

Microencapsulation of Perfumes

For

Application in Textile Industry



Microencapsulation of Perfumes for Application in Textile Industry

A Dissertation Presented to the

UNIVERSIDADE DO PORTO

For the degree of Doctor of Philosophy in Chemical Engineering

by

Carla Sofia Nogueira Rodrigues Teixeira

Supervisor: Doutora Vera Lúcia Gomes Mata

Co-supervisor: Doutora Maria Filomena Filipe Barreiro

Laboratory of Separation and Reaction Engineering

Associate Laboratory -LSRE/LCM

Department of Chemical Engineering

Faculty of Engineering

University of Porto

2010

Acknowledgements

This thesis has been a long journey and I have quite a number of people to thank for it.

I would like to express a deep sense of gratitude towards my supervisor Dr. Vera Mata, for given me this opportunity, for valuable ideas and inspiration.

I wish to express my warmest thanks to my co-supervisor Dr. Filomena Barreiro. You have helped immensely in clarifying many points. Thanks for all the support.

I wish to sincerely to thank LSRE for the support and excellent conditions at the Laboratory. I also want to thank all Professors for the sympathy and help during this journey, particularly to Professor Madalena Dias who trusted me during my other responsibilities in the LSRE besides the thesis and for all the effort during the difficult moments and disappointments, to Professor Mário Rui Costa for scientific discussions and to Professor José Miguel Loureiro for the encouragement and friendship.

I also would like to acknowledge the collaboration of the institutions involved in Scentfashion project: CITEVE, especially to Eng. José Morgado for all the patience and valuable discussions; A Penteadora, S.A., in the person of Eng. Nuno Monteiro for sharing his knowledge in textile industry; LSRE, Paula Gomes and Isabel Fernandes (IPB) for all the support on the project. To Isabel Martins I have special thanks! Thank you for all the support, for all the scientific discussions, advices, encouragement and friendship. Your size does not correspond to the great friend you are 😊

I am grateful to CEMUP, IPN and UTAD for the assistance on Scanning Electron Microscopy analysis. Thanks to Horquim, Focor and Bayer for providing commercial microcapsules samples.

I am very grateful to several other colleagues that besides not working directly with me had also contributed with their help and friendship and made my life much easier.

To Nuno Lourenço and Alexandre, for many words I write they will not be enough to thank for all your technical support, patience and encouragement (I forgot the cross-problem Nuno!!). I would like to express my gratitude to Miguel Granato

who supported me through many valuable discussions, sharing with me his long experience in textile industry and for all the help with some informatics issues!

I am very thankful to my LSRE colleagues Ana Mafalda, Eduzinho, Fatinha, Filipe Lopes, Israel, João Santos, menino Miguel (pyramidal classification!!), Oscar, Paula Pinto, Pedro Sá Gomes and Silvia, that I bothered repeatedly and was rewarded only by their kindness and generosity. Thank you to all!!! I am also grateful to my DEQmates, Daniela, Joana, Marta Campo (I will never forget that you were there!), Sofia, Vânia and Zequinha for all the effort, advices, encouragement and friendship.

I am thankful to Anabela Dias, Ana Paula Filipe, Ana Queiroz, Cristina Matos, Meriem Lamghari, and Virginia Fonseca, for their encouragement, advices, patience, and above all for being always my friends.

Ana, Goreti, Susaninha and Poeta friends thanks for being exceptional friends along all these years. I would like to express my sincere gratitude to my friend Teresa, who really supported me and for being a true friend. The best one!

I would like to especially thank my parents, M^a Cândida and Alírio, to whom I owe what I am, for their love and support. I would like to express my sincere gratitude to my sister Isabel and brother Vasco (expert in Endnote ☺), to my parents-in-law, to my sisters-in-law and brothers-in-law and to all of my nieces, Mané, Dadinha, Catarina, Benedita, and Constança, and nephews, Francisco, Afonso and Bruno, for their support and friendship. And to Teeo, for being a faithful dog ☺

This thesis is dedicated to my husband, Hugo, for his constant support of me throughout my graduate career. Congratulations to you! You had resisted to my bachelor, master and now, at the end of my doctoral, you're still here by my side!! It was not easy, I know!☺ Thank you for your patience and understanding, for supporting my choices and for always being there for me when I needed you most. I couldn't have made this far without you by my side. And I can love you for the rest of my life!!

To Hugo and my parents

Abstract

The objective of this thesis, developed in the framework of the ADI Project Scentfashion[®], is the production of polyurethane-urea (PUU) microcapsules containing perfumes to be applied in the textile industry for the manufacture of perfumed suits for men.

Commercial microcapsules with different fragrances were first characterized in terms of Particle Size Distribution and morphology using a Particle Size Analyser, Optical Microscopy, and Scanning Electron Microscopy (SEM). It was observed that they have a spherical shape with size between 2 and 6 μm . Its chemical composition was checked/confirmed by Fourier Transform Infrared Spectroscopy (FTIR) as based on melamine copolymers including melamine-formaldehyde ones.

The effectiveness of the textiles impregnation with commercial microcapsules was tested using different impregnation conditions (microcapsules concentration and type of binder) being the best results obtained with a polyurethane-based binder. The defined experimental conditions were based on industrial requirements to simulate day-to-day wear: solidness of the perfume after 5 dry cleaning washes and 9000 abrasion cycles. These tests were done at a laboratory scale using a mini-foulard. The impregnated textiles were evaluated by SEM and by Gas chromatography GC/FID/Headspace and the results showed that when using an acrylate binder, the loss of odor resulting from dry cleaning washing is around 65% against 30% when using a polyurethane binder.

Interfacial polymerization was used to produce PUU microcapsules with limonene oil and perfume as active agents for industrial application on textile substrates.

