	MiliQ water	1 ± 0.01 0.75 ± 0.05 0.45 ± 0.12	700	25	48
9 10 11	Sink water	1 ± 0.01 0.75 ± 0.09 0.45 ± 0.25	700	25	

2.6 VANILLIN SOLUTION TREATMENT

As DMF acts as polymer solvent, it is present in the polymeric solution in a notorious quantity. In a previous investigation, it was found that during the capsule formation, part of the DMF was encapsulated together with vanillin[3, 9]. This represents a huge commercial problem as DMF is harmful and toxic[30-31]. In a previous work the use of a perfume solution treatment was proposed to solve this drawback[3]. The treatment consisted in storing the capsules in a solution saturated with the perfume during 5 days. After that time, it was observed that DMF had been removed from the microcapsules. However neither the kinetics nor the exact time that DMF needed to be eliminated were reported. Therefore, with the aim to

improve this treatment, four experiments were performed: four bottles containing 100 mL of a vanillin-saturated solution and 1 g of PSf/Vanillin microcapsules were prepared and they were stirred at 700 rpm at room temperature for 1, 2, 3 and 4 days respectively. Afterwards capsules were collected and its perfume release was analysed.

2.7 ANALYTICAL TECHNIQUES

The concentration of vanillin in the release 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 at 40 °C, the analysis time was 8 min and the injection volume was 4 µL. Vanillin concentration was determined at 229 nm, showing a typical retention time of 4.2-4.5 min.[9]

2.8 XRD

X ray diffraction (XRD) is a technique that not only provides the characterization of crystal substances but it also can identify compounds, [32-33] thus, it was used with the purpose to determine if vanillin crystals were deposited over the capsule surface after the vanillin solution treatment. In this way, PSf/Vanillin microcapsules after vanillin solution treatment and PSf microcapsules without vanillin were analyzed by XRD. The experiments were performed using a siemens D5000 diffractometer (Bragg-Brentano parafocusing geometry and vertical θ-θ goniometer) fitted with a curved graphite diffracted-beam monochromator and diffracted-beam Soller slits a 0.06 º receiving slit and scintillation counter as a detector. The angular 2θ diffraction range was between 5 and 70º. Sample was dusted onto a low background Si (510) sample holder. Data were collected with an angular step of 0.05º at 3s per step and sample rotation. $Cu_{k\alpha}$ radiation was obtained from a copper X-ray tube operated at 40 kV and 30 mA.

2.9 THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TGA) is a good method to elucidate the solid content of capsules containing perfume, as it determines de lost of weights, due to the perfume release, by increasing the temperature.[34-35] In this investigation two samples were analyzed 1) PSf/Vanillin microcapsules after vanillin solution treatment and 2) PSf/Vanillin microcapsules without treatment. The equipment used was a thermogravimetric analyzer (TGA, Mettler Toledo TGA/SDTA851e) equipped with a microbalance with an accuracy of 1 µg. The microcapsules samples (about 10 mg) were introduced into an aluminium oxide crucible and analyzed by TGA under controlled temperature and a constant flow of nitrogen of

290 cm^3/min. The samples were heated from 30 to 80°C at a rate of 10°C/min and then the temperature was held at 80°C for 2 hours.

2.10 ENCAPSULATION CAPACITY

With the purpose to determine the encapsulation capacity of both: capsules prepared by the standard procedure and capsules in which the amount of vanillin was increased, vanillin remaining in the coagulation bath (200 ml of milliQ water) after capsule precipitation (from 20 ml of polymeric solution) was measured.

Encapsulation capacity was determined from the difference between the vanillin added to the polymeric solution and the vanillin detected in the precipitation water bath.

3. RESULTS AND DISCUSSION

3.1 MECHANISM OF PSF/VANILLIN MICROCAPSULES FABRICATION

PSf/Vanillin microcapsules were obtained by using an airbrush device working in semi-continuous process with a nozzle size of 80 µm. The apparatus was developed and adjusted specifically for the production of microcapsules. There is no previous investigation reported in the literature that performs dispersion followed by phase inversion precipitation technique in order to obtain PSf microcapsules. Most of the authors used a syringe needle for the formation of the polymeric micro-droplets[5-8, 36-38] and only few of them get PSf microcapsules in a semi-continuous process.[38] However, even with a semi-continuous process the microcapsules formation is quite low as only one needle is forming micro-droplets. With the airbrush device used in this investigation it is possible to obtain high production of micro-droplets in one step. Thus the production of microcapsules is notoriously increased with the airbrush device, which is capable to produce 1.5 g/min of PSf microcapsules. Moreover, our research group is still working to further improve this set-up as it shows promising results.

For the operation, the airbrush was connected to a compressed air supply valve that offered the energy required to break up the polymeric solution into micro-droplets. When the air valve was opened the device dispersed the polymeric solution by shearing action provided by a high velocity air stream (around 200 m/s). The airbrush was located 40 cm over a container with milliQ water. The outlet flow was positioned perpendicular to the surface of the coagulation bath. Thus the micro-droplets impacted directly on the water surface. Figure 2 shows a scheme of the dispersion set-up.
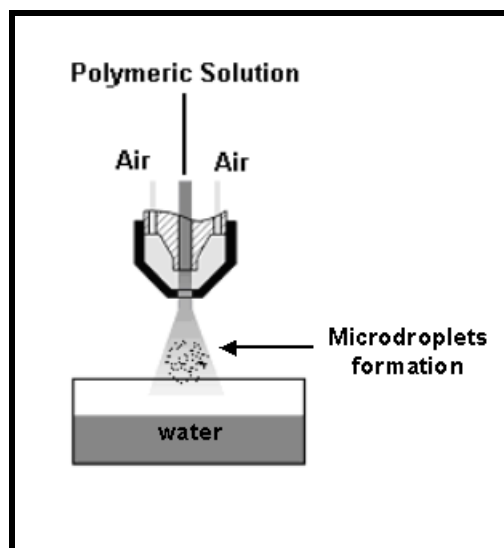
Figure 2. Schematic diagram of the atomization set – up

The polymeric solution was poured into the airbrush paint bulk just before the capsules production in order to avoid its contact with the atmospheric air that can cause the polymer precipitation because of the humidity and/or solvent evaporation.

As the precipitation of the polymer in contact with the water is very fast, the coagulation bath was stirred to prevent microcapsules aggregation.

After the dispersion, the microcapsules were floating in the coagulation bath. In order to recover them, the liquid of the coagulation bath was filtered using a 5µm nylon filter. Microcapsules that remained over the filter were stored into a desiccator in order to remove the water from them thus obtaining a dried product.

3.2 MORPHOLOGICAL CHARACTERIZATION

Morphological characterization of PSf/Vanillin microcapsules was carried out by SEM analysis. Figure 3 shows SEM micrographs of the PSf/Vanillin microcapsules. SEM micrographs show that PSf/Vanillin microcapsules present a polydisperse formation with a mean particle diameter of 17.8 µm and a standard deviation of 8.5 µm. Besides, cross-section micrographs show an empty space, which ensures a notorious volume for perfume encapsulation. Moreover, from cross-section micrographs the shell thickness was determined. It was estimated that around the 30% of the capsule diameter corresponds to the shell thickness. The polymeric shell provides good physical stability of the capsule.
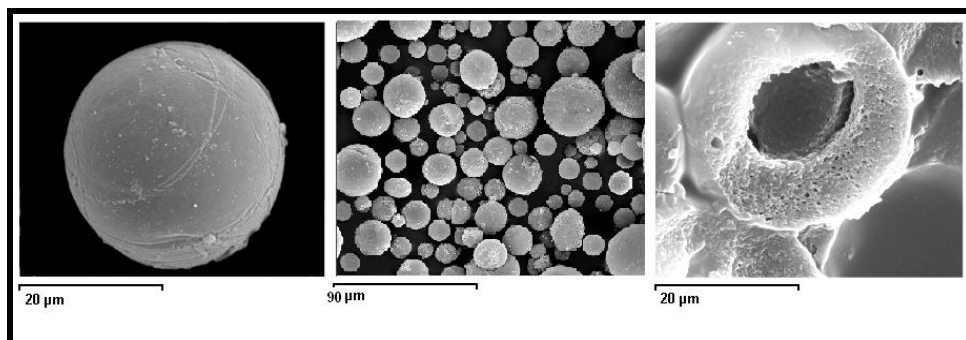
Figure 3. SEM micrograph of PSf/Vanillin microcapsules

Regarding to the porosity characterization with the N_2 gas adsorption-desorption analysis, PSf/Vanillin microcapsules present a surface area of 20.6 m^2/g and a total pore volume of 0.077 cm^3/g. The average pore width is between 1.4 and 14 nm. Thus, PSf/Vanillin microcapsules present both micro and meso pores.

3.3 RELEASE EXPERIMENTS

PSf/Vanillin microcapsules emerged with the purpose to solve several problems that commercial capsules used in detergents and fabric softeners have. Detergents and fabric softeners are products commonly used in the laundry. Depending in the region in which the laundry is carried out, water may have different nature. With the purpose to determine the effect of water nature in the perfume release behaviour, two release experiments were performed using two kinds of water: milliQ water and sink water with a high mineral content (hard water). Figure 4 and 5 show a comparison between the release results obtained with the two different kinds of water.

Figure 4 shows the release of vanillin from PSf/Vanillin microcapsules in milliQ and in sink water. The graph is plotted in terms of ppm of vanillin (released), per gram of microcapsules, versus time. As shown in Figure 4, the two curves have similar kinetics. It is observed that in both cases vanillin is rapidly released during the first 10 hours of experiment. Afterwards, from 10 to 30 h, although vanillin continues to be released from microcapsules, the release rate is considerably slower and finally it reaches a plateau. In both cases, PSf/Vanillin microcapsules released perfume continuously for 96 hours. Similar release tendencies were also observed in previous investigations with PSf/Vanillin macrocapsules. [3, 9]
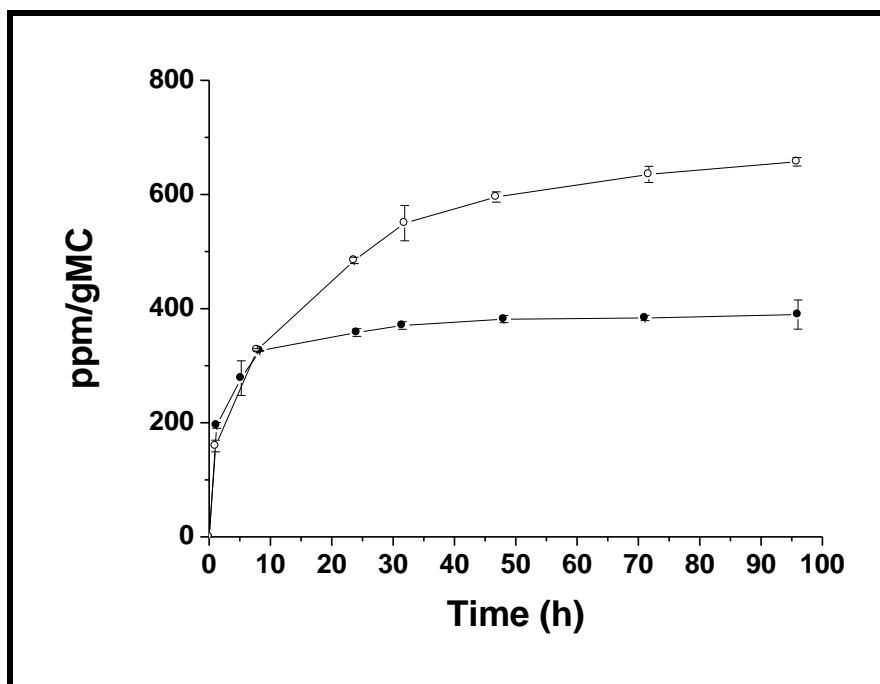
Figure 4. Vanillin release from PSf/Vanillin microcapsules: (○) using hard water as release medium; (●) using milliQ water as release medium

It seems that the release mechanism of PSf/Vanillin microcapsules is due to two main factors: 1) the capsule morphology (pore size and structure) and 2) the stirring rate. PSf/Vanillin microcapsules present a porous shell with a mean thickness of 5.34 ± 1.82 μm in which the pore width is between 1.4 to 14 nm. The molecule of vanillin (Figure 1) has a relative size of 6 A (0.6 nm). [39] Thus, it can pass through the capsule shell to the release bulk solution and may be dissolved in the aqueous medium. However without an appropriated stirring, the release of vanillin in water would not be longer. Stirring of the release medium favors the release because it helps to remove the perfume molecules from the capsule outer surface.

On the other hand, the amount of vanillin released was significantly different when hard water was used instead of milliQ water. In the case of hard water almost 90% more of vanillin was released, even when the composition of the capsules employed in both experiments was the same. According to the literature, an increase of the medium pH increases the solubility of vanillin in water. It happens due to the fact that the molecule of vanillin looses a proton, and it becomes negatively charged and more soluble in water.[39] In another investigation, in order to carry out the oxidation of the vanillin aromatic aldehyde to aromatic carboxylic a high solubility of vanillin in water was needed. Thus, the use of phosphate buffer to prevent a decrease of the pH solution and to maintain a desirable solubility of vanillin was proposed.[40]

As hard water presents high mineral content, especially of calcium Ca^{2+} and magnesium Mg^{2+} and sometimes dissolved compounds such as bicarbonates and sulfates, its pH is higher than milliQ water.[41] For this investigation, the pH of the sink water used in the experiments was 8.1, whereas the pH of milliQ water was 7.2. The measurements of the pH were made with pH meter. Thus, vanillin was more easily released in the sink water, due to its higher pH.

As was mentioned before, in previous investigation the release of DMF was also detected in PSf/Vanillin macrocapsules.[3] Unfortunately, in PSf/Vanillin microcapsules that was not an exception as DMF was also detected. Figure 5 shows the comparison of the DMF released both in hard water and in milliQ water. As shown in Figure 5, in both experiments the curves present similar kinetics, as in the case of vanillin. DMF was rapidly released during the first hours and after that it reached a plateau. However, it was observed that the final amount of DMF released was quite similar in both cases. No significant differences were observed between the DMF released in both mediums. Thus, the water nature only affects the release of Vanillin. Nevertheless, the presence of DMF into PSf/Vanillin microcapsules and its consequent release is a serious drawback as it is a harmful and toxic component .[30-31] The encapsulation of DMF may strongly limit the use of PSf/Vanillin microcapsules in human products, if it is not significantly removed from inside of PSf/Vanillin capsules. Therefore a treatment to remove DMF encapsulated has been tested.
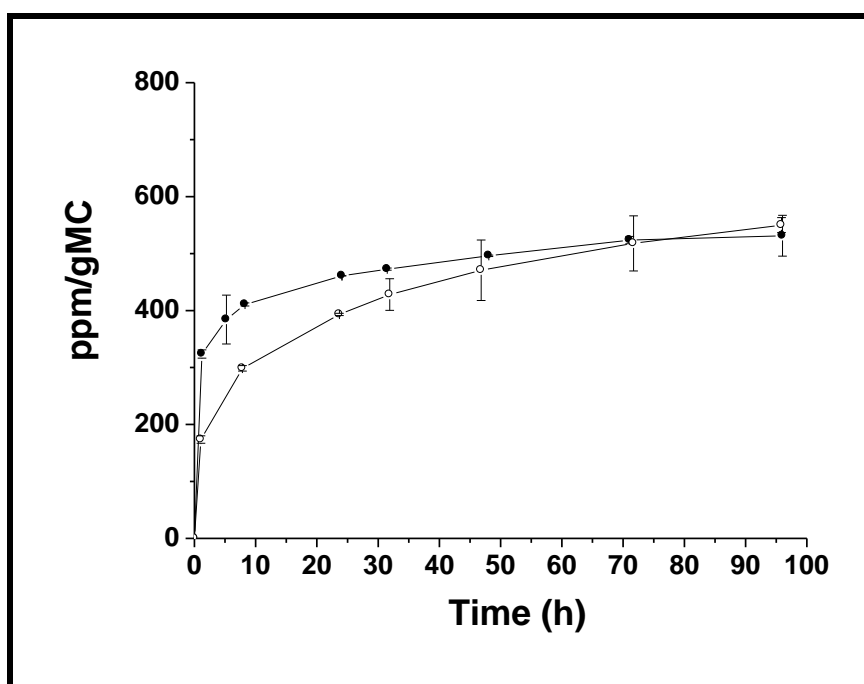

Figure 5. DMF release from PSf microcapsules: (○) using hard water as release medium; (●) using milliQ water as release medium

3.4 DMF REMOVAL

As aforementioned, the main purpose of this investigation is the production of capsules capable to offer high perfume encapsulation capacity and long lasting fragrance release. PSf/Vanillin capsules present these characteristics[3] moreover they have good physical stability.[42] PSf/Vanillin microcapsules can successfully solve the problems that have the industries of textile detergents and fabric softeners. However, the encapsulation of DMF impedes their use in human products. For this reason, DMF has to be removed from PSf/Vanillin microcapsules if they want to be used. A solution to eliminate DMF from PSf/Vanillin macrocapsules was proposed in a previous investigation.[3] It consisted in the use of a perfume-saturated solution. Capsules were stored in a vanillin-saturated solution, during 96 h, after being prepared. With this method around the 99% of DMF was removed. However, the exact time for the elimination of DMF is not known. In order to know exactly when DMF is removed with this treatment, certain experiments were performed. Table 1 collects the working conditions.

PSf/Vanillin microcapsules were treated with a vanillin-saturated solution during 1, 2, 3, 4 and 5 days. After vanillin treatment, capsules were recovered conveniently rinsed (with milliQ water) and afterwards they were immersed in fresh milliQ water with the purpose to determine the quantity of DMF removed from inside the microcapsules. Figure 6 shows the results.
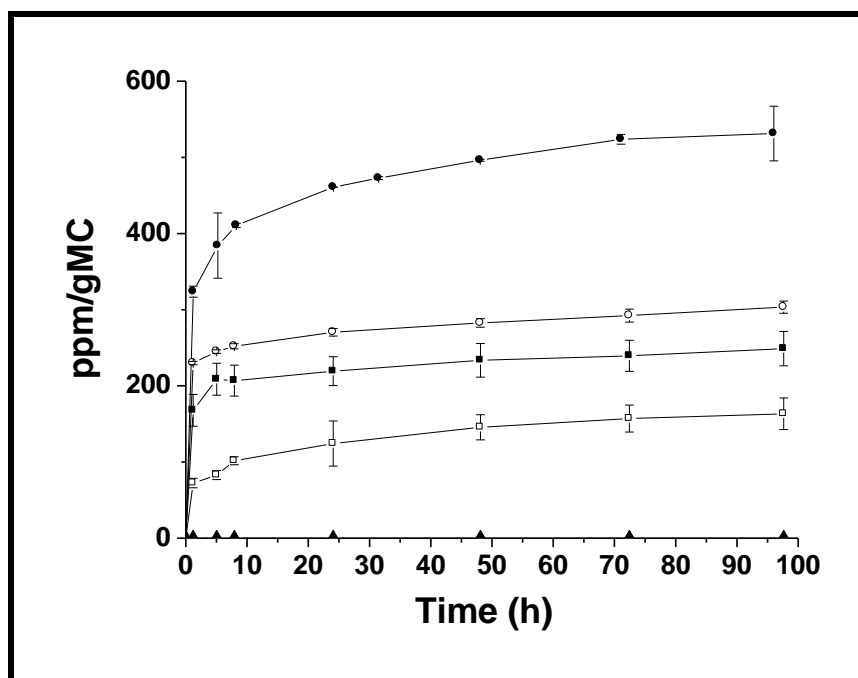

Figure 6. DMF release from PSf microcapsules pre-treated with a vanillin saturated solution. (●) Without treatment. (○) One day of treatment. (■) Two days of treatment. (□) Three days of treatment. (▲) Four days of treatment

As can be seen in Figure 6, the 42 $\pm$ 4% of DMF was eliminated in the first day of treatment. While with two days of treatment, 53 $\pm$ 3% of DMF was removed. The major elimination of DMF was observed after 3 days of treatment in which 69 $\pm$ 2% of removed DMF was achieved. At the fourth and fifth days of treatment, DMF was not detected.

The results show that the amount of DMF eliminated does not follow a proportional relation. With one more day of treatment the amount of DMF in the capsules decreased greatly. This is because an exchange between DMF and vanillin took place. DMF has a high affinity for water and vanillin, thus it is easily released to the bulk medium; whereas vanillin is more stable inside of the capsules, thus it is incorporated into the capsules. Due to these factors no equilibrium was reached between the DMF encapsulated and the DMF outside of the capsules. Moreover, after the vanillin treatment, capsules were recovered and stored into a desiccator for one day. It is probable that DMF was evaporated during the storage process. Therefore, either vanillin solution treatment as capsule storage helped removing DMF from microcapsules.

Thus, it is possible to successfully eliminate the DMF encapsulated by immersing the capsules into a vanillin-saturated solution during 4 days.

3.5 VANILLIN RELEASE AFTER THE REMOVAL OF DMF

The exact time needed to eliminate DMF from PSf/Vanillin microcapsules has been determined. However, it is also necessary to study if the treatment to remove DMF affects the release behaviour of vanillin. With this purpose, PSf/Vanillin microcapsules were recovered after the vanillin treatment, immersed both in hard water and milliQ water and finally compared with the capsules that were not pre-treated with vanillin solution. Figure 7 and 8 show the vanillin release behaviour, both in milliQ water as in hard water respectively.

As shown in Figure 7, the amount of vanillin released was greatly increased after pre-treating the capsules with a solution saturated with vanillin. The release kinetics of both capsules was quite similar. However, capsules that were treated with a vanillin-saturated solution did not reach a plateau as a considerable amount of vanillin was still released after 96 h. However their release rate is not that fast in the beginning and it starts to decrease after 50 h of experiment. Probably the extra vanillin added to the capsules was released during the first 50 h. After this time, the vanillin that was encapsulated during the capsule formation started to be released. In the case of capsules without treatment, a clear plateau is reached after 30h. In both cases, the microcapsules released perfume continuously for 96 h.

Figure 7. Vanillin release from PSf/Vanillin microcapsules in milliQ water: (○) capsules without a vanillin solution treatment; (●) capsules after a vanillin solution treatment

Moreover, Figure 7 shows that pre-treated PSf/Vanillin microcapsules had released more vanillin (nearly 400 ppm) than capsules that had not been pre-treated. The only explanation to this fact is that during the treatment an exchange of DMF, which is inside of microcapsules, by vanillin, from the bulk solution, took place.