Although PUU are very flexible polymers in terms of synthesis possibilities, these systems must be designed and optimized taking into consideration the particularities of the active agent to be encapsulated. In this work a general productive process was followed: (1) formation of an oil-in-water (o/w) emulsion;

(2) PUU formation at the interface oil-water; (3) washing to remove the remaining excess of reactants and (4) separation and storage of microcapsules.

Using FTIR it was possible to confirm the complete conversion of isocyanate groups. The produced lemon microcapsules presented spherical morphology and a bimodal particle size distribution in volume, showing a mean particle size of 10 μm . For the final microcapsules solution, the solid content was about 41% and pH of 7.18. The wall thickness of these microcapsules was estimated by SEM as 1 μm and no agglomerates were formed. SEM micrographs have also shown the good adhesion between microcapsules and textile fibers. Through GC-headspace analysis, the presence of limonene on textile substrate was quantified. During dry cleaning, the loss of limonene is of 24% in the first cycle and up to 97% after five cycles. For the abrasion tests, the loss of limonene is of 40% for 3000 cycles and up to 60% for 9000 cycles.

The same procedure was used to produce PUU microcapsules with the developed men's perfume. The encapsulation efficiency accounts for 55% of the loaded perfume in the encapsulation process. In terms of characterization (shape, size and solid content) the obtained values were similar to the ones of the limonene microcapsules. Again, no aggregation was noticed and isocyanate consumption was confirmed by FTIR. Comparing each component of the perfume with their odor threshold the results showed that musk and limonene scent odor values are the highest so these are the components that are more intensely detected. Perfume microcapsules have been used to impregnate textiles at a laboratory scale and at industrial scale. The quantification of perfume release was done by GC/FID/Headspace. Microcapsules with perfume were successfully tested using an industrial foulard. The Foulard (3 rollers) was used at a working speed of 10 m/min with fabrics of 1.55 m width and different grammages. The perfume microcapsules (50 g/L) were suspended in a 70L bath containing softener at 10 g/L (Perisoft Nano, Bayer) and a self-crosslinking agent at 50 g/L (Baypret USV, Bayer). The

impregnated textile was dried for 3 minutes at 100 °C and thermofixed at 140 °C during more 3 minutes. SEM micrographs have shown good adhesion between microcapsules and textile fibres.

For the textiles impregnated at lab-scale the loss of limonene was 38% in the first dry cleaning cycle and up to 87% after five cycles. The industrial-scale impregnated textiles also showed resistance to five dry cleaning cycles. The amount of the limonene component in the fabric was compared with its threshold and the odor value was calculated confirming that it suffers a decrease on after 5 dry cleaning cycles. The odor was also noticeable after 3000 abrasion cycles.

Concluding, in the present research a product (PUU microcapsules with limonene and men's perfume) was developed and successfully tested to impregnate textiles both at laboratory and industrial scale.

Resumo

O objectivo desta tese, desenvolvida no âmbito do Projecto ADI Scentfashion[®], consiste na produção de microcápsulas de poliuretano ureia (PUU) contendo perfumes para aplicação na indústria têxtil no fabrico de fatos de homem perfumados.

Um conjunto de microcápsulas comerciais contendo diferentes fragrâncias, foram inicialmente caracterizadas em termos de distribuição de tamanho de partícula e morfologia utilizando Dispersão Laser, Microscopia Óptica e Microscopia Electrónica de Varrimento (MEV). Observou-se que as microcápsulas têm uma forma esférica com tamanho entre 2 e 6 μm . A sua composição química foi confirmada por Espectroscopia de Infravermelhos com Transformada de Fourier (FTIR) como sendo baseada em copolímeros de melamina incluindo os de melamina-formaldeído.

A eficácia da impregnação dos tecidos com microcápsulas comerciais foi testada utilizando diferentes condições de impregnação (concentração das microcápsulas e tipo de ligante), sendo os melhores resultados obtidos com um ligante à base de poliuretano. As condições experimentais foram definidas com base nos requisitos industriais para simular o uso do dia-a-dia: solidez do perfume após 5 lavagens de limpeza a seco e 9000 ciclos de abrasão. Estes testes foram feitos à escala laboratorial usando um mini-foulard. Os tecidos impregnados foram avaliados por MEV e por cromatografia gasosa GC/FID/Headspace e os resultados mostraram que, quando se usa um ligante de base acrilato, a perda do odor resultante da limpeza a seco é cerca de 65%, sendo de 30% quando se utiliza um de base poliuretano.

A polimerização interfacial foi a técnica utilizada para produzir microcápsulas de PUU contendo limoneno e perfume como agentes activos para aplicação industrial em substratos têxteis. Embora os PUU sejam polímeros muito flexíveis em termos de possibilidades de síntese, esses sistemas devem ser concebidos e otimizados, tendo em consideração as particularidades do agente activo a ser encapsulado.

Neste trabalho, o seguinte processo geral de produção foi seguido: (1) formação de uma emulsão óleo em água (o/a); (2); formação de PUU na interface óleo-água; (3) lavagem para retirar o excesso de reagentes e (4), separação e armazenamento das microcápsulas. Utilizando FTIR foi possível confirmar a conversão completa dos grupos isocianato. As microcápsulas de limoneno apresentaram morfologia esférica e uma distribuição bimodal de tamanhos com um valor médio de 10 µm. A solução final apresentou um teor de resíduo sólido de aproximadamente 41% e um pH de 7,18. A espessura da parede das microcápsulas foi estimada por SEM como sendo 1µm e não foram formados aglomerados. As imagens de SEM mostraram também uma boa adesão entre as microcápsulas e as fibras têxteis. Através da análise de GC-FID-Headspace, a presença de limoneno no substrato têxtil foi quantificada. Durante a limpeza a seco, verificou-se uma perda de limoneno de 24% no primeiro ciclo e até 97% após cinco ciclos. Para os ensaios de abrasão, a perda de limoneno foi de 40% para os 3000 ciclos e até 60% para os 9000 ciclos.

O mesmo procedimento foi usado para produzir microcápsulas de PUU com o perfume desenvolvido para homens. Obteve-se uma eficiência de encapsulação de 55% relativa à quantidade de perfume usada no processo de encapsulação. Em termos de caracterização (forma, tamanho e teor de resíduos sólidos), os valores obtidos foram semelhantes aos das microcápsulas de limoneno. Novamente não foi notada qualquer agregação das microcápsulas e a conversão completa dos grupos isocianato foi confirmada por FTIR. Comparando cada componente do perfume com o seu limiar de odor, os resultados mostraram que as fragrâncias de musk e limoneno são as que apresentam valores de odor superiores e por isso são estes os componentes que são detectados mais intensamente. As microcápsulas com perfume foram utilizadas para impregnar têxteis à escala laboratorial e industrial.

A quantificação da libertação do perfume foi feita por GC-FID-Headspace. As microcápsulas de perfume foram testadas ao nível da aplicação industrial com

sucesso (foulard industrial). O Foulard (3 rolos) foi utilizado à velocidade de trabalho de 10 m/min, com tecidos de 1,55 m de largura e de diferentes gramagens. As microcápsulas de perfume (50 g/L) foram suspensas num banho de 70L contendo 10 g/L de um amaciador (Perisoft Nano, Bayer) e 50 g/L de um ligante (Baypret USV, Bayer). O tecido impregnado foi seco durante 3 minutos a 100 °C e termofixado a 140 °C durante mais 3 minutos. As imagens de SEM mostraram uma boa adesão entre as microcápsulas e as fibras têxteis.

Para os tecidos impregnados à escala laboratorial, verificou-se uma perda de limoneno de 38% no primeiro ciclo de limpeza a seco e até 87% após cinco ciclos. Os tecidos impregnados à escala industrial também apresentaram resistência a cinco ciclos de limpeza a seco. A quantidade do componente limoneno no tecido foi comparada com o seu limiar de odor e foi calculada a intensidade do odor confirmando que sofre uma perda depois de 5 ciclos de limpeza a seco. O odor continuou perceptível após 3000 ciclos de abrasão.

Concluindo, na presente investigação, um produto (microcápsulas de PUU com limoneno e perfume masculino) foi desenvolvido e testado com sucesso para impregnar tecidos tanto à escala laboratorial como industrial.

Sommaire

Le but de cette thèse, déroulée dans le cadre du projet ADI Scentfashion[®], est la production de microcapsules en polyuréthane-urée (PUU) contenant des parfums pour l'application en industrie textile en vue de la fabrication de costumes masculins parfumés.

Des microcapsules commerciales à des arômes diverses ont été d'abord analysées en ce qui concerne leur distribution de tailles de particules et morphologie à l'aide de diffusion de lumière (compteur Coulter), microscopie optique et microscopie électronique à balayage *Scanning Electron Microscopy* (SEM). D'après ces observations, on a pu constater une forme sphérique à diamètre compris entre 2 et 6 μm . Leur composition chimique a été vérifiée / confirmée par spectroscopie infra-rouge Fourier Transform Infrared Spectroscopy (FTIR) et consiste à des copolymères de mélamine-formaldéhyde.

La performance de l'imprégnation des textiles avec microcapsules commerciales a été essayée avec plusieurs conditions opérationnelles (concentration de microcapsules et nature du liant). Les meilleurs résultats ont été obtenus avec un liant de base polyuréthane. Les conditions expérimentales choisies ont pris en compte les contraintes de la dégradation due à l'usage journalier: tenue du parfum après 5 nettoyages à sec et 9000 cycles d'abrasion. Ces essais ont été exécutés en laboratoire à l'aide d'un mini-foulard. Les tissus imprégnés ont été évalués par SEM et chromatographie en phase gazeuse GC/FID/Headspace et les résultats ont montré que, en présence d'un liant acrylate, la perte d'odeur en résultat du nettoyage à sec est environ 65% en comparaison avec une perte de 30% observée avec un liant polyuréthane.

La polymérisation interfaciale a été choisie pour la production de microcapsules PUU à l'huile de limonène et parfum qui jouaient le rôle d'agents actifs pour l'application industrielle sur des substrats textiles.

Bien que les PUU soient des polymères très flexibles en ce qui concerne les possibilités de synthèse, ces systèmes doivent être conçus et optimisés en tenant compte des particularités de l'agent actif à encapsuler. Dans ce travail, un procédé de production standard a été choisi, lequel consistait à: (1) formation d'une émulsion huile-dans-l'eau *oil-in-water* émulsion (o/w); (2) formation de PUU à l'interface huile-eau; (3) rinçage pour enlever l'excès de réactifs et (4) séparation et stockage des microcapsules.

L'usage de FTIR a permis de confirmer la conversion complète de groupes isocyanate. Les microcapsules produites à l'odeur de citron présentaient une morphologie sphérique et une distribution en volume de tailles de particules bimodale, à une taille moyenne de 10 µm. La suspension finale de microcapsules avait une teneur de solides environ 41% et pH 7.18. L'épaisseur de paroi de ces microcapsules a été estimée par SEM à 1 µm et des agglomérats n'ont pas été formés. Les micrographies SEM ont aussi montré la bonne adhésion entre microcapsules et fibres textiles. D'après l'analyse par chromatographie en phase gazeuse de la vapeur GC-*headspace*, la présence de limonène accompagnant le substrat textile a pu être quantifié. Pendant le nettoyage à sec, la perte de limonène est 24% pour le premier cycle et jusqu'à 97% après cinq cycles. Pour les essais d'abrasion, la perte de limonène est 40% pour 3000 cycles et jusqu'à 60% pour 9000 cycles.