On the other hand, as shown in Figure 8, in the case in which hard water was used as a release medium a plateau was reached after 30 h of experiment both in the capsules that were pre-treated as in those that were not pre-treated. In addition, the amount of vanillin released was higher in hard water than in Milli-Q water. Capsules pre-treated with vanillin solution show a higher release also in these conditions. As was explained before, vanillin is better dissolved when the pH of the water is higher. Thus, the use of hard water facilities the release of vanillin.
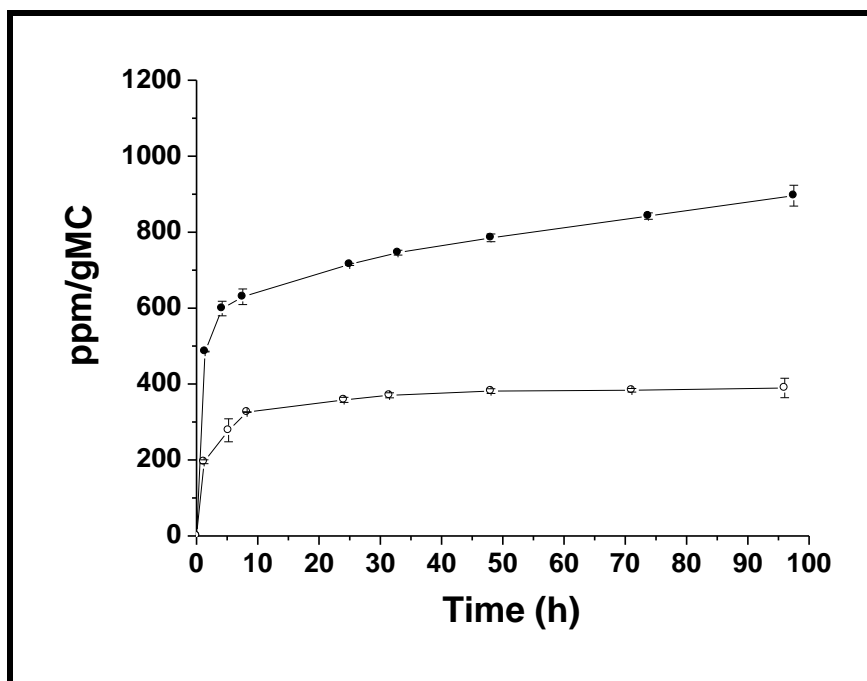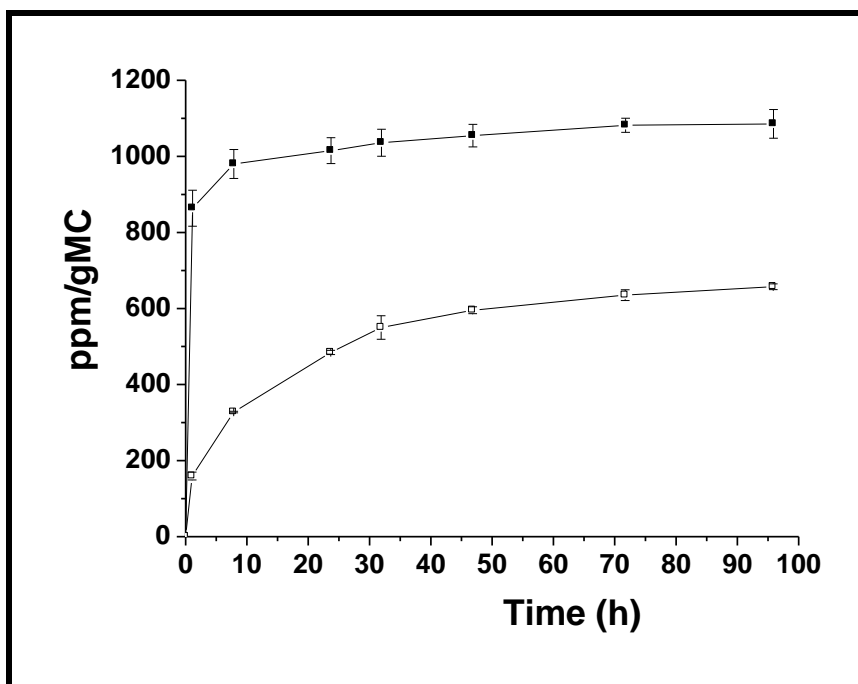
Figure 8. Vanillin release from PSf/Vanillin microcapsules in hard water: (□) capsules without a vanillin solution treatment; (■) capsules after a vanillin solution treatment

Until here, it is known that the use of a vanillin-saturated solution allows to eliminate the DMF encapsulated and greatly increases the amount of vanillin in the capsule. However, it is possible that this extra vanillin could have been incorporated over the capsule surface. If it is the case, the perfume would not be protected and therefore it could be released immediately. To elucidate if vanillin crystals are located over the capsule surface after the vanillin treatment, SEM and XRD analysis were performed.

Figure 9 shows the comparison of capsules surface between capsules that were treated with a vanillin saturated solution and capsules that were not treated. As can be observed in Figure 9, certain differences between the images were encountered, however it could not be determined if these differences are due to the presence of vanillin in the capsule surface.

Figure 10 shows the XRD analysis of PSf/Vanillin microcapsules after vanillin solution treatment and PSf microcapsules prepared without vanillin. As can be seen in Figure 10, both microcapsules presented similar spectra. However the results show that both capsules have an amorphous material. In a previous investigation it was reported that vanillin is a very crystalline material and it most intense XRD signal appears at 13º of 2ɵ.[43] If PSf/Vanillin microcapsules present vanillin crystals over their surface, it was expected to find a sharp and intense peak of vanillin at 13º of 2ɵ. However it was not the case. Thus, PSf/Vanillin

microcapsules have an amorphous material that means that not crystals of vanillin were detected by XRD. This indicates that vanillin enters into the capsule pores after the vanillin solution treatment. Therefore, the treatment of PSf/Vanillin microcapsules with an aqueous solution saturated with vanillin not only removes DMF from PSf/Vanillin microcapsules but also greatly improves the amount of vanillin inside the capsules (the so called encapsulation capacity). Therefore, capsules could be stored in this medium before their final application.
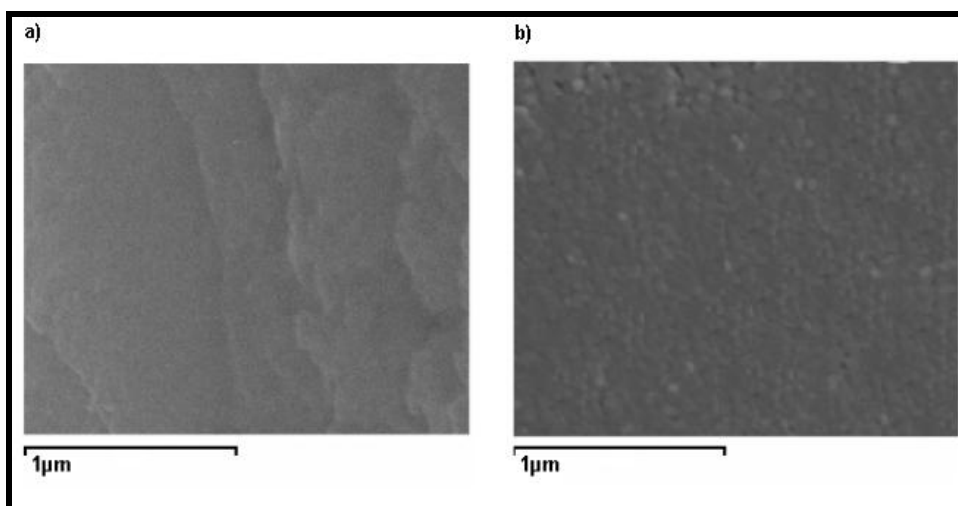

Figure 9. SEM micrograph of PSf/Vanillin microcapsules. a) PSf/vanillin microcapsules without a vanillin solution treatment. b) PSf/Vanillin microcapsules treated with a solution saturated with vanillin
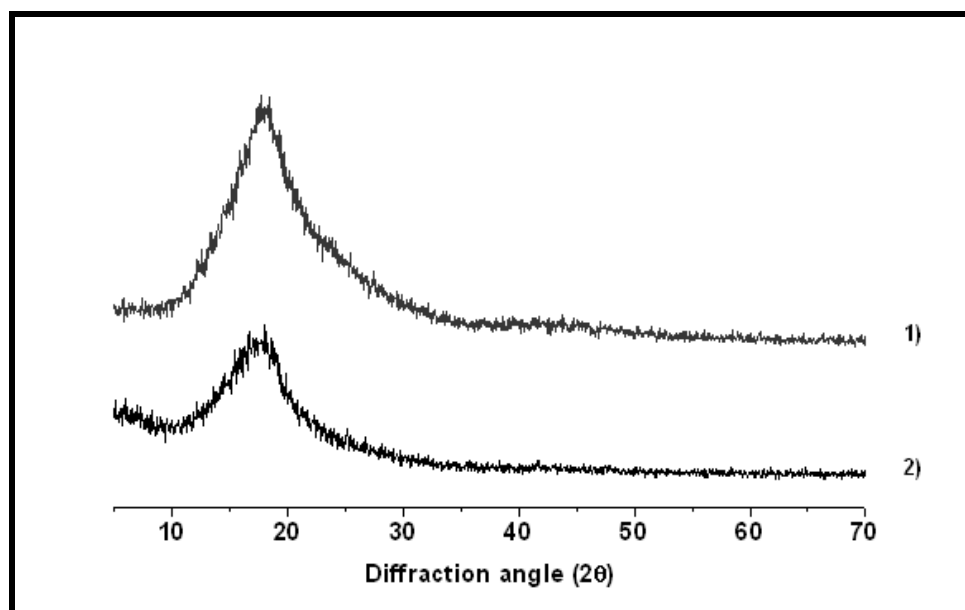
Figure 10. XRD analysis: 1) PSf/Vanillin microcapsules after a vanillin solution treatment. 2) PSf microcapsules prepared without vanillin

3.6 THERMOGRAVIMETRIC ANALYSIS

PSf/Vanillin microcapsules were investigated by thermogravimetric analysis with the purpose to determine their solid content and their perfume retention after the vanillin treatment. In this way two samples were analysed 1) PSf/Vanillin microcapsules treated with a vanillin-saturated solution and 2) PSf/Vanillin microcapsules that were not pre-treated. Figure 11 shows the results of both capsules.
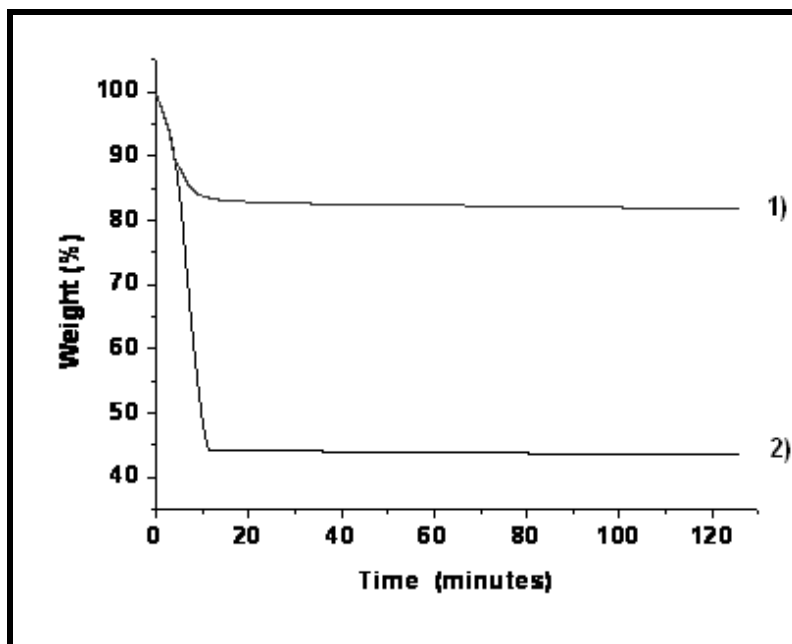
Figure 11. Thermogravimetric analysis. 1) PSf/Vanillin microcapsules without a vanillin solution treatment. 2) PSf/Vanillin microcapsules with a vanillin solution treatment

As can be seen in Figure 11, the results show that both kinds of capsules, pre-treated and not pre-treated, present two principal regions of weight loss. First, a faster one that took place after 10 minutes of analysis and, in which, the lost of weight rapidly increase. And a second region in which the lost of weight slowly increased achieving a plateau. However, it is also possible to observe other regions represented by small weight loss. The first weight loss region is probably dominated by the evaporation of water and by the release of vanillin trapped into the pores of the capsule surface. The second one could be attributed to the perfume deeply encapsulated, which release is more limited due to the fact that vanillin has to diffuse through the capsule material. While the other regions, represented by small lost of weight, can be associated to perfume located more deeply into the capsule. Probably, the perfume is strongly trapped into the capsule

and it seems that it has not been released completely. That could be the reason that the regions represented by the small weight loss were observed.