Le même procédé a servi pour produire microcapsules en PUU avec le parfum pour homme développé en ce projet. L'efficacité du procédé d'encapsulation par rapport à la quantité de parfum au départ a été 55%. Les caractéristiques du produit (forme, taille et teneur en solides) ont été similaires à ceux des microcapsules à limonène. À nouveau, de l'agrégation n'a pas été remarquée et la consommation d'isocyanates a été confirmée par FTIR. La comparaison pour chaque composant du parfum de sa valeur limite d'odeur détectable a montré que le musc et le limonène étaient ceux les plus intensément aperçus. Des microcapsules de parfums ont servi pour imprégner des textiles non seulement à

l'échelle du laboratoire mais aussi à l'échelle industrielle. La mesure de la quantité de parfum libérée a été faite par GC/FID/Headspace. Des microcapsules à parfum ont été testées avec succès à l'aide d'un foulard industriel. Ce foulard (à 3 rouleaux) a été opéré à une vitesse de 10 m/min avec des tissus à largeur 1.55 m et différents grammages. Les microcapsules à parfum (50 g/L) ont été suspendues dans un bac de 70 L contenant 10 g/L d'adoucissant (Perisoft Nano, Bayer) et un agent de réticulation à concentration 50 g/L (Baypret USV, Bayer). Le tissu imprégné a été séché pendant 3 minutes à 100 °C et a subi une thermofixation à 140 °C pendant plus de 3 minutes. Des micrographies SEM ont montré une bonne adhésion entre les microcapsules et les fibres textiles.

Pour ces tissus imprégnés à l'échelle du laboratoire la perte de limonène a été 38% pour le premier cycle de nettoyage à sec et jusqu'à 87% après cinq cycles. Les tissus imprégnés à l'échelle industrielle ont aussi montré de la résistance après cinq cycles de nettoyage à sec. La teneur du composant limonène dans le tissu a été comparée avec sa limite d'odeur détectable et cette valeur a confirmé la chute après cinq cycles de nettoyage à sec. L'odeur pouvait encore être aperçue après 3000 cycles d'abrasion.

En conclusion, cette recherche a développé un produit (microcapsules en PUU avec limonène et un parfum pour homme) qui a été essayé avec succès pour l'imprégnation de textiles soit à l'échelle du laboratoire, soit à l'échelle industrielle.

Table of contents

Abstract
Resumo
Sommaire

Table of contents.....	i
List of Figures.....	v
List of Tables.....	xiii
1. Introduction	1
1.1 Relevance and motivation	3
1.2 Objectives and outline	8
2. State of the art.....	11
2.1 Introduction	13
2.2 Microencapsulation and techniques.....	14
2.2.1 In situ polymerization	16
2.2.2 Emulsion crosslinking	17
2.2.3 Suspension polymerization.....	18
2.2.4 Molecular encapsulation using cyclodextrins	19
2.2.5 Processes based on supercritical fluids	20
2.2.6 Coacervation.....	21
2.2.7 Spray drying.....	23
2.2.8 Fluid bed coating	24
2.2.9 Extrusion technology	25
2.2.10 Interfacial polymerization.....	26
2.3 Selection of “target perfumes” for encapsulation.....	33
2.3.1 Perfumes structure – Fragrances pyramid	34
2.3.2 Fragrance family – Types of perfumes	35
2.4 Encapsulation techniques in textile industry	36
2.4.1 Patent review.....	36
2.4.2 Application of microcapsules on textile industry	39
3. Materials and Methods	45
3.1 Chemical compounds and reagents.....	47
3.2 Experimental facilities.....	48
3.2.1 Microcapsules production	48
3.2.2 Impregnation of microcapsules on textile substrate.....	50
3.2.3 Binder selection	52
3.3 Techniques for microcapsules and fabrics characterization.....	59
3.3.1 Mean particle size and particle size distribution (Laser dispersion).	59
3.3.2 Optical microscopy.	59
3.3.3 Scanning electron microscopy (SEM).	60

3.3.4	Determination of solid content and pH.....	61
3.3.5	Fourier Transform Infrared spectroscopy (FTIR).	61
3.3.6	Gas chromatography GC-FID-Headspace and GC-MS.	62
3.3.7	Solidness of the aromas by abrasion, dry cleaning and washing tests.	65
4.	Commercial samples characterization	69
4.1	Commercial microcapsules and impregnated textiles characterization... ..	71
4.1.1	Laser dispersion	72
4.1.2	Optical microscopy	73
4.1.3	Scanning Electron Microscopy (SEM) and Environmental Scanning Electron microscopy (ESEM)	76
4.1.4	FTIR	80
4.1.5	Solid Content and pH.....	82
4.1.6	SEM of impregnated textiles with lemon microcapsules	83
4.1.7	GC-headspace analyses of commercial lemon microcapsules	87
4.1.8	Headspace Analysis of impregnated textiles with commercial microcapsules	88
4.2	Conclusions	91
5.	Microencapsulation of Limonene	95
5.1	Formulation A.....	98
5.1.1	Characterization of produced microcapsules using formulation A	100
5.2	Formulation B.....	109
5.2.1	Characterization of produced microcapsules using formulation B	112
5.3	Formulation C, D and E	120
5.3.1	Characterization of produced microcapsules using formulation C, D and E	126
5.4	Improvement of formulation C	136
5.5	Final formulation.....	142
5.5.1	Microcapsules preparation.....	142
5.5.2	Impregnation of microcapsules on textile substrate.....	147
5.5.3	Characterization of the microcapsules solution	148
5.5.4	Textile impregnated with microcapsules characterisation.....	152
6.	Microencapsulation of Perfumes	159
6.1	Preparation of PUU microcapsules	161
6.2	Preparation of perfume	161
6.3	Impregnation of microcapsules on textile substrate	164
6.4	Results and discussion	165
7.	Conclusions and Future work	179
	Acknowledgements	187
	References	189
	Press release.....	199

List of Figures

Chapter 1. Introduction

Figure 1.1. Number of patents and publications in the period from 1970 to 2010 (obtained on free patents online database and ISI web of knowledge, April 2010; keyword:microencapsulation).....	6
Figure 1.2. Number of patents registered in the period from 1950 to 2010 (obtained on free patents online database, April 2010; keywords: microencapsulation, fragrances and textiles).	6

Chapter 2. State of the art

Figure 2.1. Schematic representation of the release of the active agent on the skin. 1. Textile fibre; 2.Release of the active agent on the skin; 3.Binder.....	14
Figure 2.2. Microcapsules basic structures. (Courtesy of Ronald T. Dodge 2009)...	15
Figure 2.3. ESEM image of urea-formaldehyde microcapsules containing dicyclopentadiene core [42].....	17
Figure 2.4. Process scheme for based emulsion technique [53].	18
Figure 2.5. SEM micrographs of a batch of microcapsules containing PRS® paraffin wax [55].	19
Figure 2.6. Scheme of odor molecules caption using cyclodextrins [70].....	20
Figure 2.7. Scheme of encapsulation and microsphere formation using supercritical fluids [76].....	21
Figure 2.8. Microcapsules containing thyme oil obtained by coacervation (optical microscopy with magnification of 1000x) [90].....	22
Figure 2.9. A spray dryer layout from Gea Process Engineering Inc [99].....	23
Figure 2.10. Scheme of the fluidized bed principle [103].	25
Figure 2.11. Schematic representation of an extruder for microencapsulation [110].	26
Figure 2.12. SEM photographs of microcapsules produced by Interfacial Polymerisation [124]	27
Figure 2.13. General process scheme for microcapsules preparation by interfacial polymerisation. 1) Aqueous phase with a protective colloid, 2) oil active principal with monomer A; 3) formation of the wall material at the interface due to the reaction of monomer A with monomer B (added to the continuous phase); 4) formed microcapsules.	28
Figure 2.14. Reaction scheme for urethane formation.	30
Figure 2.15. Reaction scheme for ureas or polyurethanes/ureas formation	30
Figure 2.16. Reaction scheme for ureas formation.	30
Figure 2.17. Chemical structure of aromatic and aliphatic isocynates.	31
Figure 2.18. Chemical structure of polyester and polyether polyols.....	32
Figure 2.19. Classical perfume pyramid structure.	35
Figure 2.20. Example of classification methodology in men's fragrance families ...	35

Figure 2.21. Schematic representation of the microcapsules application in fabrics using a Foulard. 1. Untreated fabric; 2. Microcapsules bath; 3.Squeezing; 4.Drying and curing; 5. Fabric treated containing microcapsules.	39
Figure 2.22. Critical factors of new product development (adapted from Scentfashion project report [151]).	41
Figure 2.23. Fragrances microcapsules application conditioning factors on textile substrates (adapted from Scentfashion project report [151]).	42

Chapter 3. Materials and Methods

Figure 3.1. Experimental set-up for the production of microcapsules by interfacial polymerization: (1) reactor vessel; (2) ultraturrax; (3) overhead stirring drive and (4) thermostatic bath.	49
Figure 3.2. a) Laboratory horizontal foulard; b) Laboratory dryer [153].	50
Figure 3.3. Several views of the industrial Foulard during the impregnation process of scented microcapsules. a) Overview of the Foulard; b) View of the fabric entry in the oven for the thermofixing and curing steps. c) View of the output of the final fabric with impregnated microcapsules.	51
Figure 3.4. FID chromatograms of the textiles impregnated with mint microcapsules (Horquim) using the acrylate binder after 0, 1, 2, 3, 4 and 5 washes.	53
Figure 3.5. Relative weight of menthol present in the textiles impregnated with mint microcapsules using the acrylate binder, as a function of dry washes number.	54
Figure 3.6. FID chromatograms of the textiles impregnated with mint microcapsules (Horquim) using the acrylate binder after 0, 3000, 6000 and 9000 abrasion cycles.	55
Figure 3.7. Relative weight of menthol present in textiles impregnated with mint microcapsules using the acrylate binder, as a function of abrasion cycles.....	56
Figure 3.8. FID chromatograms of the textiles impregnated with mint microcapsules (Horquim) using the urethane binder after 0, 1, 2, 3, 4 and 5 washes.	57
Figure 3.9. Relative weight of menthol present in the textiles impregnated with mint microcapsules using the polyurethane binder, as a function of dry washes number.	58
Figure 3.10. Laser Diffraction Particle Size Analyzer COULTER LS230.	59
Figure 3.11. Optical microscope- Leica DM 2000.....	60
Figure 3.12. Scanning electron microscope JEOL JSM-6301S.	60
Figure 3.13. FTIR BOMEN (model MB 104).	62
Figure 3.14. GC-FID-Headspace equipment with an automatic sampler coupled..	63
Figure 3.15. Vial of headspace analysis; Headspace phases: G = the gas phase (headspace); S = the sample phase; MC= Microcapsules.	64
Figure 3.16. Impregnated fabric isolated on plastic bag (a) for GC headspace analyses (b).....	64
Figure 3.17. Martindale abrasion tester [154].	65