On the other hand, significant differences were encountered in the weight loss between both capsules. PSf/Vanillin microcapsules that were treated with a vanillin saturated solution lost around 55% of weight during the first 10 minutes. While PSf/Vanillin microcapsules that were not treated with a vanillin solution only lost nearly 25% of weight. This analysis corroborate that the extra-vanillin is located into the porosity of the capsule surface. That is why it is easily released under the thermogravimetric analysis conditions.

3.7 RELEASE MEDIUM RENEWAL

With the purpose to determine the influence of water nature in the maximum perfume release capacity of PSf microcapsules, treated with an aqueous solution saturated with vanillin, certain experiments, involving release medium renewal, were carried out. Table 1 collects the experimental conditions and Figure 12 shows the corresponding results.
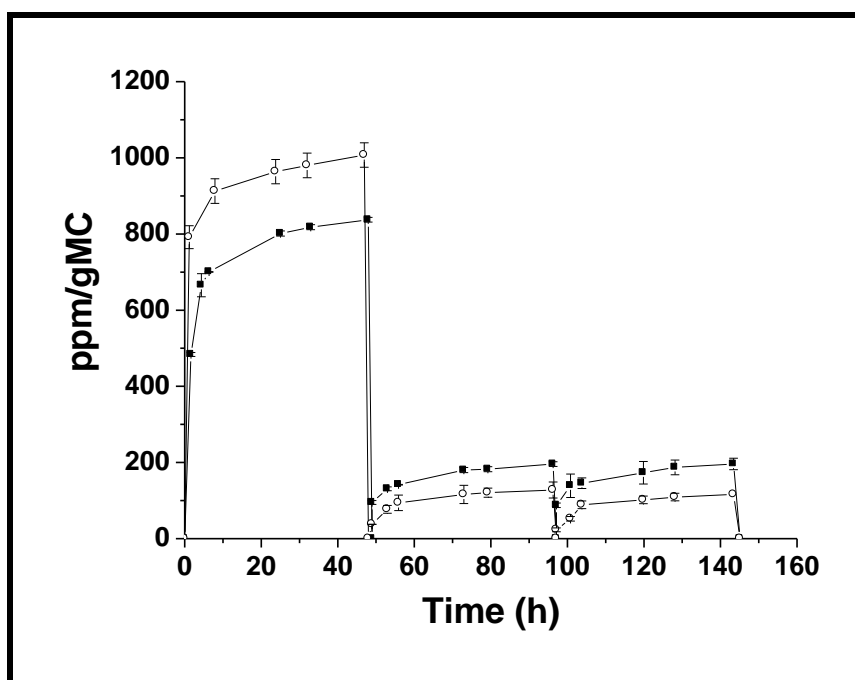
Figure 12. Vanillin release with release medium renewal from PSf microcapsules pre-treated with a vanillin saturated solution: (○) using hard water as a release medium and (■) using milliQ water as release medium

As can be observed in Figure 12, when milliQ water was used as release medium, around 60% of vanillin release took place during the first 48h. While in hard water, it was nearly the 80%. After renewing the release medium, the amount of vanillin

released in hard water was lower than in milliQ water. Probably the extra vanillin was already released during the first 48 h because it was added into the pores of the capsule surface and also because hard water facilitates the vanillin release. In the case of milliQ water, the extra vanillin was still released after the first release medium renewal.

However, in both cases the release of the perfume continued, for more than 144 h (6 days). PSf/Vanillin microcapsules present promising results for applications in which long release times are required.

3.8 PSf MACRO AND MICROCAPSULES COMPARISON

As mentioned before, PSf macrocapsules had been already investigated and they showed promising results in terms of encapsulation capacity, release behavior and stability.[3, 9] However, their size is not suitable for final applications in textile detergents and fabric softeners. This is the reason why PSf microcapsules were developed and investigated in this work.

In order to prove whether PSf macrocapsules performance may be extrapolated to microcapsules, results obtained with both kinds of capsules have been compared. Table 2 shows corresponding parameters of both micro and macrocapsules.

PSf microcapsules and macrocapsules present similar characteristics, such as; the encapsulation capacity, perfume release time and percent of DMF removed after vanillin treatment. However, in the case of PSf macrocapsules nearly 30% of vanillin was lost during vanillin treatment.

Table 2. Comparison between PSf macro and microcapsules

	PSf macrocapsules	PSf microcapsules
Encapsulation capacity of vanillin (%)	More than 50	45
Perfume release time without vanillin treatment (h)	96	96
DMF removed after vanillin treatment (%)	99	100
Vanillin added after vanillin treatment (%)	- 30	Around 100
Perfume release time after vanillin treatment (h)	120	144

It is due to the fact that vanillin is highly soluble in DMF. Therefore, a part of vanillin was solubilized into DMF and vanillin was released together with the DMF to the

bulk solution medium.[3] This effect was completely contrary in PSf microcapsules, in which the amount of vanillin greatly increased after the treatment.

To understand this fact is necessary to analyze the morphological characteristics of micro and macrocapsules. PSf macrocapsules presented diameters around 3 mm, shell thickness close to 1 mm and a free volume inside of about 1 mm.[3] Whereas PSf microcapsules show diameters of 17.8 $\pm$ 8.5 µm, shells thickness of 5.34 $\pm$ 1.82 µm and free volumes of 10.51 $\pm$ 5.5 µm. Comparing these values, it may be observed that macrocapsules have a relatively higher internal volume and higher release area than microcapsules. This will have an influence on the amount of DMF encapsulated and therefore in the possibility of vanillin dissolution on DMF. On the other hand, both 1 g of macrocapsules and 1 g of microcapsules have equivalent composition in terms of DMF and vanillin encapsulated. However, the amount of DMF in one macrocapsule is far different from the amount of DMF encountered in one microcapsule. Thus, in the case of the microcapsules the vanillin loss during the vanillin solution treatment was not observed because the amount of DMF present in one microcapsule was not enough to dissolve the vanillin encapsulated. In addition as the microcapsules shell thickness is only of few micrometers, DMF is easily lost during the drying step. As a consequence, the amount of DMF released from microcapsules was lower than the amount of DMF released from macrocapsules. Therefore, PSf microcapsules not only present the same advantages than PSf macrocapsules, but also they can incorporate new vanillin after capsule formation if they are conveniently treated.

3.9 ENCAPSULATION CAPACITY

PSf/Vanillin capsules prepared from a polymeric solution containing 10% (w/w) of vanillin, 15% (w/w) of PSf and 75% (w/w) of DMF have been studied. They presented good encapsulation capacity and high physical stability.[3, 42] One of the principal objectives of the present investigation is the production of capsules with high perfume encapsulation capacity. It was observed that treating the capsules with a vanillin solution successfully increases the encapsulation capacity of PSf/Vanillin microcapsules. However, this vanillin is added after the capsule formation. Thus, in order to estimate the maximum perfume encapsulation capacity of PSf/Vanillin microcapsules during the capsule formation, the encapsulation capacity of several capsules prepared with different vanillin concentration need to be analysed. Table 3 shows the results obtained.

As can been seen in Table 3, the maximum vanillin encapsulation capacity of PSf/Vanillin microcapsules prepared by the standard composition (with 10% (w/w) of vanillin) was found to be around 45% of the total perfume added. On the other hand, when vanillin concentration was increased in the polymeric solution, the

amount of vanillin encapsulated had a notorious increment. It seems that the extra vanillin added into the polymeric solution is not lost in the coagulation bath. Vanillin tends to be encapsulated by the polymeric matrix. The results show that PSf/Vanillin microcapsules can incorporate more vanillin during the capsule formation. This corroborates the results obtained with the vanillin treatment.

Table 3. Material balance of vanillin

% of vanillin in the polymeric solution	g of vanillin in the polymeric solution	g of vanillin in the coagulation bath	g of vanillin in PSf/Vanillin microcapsules	Encapsulation capacity (%)
10	2.05	1.14	0.91	44.4
15	2.76	1.07	1.69	61.2
20	3.62	1.39	2.23	61.6
25	4.55	1.74	2.81	61.8
30	5.28	2.03	3.25	61.6
35	6.28	1.91	4.37	69.6

However, the use of PSf/Vanillin microcapsules prepared by the standard composition is recommended for two reasons: (1) in a previous investigation it was demonstrated that the incorporation of vanillin into the polymeric solution decreases the elongation property of the PSf material as vanillin favours the formation of larger pores.[42] Thus the addition of vanillin during the capsule formation could affect the capsule material. (2) In this study it was found that encapsulation capacity of PSf/Vanillin microcapsules increased almost in a 100% with a vanillin treatment. Thus, capsules prepared by the standard procedure can have a similar encapsulation capacity than those capsules prepared with 35% (w/w) of vanillin and they can preserve their good physical properties and stability.

4. CONCLUSIONS

PSf/Vanillin microcapsules were prepared successfully by phase inversion precipitation technique using an airbrush device developed specially for this investigation. The maximum amount of vanillin encapsulated has been estimated to be nearly 45% from the total perfume added to the polymeric solution. A good way to avoid the presence of DMF in the capsules was tested. It consists in storing the capsules in a saturated vanillin aqueous solution for 4 days. With this procedure, not only DMF was removed from inside of the microcapsules but also the amount of vanillin encapsulated increased around 100%. Concerning the effect of the water nature in the perfume release behavior, it was found that vanillin was more rapidly released in hard water than in pure Milli-Q water. However, in both release media, the total release time encountered after vanillin treatment has been of at least 144 h (6 days).

5. ACKNOWLEDGEMENTS

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CHAPTER 5

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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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 detergents 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 due to 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 already investigated.[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 to 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 these 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 MICROCAPSULES 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 MICROCAPSULES 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.

2.3 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 of PSf, 10 % w/w of vanillin and 75% of DMF or (b) 15% w/w of PSf and 85% of 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 x 20 cm^2) using a casting

knife, providing 50 μm thick films, which was pushed by an applicator (K-Paint applicator, United kingdom) at a constant velocity of 3 m/min. Afterwards, the glass with the liquid polymeric film on top was immersed into a coagulation bath of MilliQ 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 x 20 cm^2.

2.4 SAMPLES 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 vacuum at 50 °C during 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, afterwards 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.

Table 1.Sample preparation conditions for each analysis

	Sample preparation	characterization techniques				
		^{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_2O	*				
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 ºC for 12h			*		*
13	PSf/Vanillin microcapsules were dried under vacuum at 50 ºC for 12h					*
14	PSf/Vanillin microcapsules were dried under vacuum at 50 ºC for 12h, were added in a release treatment with water during 96 h and were dried again under vacuum at 50 ºC for 12h.					*

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 ($\pm$ 0.1) K.