Chapter 4. Commercial microcapsules characterization

Figure 4.1. Particle size distribution (in volume) for the samples Lemon (Bayer, Focor and Horquim), Jasmine (Focor) and Strawberry (Horquim).....	72
Figure 4.2. Particle size distribution (in number) for the samples Lemon (Bayer, Focor and Horquim), Jasmine (Focor) and Strawberry (Horquim).....	72
Figure 4.3. Optical micrographs with magnification of 1000x of commercial microcapsules.....	75
Figure 4.4. SEM micrographs of strawberry microcapsules from Horquim with magnification of 500x and 2000x.	76
Figure 4.5. SEM micrographs of lemon microcapsules from Horquim with magnification of 500x and 2000x.	76
Figure 4.6. ESEM micrographs of commercial microcapsules. a) Lemon from Bayer, b) Lemon from Focor, c) Lemon from Horquim, d) Strawberry from Horquim, e) Jasmine from Focor.	79
Figure 4.7. SEM micrographs after domestic washing process of impregnated textiles with commercial lemon microcapsules from Horquim.	86
Figure 4.8. MS Chromatogramms of lemon commercial samples.....	87
Figure 4.9. Comparison of MS chromatograms of the commercial sample of lemon from Horquim and essential oil of lemon.	88
Figure 4.10. FID chromatograms of limonene and impregnated textiles samples with microcapsules of Horquim after 0, 1 and 20 washes.	89
Figure 4.11. Calibration curve of limonene.....	90
Figure 4.12. Values of the mass of limonene-based on calibration curve of limonene.....	90
Figure 4.13. Panel list evaluation of impregnated textiles subjected to domestic washes. Where: A – Intense aroma, B - Slightly less intense aroma, C - Aroma exists but with low intensity, D - Aroma exists but with very low intensity, E - Do not smell the aroma.....	91

Chapter 5. Microencapsulation of limonene

Figure 5.1. Differential and cumulative particle size distribution in volume of limonene microcapsules obtained with formulation A.....	100
Figure 5.2. Differential and cumulative particle size distribution in number of limonene microcapsules obtained with formulation A.....	101
Figure 5.3. Optical microscopy in bright field with magnification 1000x. Formulation A-using the base formulation.	101
Figure 5.4. Optical microscopy in bright field with magnification 1000x. Formulation A after reduction of acetone content (50%).	102
Figure 5.5. SEM micrographs of the whole microcapsules solution and concentrated phase solution obtained with formulation A (magnification of 1500X).	103
Figure 5.6. SEM micrographs of the impregnated textile with produced lemon microcapsules by formulation A with magnification of 500x.....	104

Figure 5.7. Comparison between the FID chromatograms obtained for the microcapsules solutions produced with 1% (red) and 5% (green) of limonene using formulation A.....	105
Figure 5.8. FID chromatograms of the blank sample (blue) and textiles impregnated with microcapsules solutions produced with 1% (red) and 5% (green) of limonene using formulation without washing.	106
Figure 5.9. Chromatograms of the impregnated textiles with microcapsules of Formulation A after 0, 1, 2 and 3 dry cleaning cycles.	107
Figure 5.10. Mass of limonene remaining after 1, 2 and 3 dry cleaning cycles relative to the initial mass of limonene in the fabric.	108
Figure 5.11. Differential and cumulative particle size distribution in volume of limonene microcapsules obtained with formulation B.	112
Figure 5.12. Differential and cumulative particle size distribution in number of limonene microcapsules obtained with formulation B.	113
Figure 5.13. Photos of optical microscopy in bright field mode with magnifications of 400x (left) and 1000x (right)of the microcapsules produced using formulation B.	113
Figure 5.14. SEM micrographs of the textile covered with the produced lemon microcapsules according to formulation B dried at room temperature. Magnifications of 500x (left) and 2000x (right).....	114
Figure 5.15. SEM micrographs of the textile covered with produced lemon microcapsules by formulation B and dried at 165°C with magnification of 500x (left) and 2000x (right).	115
Figure 5.16. SEM micrographs of the impregnated textiles with lemon microcapsules (concentration 40 g/L) using a polyurethane binder (magnification of 500x (left) and 1000x (right)).	116
Figure 5.17. FID chromatograms of the limonene PUU microcapsules (Formulation B) impregnated textiles using different impregnation conditions (microcapsules concentration and the effect of presence and absence of a thermofixation process).	117
Figure 5.18. Relative weight of limonene present in the impregnated textiles with limonene microcapsules (sample 2) using the polyurethane binder, as a function of dry washes number.	118
Figure 5.19. Particle Size distribution in volume for the limonene microcapsules produced by: a) Formulation C: Polyurethane-urea; b) Formulation D: Polyurethane; c) Formulation E: Polyurea.....	127
Figure 5.20. Particle Size distribution in volume for the limonene microcapsules produced by: a) Formulation C: Polyurethane-urea; b) Formulation D: Polyurethane; c) Formulation E: Polyurea.....	127
Figure 5.21. Photos of optical microscopy in bright field mode using a magnification of 400x (left) and 1000x (right) of microcapsules produced using: a) formulation C; b) formulation D; c) formulation E).	129
Figure 5.22. Infrared spectra (FTIR) of the microcapsules obtained using: (a) formulation C, (b) formulation D and (c) formulation E.....	131

Figure 5.23. FID chromatograms of the original impregnated textiles with limonene microcapsules produced using formulations C, D and E without washing.	133
Figure 5.24. Relative weight of limonene present in impregnated textiles with limonene microcapsules produced using formulation C, depending on the number of wash cycles.	134
Figure 5.25. Relative weight of limonene present in impregnated textiles with limonene microcapsules using formulation C, depending on the number of abrasion cycles.	135
Figure 5.26. Infrared spectra (FTIR) of the microcapsules obtained using formulation C with the introduction of hydrazine in the formulation.	137
Figure 5.27. Comparison of the limonene amount detected by headspace among samples (i) Original formulation C - MC000, (ii) Formulation C optimized - MC003-MC023 and (iii) commercial lemon microcapsules - Horquim.	140
Figure 5.28. SEM micrographs of the impregnated textiles with limonene microcapsules produced using formulation C: (i) Original formulation C - MC000, (ii) optimized formulation C - MC003 and (iii) optimized formulation C - MC009.	141
Figure 5.29. Reaction scheme for polyurethane-urea microcapsules production.	143
Figure 5.30. Microencapsulation process of limonene by interfacial polymerization.	145
Figure 5.31. FTIR spectrum of polyurethane-urea microcapsules.	149
Figure 5.32. Particle size distribution in volume of polyurethane-urea microcapsules with limonene oil.	150
Figure 5.33. Particle size distribution in number of polyurethane-urea microcapsules with limonene oil.	150
Figure 5.34. Optical microscopy of microcapsules solution. a) 200x; b) 1000x.	151
Figure 5.35. SEM micrographs of the impregnated textiles with lemonene microcapsules using different magnifications.	153
Figure 5.36. Chromatograms obtained by GC-FID-Headspace of textile substrates impregnated with microcapsules and subject to the dry cleaning. 1) with one dry cleaning; 2) with two dry cleaning; 3) with three dry cleaning; 4) with four dry cleaning and 5) with five dry cleaning.	154
Figure 5.37. Relative weight of limonene present in impregnated textiles with lemon microcapsules, depending on the number of wash cycles.	155
Figure 5.38. Relative weight of limonene present in impregnated textiles with lemon microcapsules, depending on the number of abrasion cycles.	156