The average number of scans recorded for all the samples analyzed, was 128. The 90° pulse length was typically 10μs and the relaxation time (t1) was 6s. Chemical shifts ($δ$) were determined from two external references of residual protons in fully deuterated benzene ($δ$=7.157 ppm) with an aliquot of tetramethylsilane (TMS) ($δ$=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 ($\pm$ 0.1) K using a Bruker spectrometer. All chemical shifts were recovered from the external references: deuterated benzene (δ=128.39 ppm) with an aliquot of tetramethylsilane (TMS) (δ = 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 10μs with a relaxation time (t1) of 1 s 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 ($\pm$ 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, 1g 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, 1g 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.

2.9 ANALYTICAL DETERMINATION OF VANILLIN AND DMF

The concentration of DMF and vanillin in water medium samples was determined b*y* 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 μL. 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 Table 2 and 3.

Table 2 ^{1}H NMR shifts of Vanillin in different systems

System	Vanillin proton resonance (ppm)				
	$H_3CO(a)$	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 7.506 - 7.511	9.641
Vaniilin concentrated	3.801	6.899- 6.919	7.279 - 7.284	7.355 - 7.359 7.375 - 7.379	9.553
Vanillin less concentrated	3.818	6.912 - 6.932	7.302 - 7.306	7.372 - 7.376 7.392 - 7.396	9.566

Table 3 ^{1}H NMR shifts of DMF in different systems

System	DMF protons resonance (ppm)		
	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

As may be observed PSf/Vanillin microcapsules, suspended in a D_2O solution containing vanillin and DMF, show five kinds of protons corresponding to vanillin and another three corresponding to DMF. As can be seen in Table 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. 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$_2$O solution of vanillin and DMF, (2) a concentrated D$_2$O solution of vanillin and (3) a diluted D$_2$O solution of vanillin.
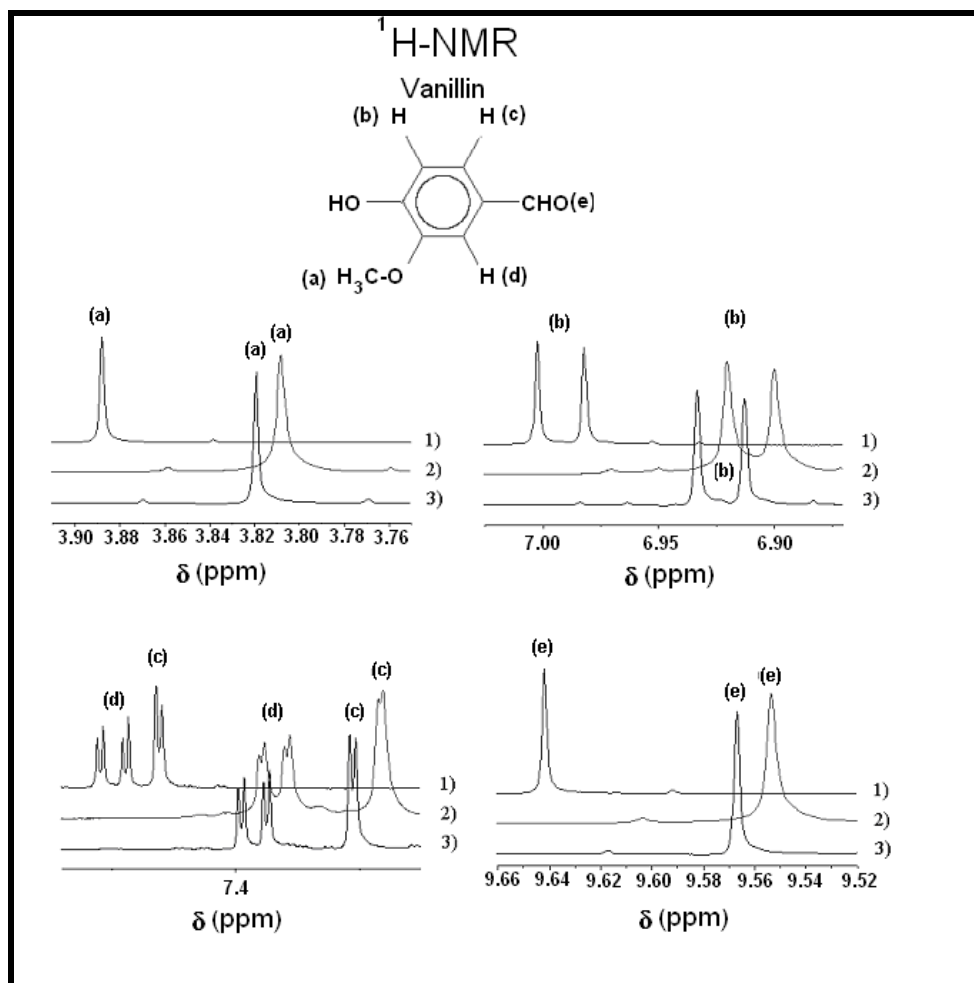

Figure 1. ^{1}H NMR spectra. Vanillin resonance. (1) PSf/vanillin microcapsules in a DMF/Vanillin/D$_2$O solution, (2) Concentrated Vanillin/D$_2$O solution and (3) diluted Vanillin/D$_2$O solution

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$_2$O, probably certain transient ionic interactions took place between the D$_2$O and the vanillin protons. In the case of the vanillin signals detected in PSf/Vanillin microcapsules sample, not only D$_2$O 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.
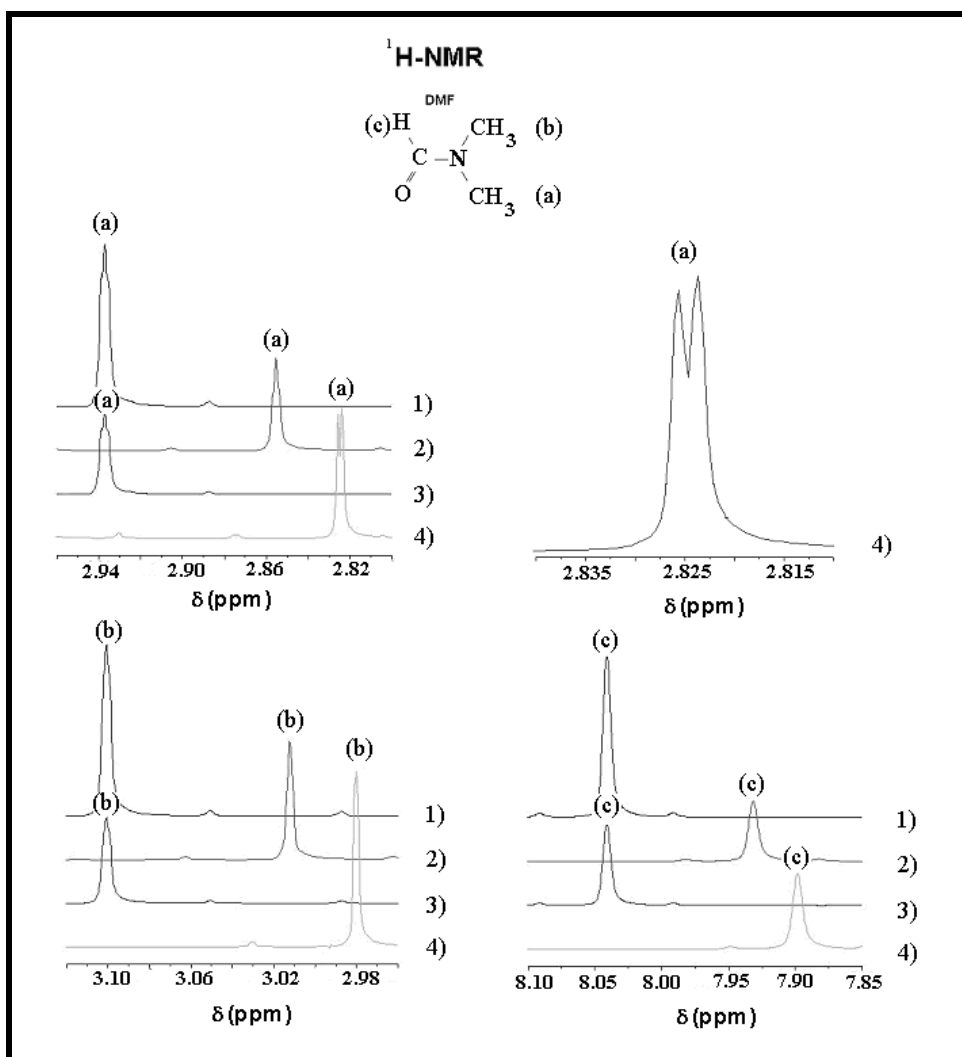

Figure 2. ^{1}H NMR spectra. DMF resonances. (1) Concentrated DMF/D_2O solution, (2) diluted DMF/D_2O solution, (3) PSf microcapsules in a DMF/D_2O solution, (4) PSf/vanillin microcapsules in a $DMF/Vanillin/D_2O$ solution

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/Vanillin 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 minutes) 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.
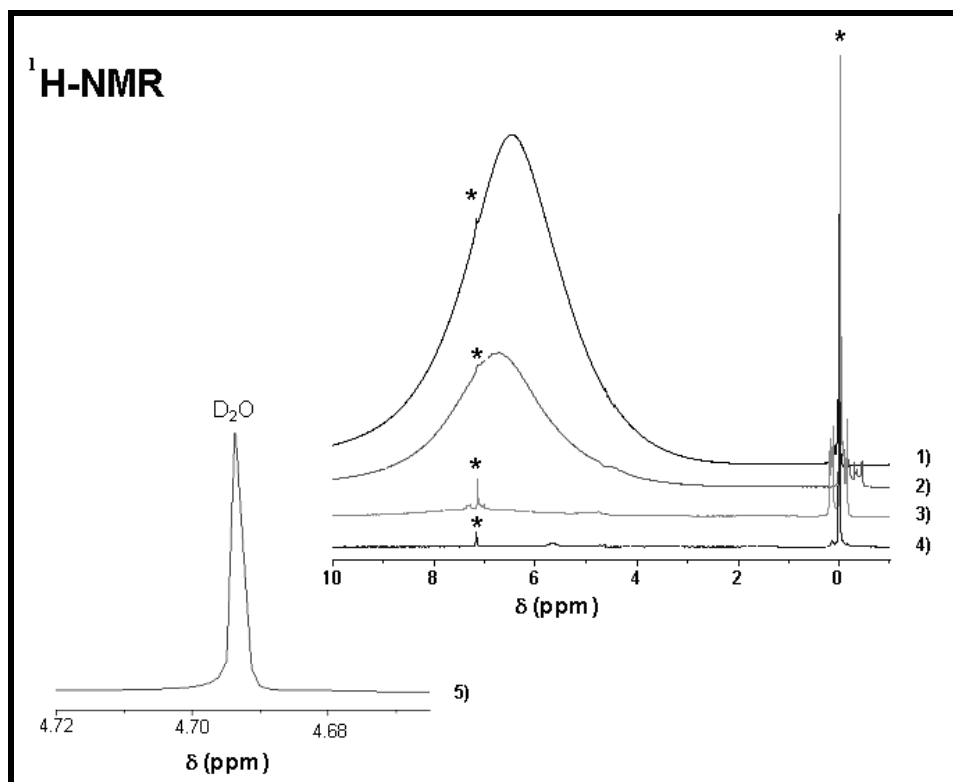
Figure 3. ^{1}H NMR spectra. (1) PSf/Vanillin microcapsules dried at room temperature spectrum. (2) PSf/Vanillin microcapsules dried at room temperature under vacuum during 5 min spectrum. (3) PSf/Vanillin microcapsules dried at room temperature under vacuum during 10 min spectrum. (4) PSf/Vanillin microcapsules dried at room temperature under vacuum during 15 min spectrum. 5) D$_2$O. * External references

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$_2$O 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 ºC 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 afterwards 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 ºC were compared with the liquid-state ^{13}C-NMR spectrum of DMF Figure 6 shows the results.