Chapter 6. Microencapsulation of perfume

Figure 6.1. Pyramid structures on these men's fragrance.	162
Figure 6.2. FTIR spectrum of the encapsulated perfume with the following composition: limonene (19.51%), musk (9.15%), jasmine (35.67%) and vetiver (35.67%).	166
Figure 6.3. FTIR spectrum of polyurethane-urea microcapsules with perfume.	166

Figure 6.4. Differential and cumulative Particle size distribution in volume (a) and number (b) of polyurethane-urea microcapsules with perfume.	168
Figure 6.5. Optical micrographs of microcapsules containing perfumes. A)100x; b)200x; c)400x; d)1000x.	169
Figure 6.6. SEM photographs of fabrics in laboratory application.....	170
Figure 6.7. SEM photographs of fabrics in industrial application.	171
Figure 6.8. Quantity of limonene present in the headspace according to the number of dry cleaning cycles.	175

List of Tables

Chapter 1. Introduction

Table 1.1. Methods of encapsulation, particle size and applications of different methods [1].	5
Table 1.2. Functional fabrics commercially available.....	7

Chapter 2. State of the art

Table 2.1. Several techniques used for the production of microcapsules.	16
Table 2.2. Classification of perfume notes according to their volatility	34
Table 2.3. Patented processes for microencapsulation of flavours and fragrances and applications in textile industry.	36

Chapter 3. Materials and methods

Table 3.1. Conditions of dry cleaning cycles.	66
Table 3.2. Washing conditions for domestic laundering.....	66

Chapter 4. Commercial microcapsules characterization

Table 4.1. Fragrances and suppliers of the commercial microcapsules.....	71
Table 4.2. Microcapsules mean size based on volume distribution	73
Table 4.3. Data relating to commercial microcapsule of lavender and mints.	80
Table 4.4. FTIR analyses of commercial microcapsules.....	81
Table 4.5. Solid content and pH of samples of commercial microcapsules.....	83
Table 4.6. Application conditions of microcapsules on textiles	84

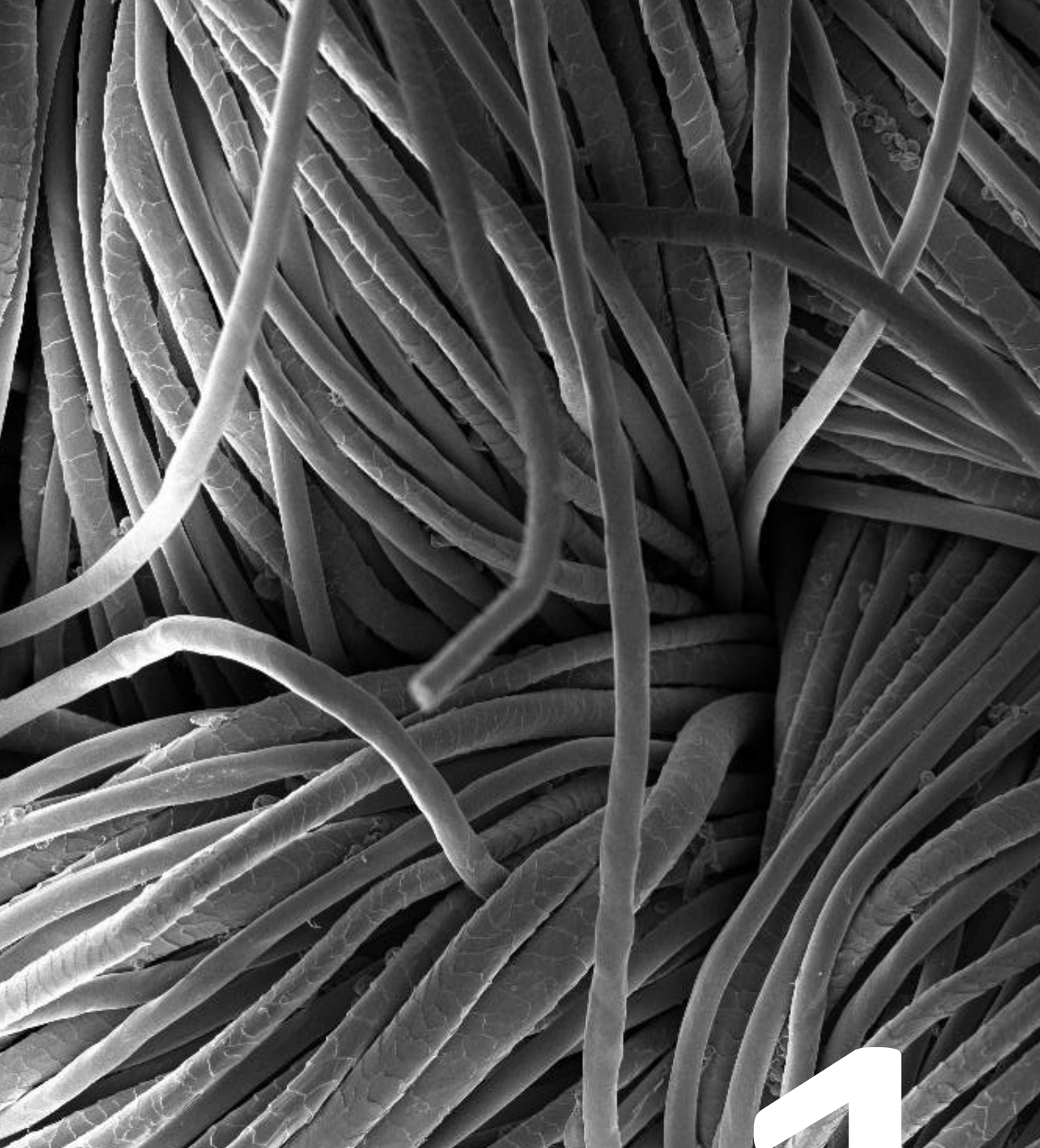
Chapter 5. Microencapsulation of limonene