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 analysed 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 analyse the effect that the increment of the vanillin amount in the polymeric solution has on the encapsulation of DMF.
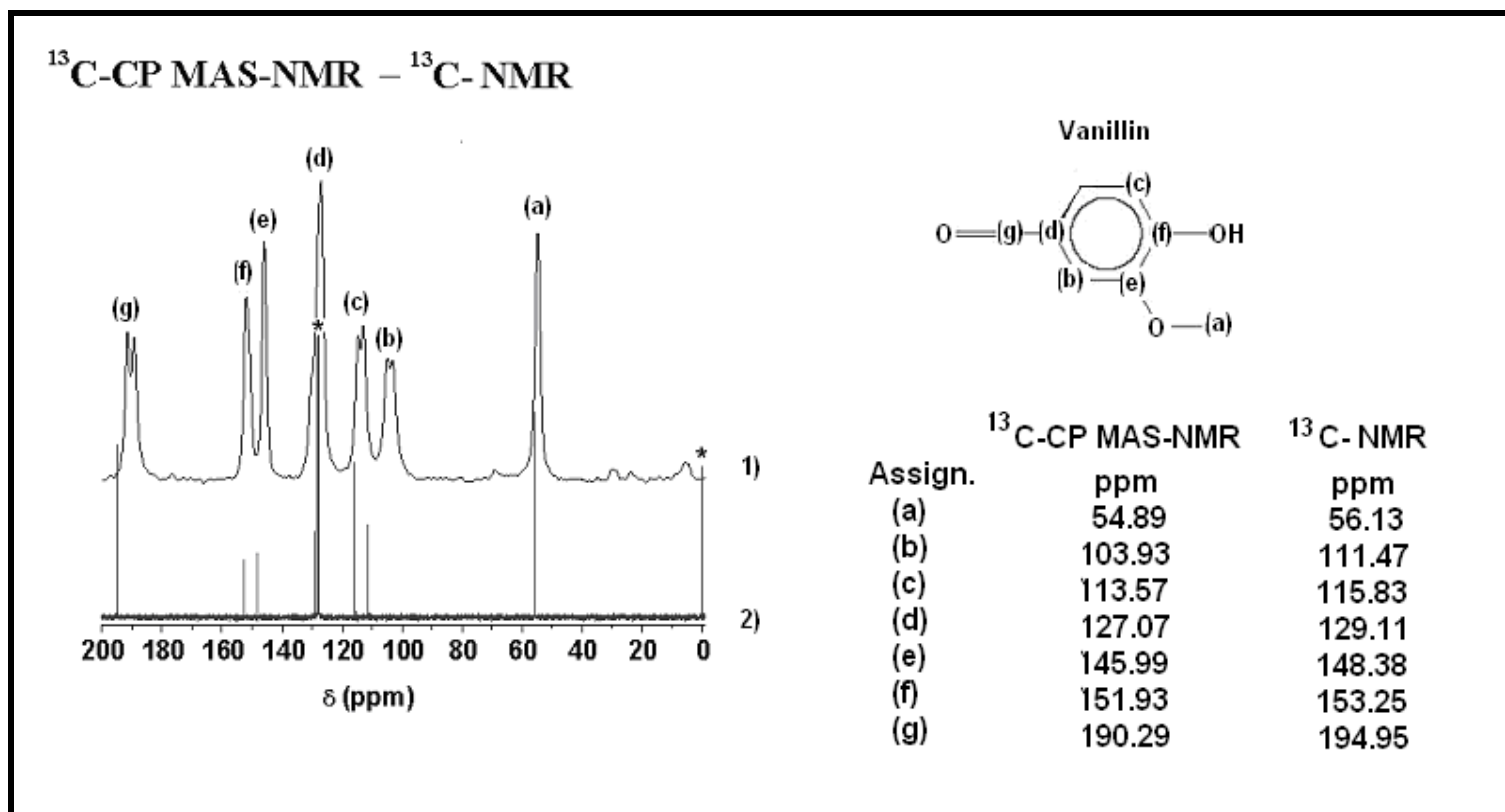
Figure 4. Solid-state ^{13}C-CP MAS-NMR and ^{13}C NMR spectra of vanillin. (1) ^{13}C-CP MAS-NMR spectrum of vanillin. (2) ^{13}C NMR spectrum of vanillin. * External references
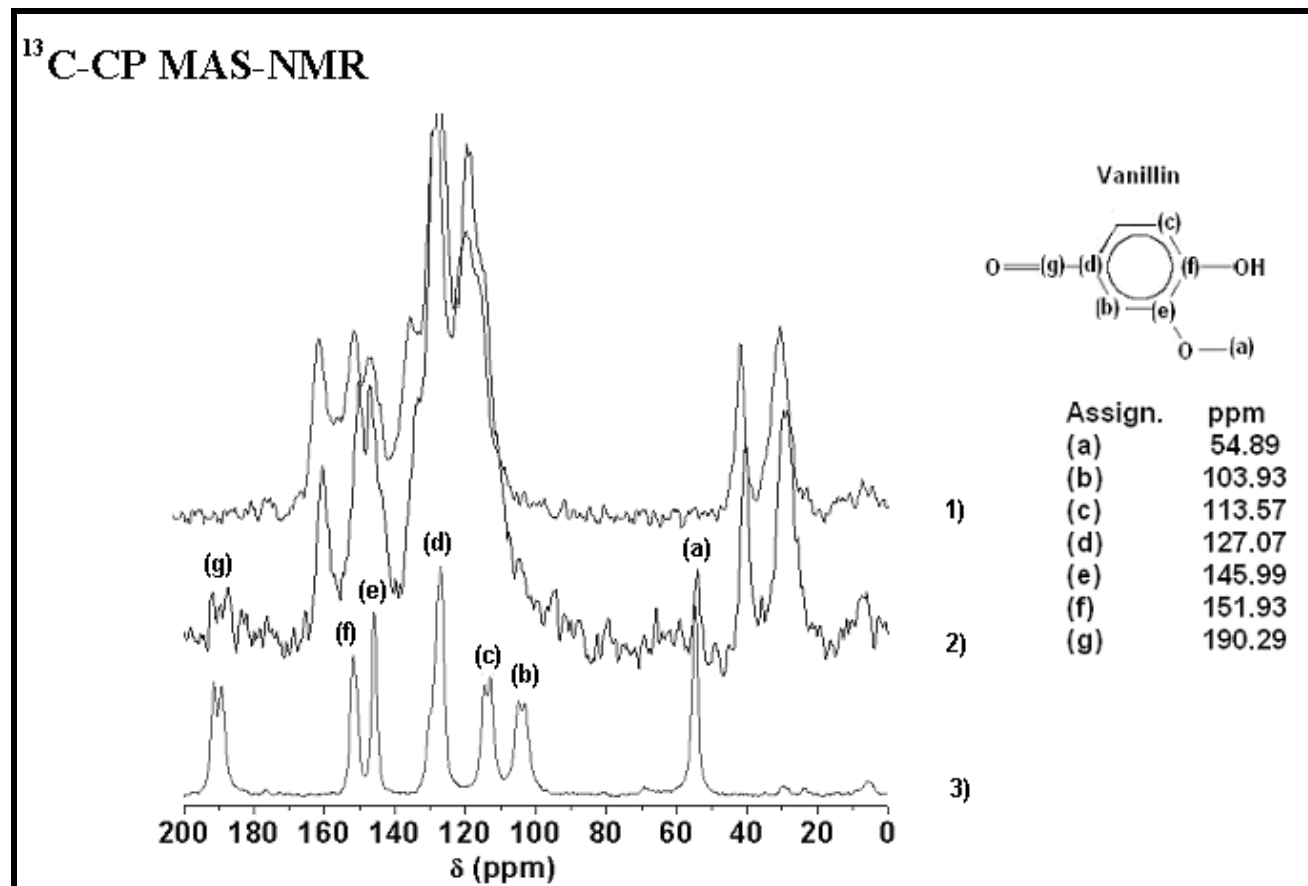
Figure 5. Solid-state ^{13}C-CP MAS-NMR spectra. (1) Dry PSf microcapsules spectrum. (2) PSf/vanillin microcapsules spectrum. (3) Vanillin spectrum
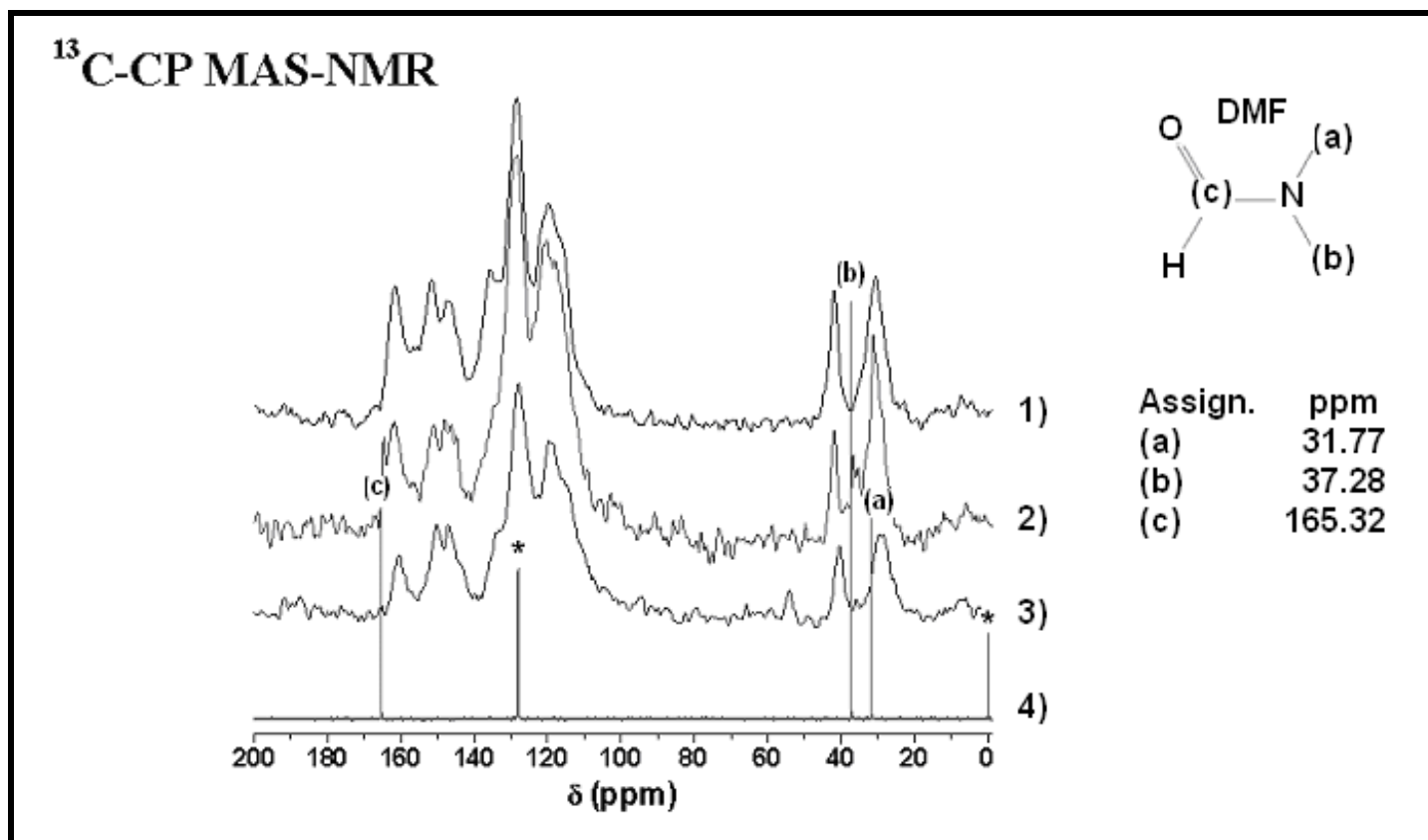
Figure 6. Solid-state ^{13}C-CP MAS-NMR spectra of (1) PSf microcapsules dried at 50 ºC under vacuum. (2) PSf microcapsules. (3) PSf/Vanillin microcapsules. (4) DMF/D$_2$O solution. * External references

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.

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 $\pm$ 0	697.5 $\pm$ 0
15	346.9 $\pm$ 3	517.4 $\pm$ 10
10	355.2 $\pm$ 3	451.3 $\pm$ 12
5	371.6 $\pm$ 4	272.1 $\pm$ 11
0	880.5 $\pm$ 3	0

3.3 MORPHOLOGICAL CHARACTERIZATION

Morphological characterization, of PSf microcapsules with and without vanillin, was carried out by SEM and AFM analysis.
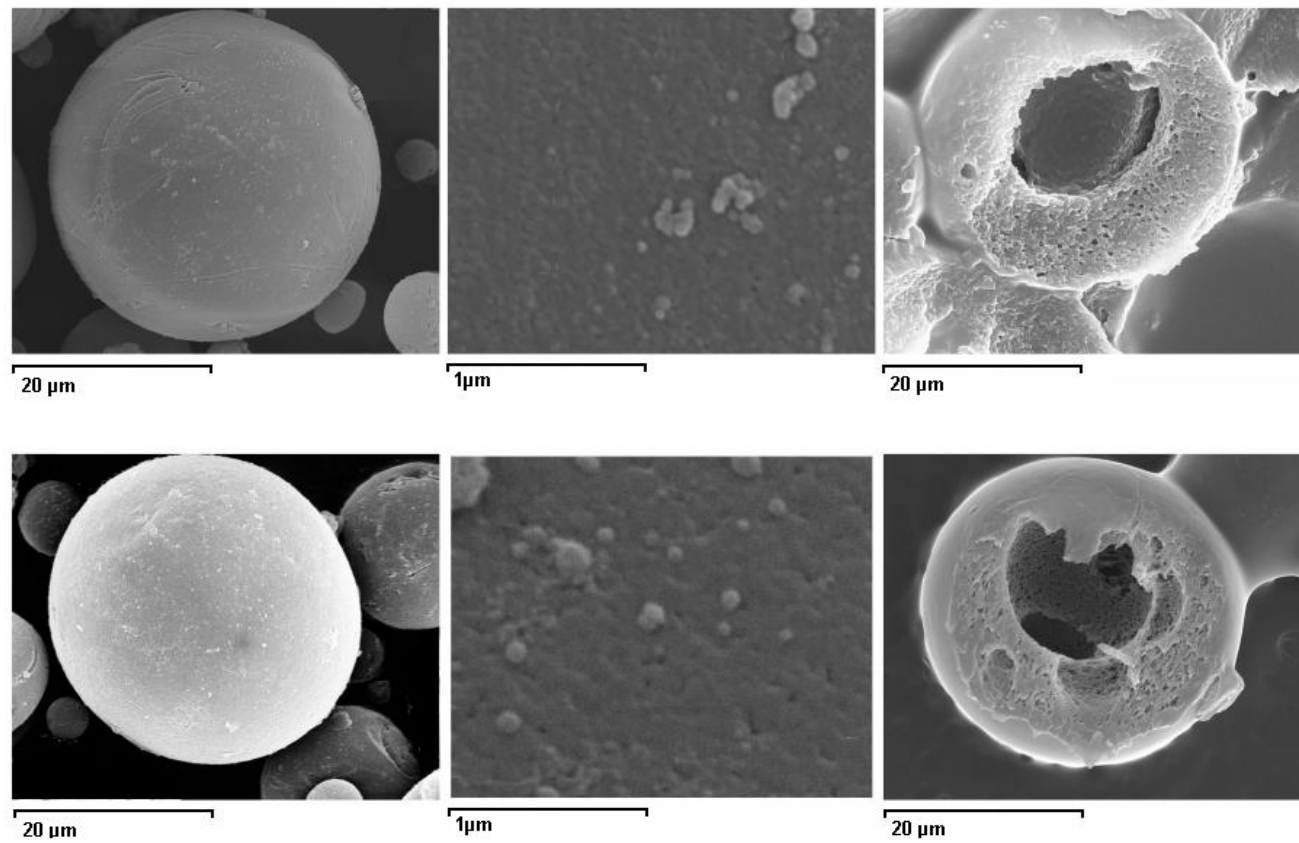
Figure 7. SEM micrographs (top, PSf/Vanillin microcapsules; bottom, PSf microcapsules)

Figure 7 shows SEM micrographs of PSf and PSf/Vanillin microcapsules. SEM micrographs show that PSf microcapsules present diameters around 30 µm 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.
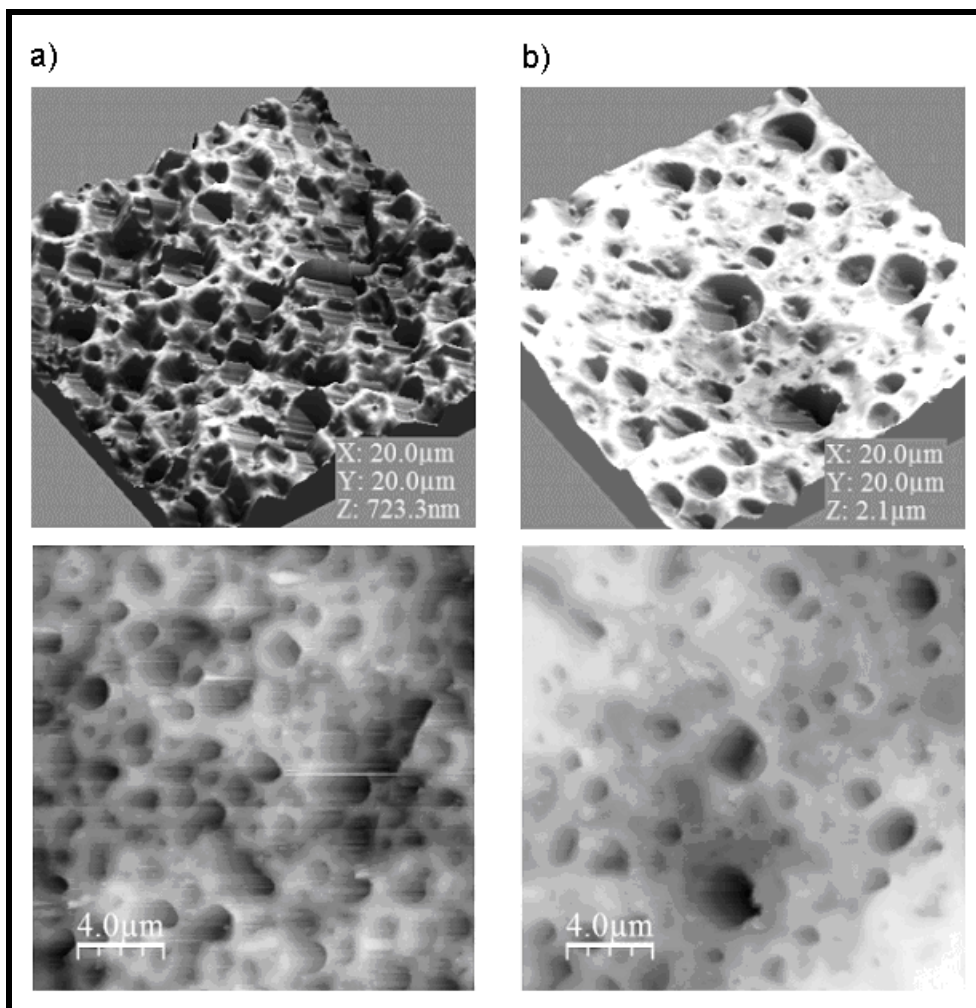

Figure 8. AFM micrographs. From left to right: (a) PSf films and (b) PSf/Vanillin films

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 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 leading 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 Figures 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 slit-like 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 meso-pores.

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

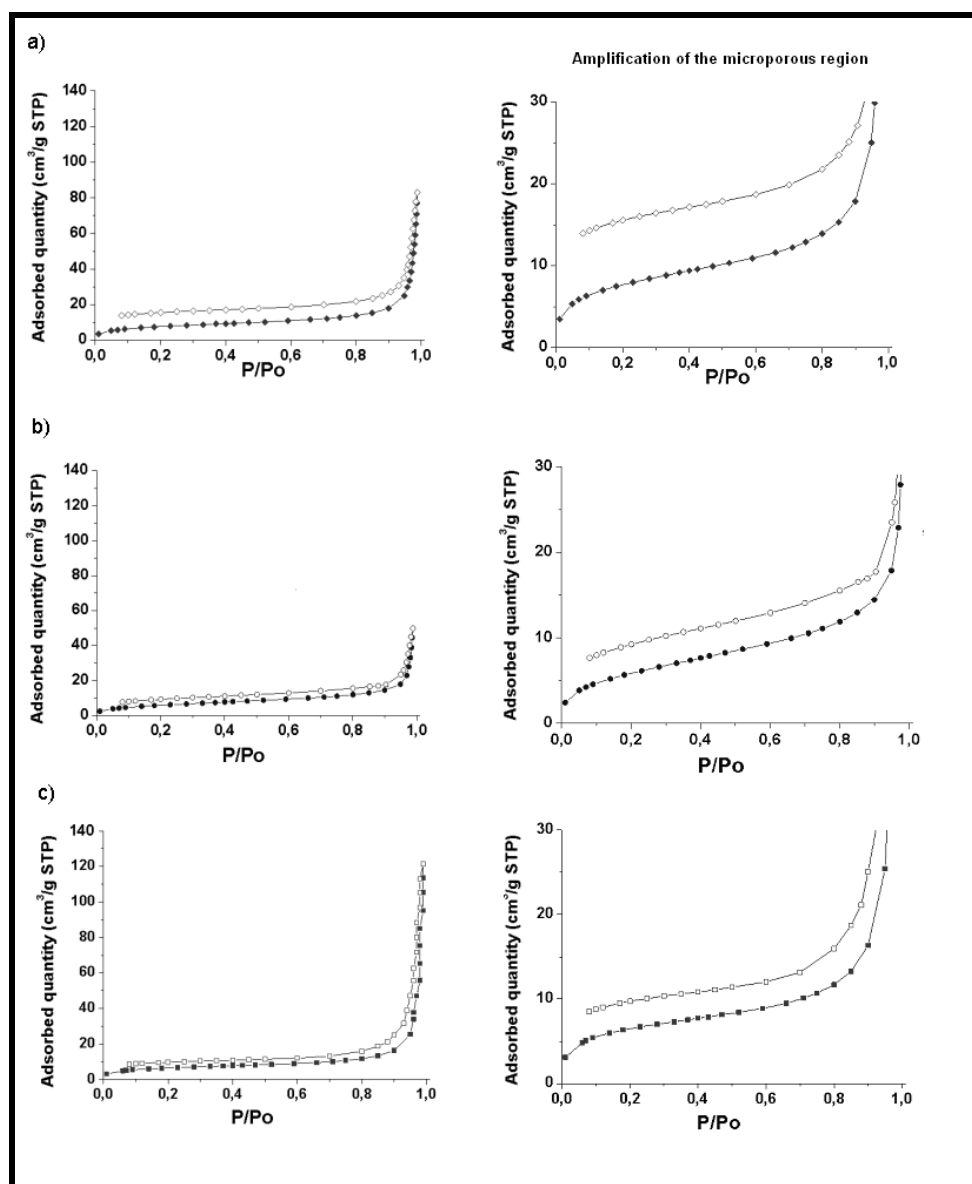Figure 9. Adsorption-desorption isotherms. (a) PSf microcapsules dried at 50°C under vacuum. (b) PSf/Vanillin microcapsules dried at 50°C under vacuum. (c) PSf/Vanillin microcapsules dried at 50°C under vacuum, afterwards immersed in water for a release treatment and finally, dried again at 50°C under vacuum. Right images: normal adsorption-desorption isotherms. Left images: amplification of the microporous region.
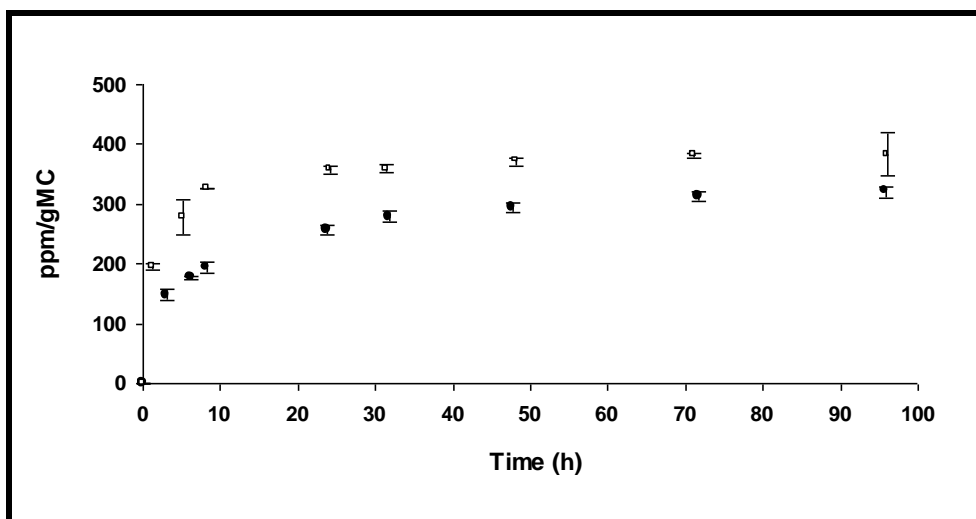
Figure 10. Vanillin release from PSf/Vanillin microcapsules. □, PSf/Vanillin microcapsules without treatment; ●, PSf/Vanillin microcapsules after drying treatment

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 hours 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. As can be seen in figure 9c, the microporous region barely changed in comparison with PSf/Vanillin microcapsules without release treatment. However, a greater amount 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.

4. 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 ºC 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 ensure perfume preservation and a long lasting fragrance release.

5. ACKNOWLEDGEMENTS

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CHAPTER 6

GENERAL CONCLUSIONS AND FURTHER WORK

GENERAL CONCLUSIONS

- Macro and microcapsules of PSf/Vanillin have been successfully obtained by phase inversion precipitation technique.

- The morphological characterization of PSf/Vanillin Macrocapsules and PSf/Vanillin microcapsules has been carried out by SEM analysis. PSf/Vanillin macrocapsules presented a monodisperse formation, in which a lentil shape has been observed. Cross-section micrographs showed the presence of a notorious volume inside as well as highly porous configuration. The mean macrocapsule diameter has been estimated to be 3.48 $\pm$ 0.53 mm, with a shell thickness size close to 1mm and a free volume inside of about 1 mm.   Whereas, PSf/Vanillin microcapsules showed a well-defined spherical shape, in which a polydisperse formation has been observed. Besides, cross-section micrographs also showed a remarkable empty space in the middle of the capsule as well as a vastly porous configuration. The mean particle diameter of microcapsules has been found to be 17.8 $\pm$ 8.5μ, with shells thickness of 5.34 $\pm$ 1.82μ and a free volume of 10.51 $\pm$ 5.5μ. Both PSf/Vanillin macro and microcapsules belong to the poly-core type of encapsulates.

- Regarding the encapsulation capacity and release behavior it was observed that PSf/Vanillin macrocapsules achieved to encapsulate more than 50% of the total vanillin added to the polymeric solution, however during the elimination of DMF, 30% of vanillin encapsulated was lost; nevertheless they release perfume in water for 120 h. On the other hand, PSf/Vanillin microcapsules presented a vanillin encapsulation capacity of 45% from the total perfume added to the polymeric solution but after the treatment to eliminate DMF, the amount of vanillin greatly increased in almost 100%. The perfume release time encountered in PSf/Vanillin microcapsules has been more than 144 h.

- Physical analyses demonstrate that vanillin affects the material structure of PSf. AFM micrographs and N$_2$ isotherms showed that vanillin is trapped in the capsule porosity and when it is released, it deformed the pores making them larger. However, tensile and protrusion studies demonstrated that this deformation only affected the maximum strain percentage capacity of the material, remaining constant the rest of the mechanical properties of the material. Moreover, the pre-treatment of gas adsorption studies demonstrated that vanillin is strongly trapped in all the capsule porosity due to the fact that even heating the capsules at 50 °C under vacuum for

12 h the perfume was not released completely. TGA analysis showed similar results in which three steps of release have been identified: (1) one corresponding to water and perfume from the capsule surface; (2) one due to the perfume from the channels of the capsule and (3) another one that corresponds to the perfume located in the middle of the capsule. Therefore, PSf/Vanillin capsules offer a suitable encapsulation system that ensures a long lasting perfume release.

- Chemical analysis elucidated the aggregate state that vanillin has inside of both PSf macro and microcapsules. ATR-IR identified vanillin, water and DMF in the liquid obtained by pressing PSf/Vanillin macrocapsules. While solid NMR studies showed that vanillin is in solid state in PSf/Vanillin microcapsules. H^1 NMR has not identified signals of vanillin or DMF in PSf/Vanillin microcapsules. The results may explain why vanillin was lost during the elimination of DMF in PSf macrocapsules. As vanillin was dissolved in DMF, it was released together with the DMF in the vanillin solution treatment. On the other hand, the incorporation of new vanillin was observed in PSf/Vanillin microcapsules. It seems that vanillin in solution, from the solution treatment, entered into the microcapsule porosity and because of the small pore size, it was trapped inside leading to the incorporation of new vanillin. XRD results showed that the new vanillin incorporated in PSf/Vanillin microcapsules was not located over the capsule surface; thus this vanillin may be considered for the encapsulation capacity of PSf/Vanillin microcapsules.

- In conclusion, this investigation offers an excellent vanillin encapsulated system that posses a high encapsulation capacity, a long lasting fragrance release, good material stability, and ensures a perfume protection. Due to all this qualities, PSf/Vanillin microcapsules have the potential to be used not only in detergents and softeners but also in other textile products. Moreover, due to the antibacterial and antimycotic properties of vanillin, these capsules may be used in fabrics that search for an antibacterial and antimycotic protection, by instant in sheets, pillowcases, mattress protectors or towels.

FURTHER WORK

Currently, PSf/Vanillin capsules are under investigation for their application in cotton fabrics, due to the fact that they have been shown promising results related to encapsulation capacity, material stability, long lasting fragrances released and fragrance protection, and because of the antibacterial and antimycotic properties of vanillin.

ANNEX A

LIST OF PUBLICATIONS AND COMMUNICATIONS

LIST OF PUBLICATIONS AND COMMUNICATIONS

ARTICLES

<u>Directly related with the thesis:</u>

Authors: Peña, B.; Casals, M.; Torras, C.; Gumí, T.; Garcia-Valls, R.

Title: Vanillin release from polysulfone macrocapsules

Journal: Industrial & Engineering chemistry research

Volume: 48   **Pages:** 1562-1565.   **Year:** 2009

Impact index: 2.072

ISI category: Engineering, Chemical

AIF (AIF): 1.888

Position in the category: 29

Authors: Peña, B.; Ferré, L.; Garcia-Valls, R.; Ferrando, F.; Gumi T.

Title: Study of the mechanical properties of PSf/Vanillin films

Influence of temperature treatments.

Journal: Industrial & Engineering chemistry research

Volume: 50   **Pages:** 2073-2079   **Year:** 2011

Impact index: 2.072

ISI category: Engineering, Chemical

AIF (AIF): 1.888

Position in the category: 29

Authors: Peña, B.; de Ménorval L. C.; Garcia-Valls, R.; Gumi, T.

Title: 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

Journal: ACS Applied Materials & Interfaces

Volume: 3   **Pages:** 4420–4430   **Year:** 2011

Impact index: 2.925

ISI category: Materials science, Multidisciplinary

AIF (AIF): 2.795

Position in the category: 38

Authors: Peña, B.; Panisello, C.; Aresté, G.; Garcia-Valls, R.; Gumi, T.

Title: Preparation and characterization of polysulfone microcapsules for perfume release

Journal: Chemical Engineering Journal

Volume: 179 **Pages:** 394– 403 **Year:** 2012

Impact index: 3.074

ISI category: Engineering, Chemical

AIF (AIF): 1.888

Position in the category: 10

Derived from other research lines different of the thesis:

Authors: Fuentes, M.; Peña, B.; Contreras, C.; Montero, A.; Chianelli, R.; Alvarado, M.; Olivas, R.; Rodríguez, L.; Camacho, H.; Montero-Cabrera, L.

Title: Quantum Mechanical Model for Maya Blue

Journal: International Journal of Quantum Chemistry

Volume:108 **Pages:**1664-1673 **Year:** 2008

Impact index: 1.302

ISI category: Mathematics, Interdisciplinary Applications

AIF (AIF): 1.348

Position in the category: 29

CONGRESS CONTRIBUTIONS

Authors: Peña, B.; Torras, C.; Ballinas, M.; Fuentes, M.; Gumí, T.; García–Valls, R.

Title: Preparation and characterization of polymeric macrocapsules containing perfume

Congress: Lignocarb meeting

Format (poster or oral): Poster

Dates: December 2007 **Place:** Nancy France

Authors: Gumí, T.; Peña, B.; Casals, M.; Torras, C.; Garcia-Valls, R.

Title: Vanillin release from polysulfone capsules

Congress: Engineering with Membranes

Format (poster or oral): Poster

Dates: May 2008 **Place:** Algarve, Portugal

Authors: Peña, B.; Garcia-Valls, R.; Gumí, T.

Title: Perfume release from Polysulfone Macrocapsules

Congress: Network young membrains (NYM)

Format (poster or oral): Oral

Dates: September 2009 **Place:** Mèze France

Authors: Peña, B.; Ferré, L.; Garcia-Valls, R.; Ferrando, F.; Gumí, T.

Title: Temperature influence on the mechanical properties of polysulfone films

Congress: Euromembrane meeting

Format (poster or oral): Poster

Dates: September 2009 **Place:** Montpellier France

Authors: Peña, B.; Aresté, G.; Garcia-Valls, R.; Gumí, T.

Title: Perfume release from Polysulfone microcapsules

Congress: PERMEA meeting

Format (poster or oral): Poster

Dates: September 2010 **Place:** Tatranské Matliare Slovakia

Authors: Peña, B.; Gumí, T.; Garcia-Valls, R.

Title: Perfume release from Polysulfone capsules

Congress: XIX International Conference on Bioencapsulation

Format (poster or oral): Poster

Dates: October 2011 **Place:** Amboise France