Table 5.1. Base formulation (type of materials and amount used) and operating conditions used in the production of limonene microcapsules according to formulation A.	98
Table 5.2. Experimental steps used in the preparation of limonene microcapsules according to formulation A.	99
Table 5.3. Application conditions of microcapsules on textiles	103
Table 5.4. Base formulation (type of materials and amount used) and operating conditions used in the production of limonene microcapsules according to formulation B.	110
Table 5.5. Experimental steps used in the preparation of microcapsules– according to formulation B.	111
Table 5.6. Application conditions of microcapsules on textiles	116
Table 5.7. Base formulation (type of materials and amount used) and operating conditions used in the production of limonene microcapsules according to formulation C.....	121

Table 5.8. Experimental steps used in the preparation of these microcapsules– formulation C.....	121
Table 5.9. Base formulation (type of materials and amount used) and operating conditions used in the production of limonene microcapsules according to formulation D.	123
Table 5.10. Materials and operating conditions used in the production of MC - formulation D.	123
Table 5.11. Base formulation (type of materials and amount used) and operating conditions used in the production of limonene microcapsules according to formulation E.....	125
Table 5.12. Materials and operating conditions used in the production of MC - formulation E.....	125
Table 5.13 Average size diameter of the microcapsules obtained using the formulations C, D and E.	128
Table 5.14. Application conditions of microcapsules on textiles	132
Table 5.15. Summary of data related to the used emulsifiers.	138
Table 5.16. Results obtained in formulating the post-synthesis.	138
Table 5.17. Average diameter size of the microcapsules obtained using the formulations C optimized.	139
Table 5.18. Chemical system and composition of oil and aqueous phases.	144
Table 5.19. Conditions of textile impregnation process	147
Table 5.20. Values of solid content and pH determined for the produced microcapsules.....	152

Chapter 6. Microencapsulation of perfume

Table 6.1. Floral-Woody-Musk fragrance compounds	162
Table 6.2. Floral-Woody-Musk fragrance: vapour pressure and threshold values of components.....	164
Table 6.3. Fragrance components in liquid and gas phases.	172
Table 6.4. Total, encapsulated and nonencapsulated masses discriminated by perfume components and encapsulation efficiency.	173



Introduction

1

1.1 Relevance and motivation

The competitiveness of the textile sector depends on the capability to understand and answer to the customer needs by adjusting to the evolution of technologies and mobility of human resources. The introduction of a “new” technology: microencapsulation, in a traditional industrial sector such as the textile, will help making products in response to the requirements of fashion, reducing competition with products from countries with lower labour cost and little social concern.

The Portuguese textile industry is in the midst of a second industrial revolution that assumes global proportions. This requires a tremendous versatility, both in products and processes, of this fashion business. Flexible and environmentally friendly productive processes are needed to respond more quickly to market demands, thus satisfying the customer needs and making this industry competitive, betting on quality and innovation.

Potential markets are numerous and beyond the traditional textile sector. In this context it is promising to expand the textile sector into the field of 'interactive' textiles, a term that refers to multifunctional textiles exhibiting unique and valuable properties considered as "intelligent." Most of these functionalities may be incorporated into textile substrates by microencapsulation processes, a technology with great potential in today's world. However, it is still important to overcome some problems:

1) In Portugal, for example, there is a growing concern of textile companies in this type of products that enable differentiation and increased competitiveness of the "Portuguese textile" in added-value markets. There is at the moment only one company (Micropolis, now part of Devan Chemicals), able to produce microcapsules with fragrances; therefore, fragrance microcapsules are imported at prices between 270 and 375€/kg, sometimes with characteristics and quantities inadequate to the needs, which raise some problems such as storage due to the

instability of these products. The same lack of knowledge occurs in other countries worldwide.

2) Perfumes are complex mixtures of essential oils (EO) containing many aromatic compounds with very different volatilities, classified into three types: top notes (lasting only a few minutes), middle notes (lasting 2-5 hours and giving the main character to the perfume) and base notes (may last more than 8 hours and act as fixatives, increasing the lifetime of the perfume). This complexity results in large difficulties in their encapsulation, when compared to other single-molecule core materials.

3) Current treatments consist of fixing the microcapsules using a conventional binder, as for example an acrylic polymer. This type of fixation appears very vulnerable to laundering operations in which the link is removed slowly and the capsule is destroyed. From the point of view of the customer, the functionality of textiles disappears after 2 or 3 cycles of washing which is not acceptable. If we consider the cost of raw material/process inherent to the valorisation of textiles, we may conclude that the quality/price is not appealing to the consumer.

Microencapsulation is the involvement of small solid particles, liquid droplets or bubbles of gas, with a coating. It can be considered as a type of packaging for protection against external degradation, or controlled release.

There are different industrial applications of microcapsules: “scratch and sniff” fragrance sampling, controlled release of drugs and cosmetics, medicine, food, and textile applications. Examples of microencapsulation techniques and existing applications are listed in

Table 1.1. The selection of the process and the wall material is made based on the core material, on physical and chemical stability, concentration, desired particle size, release mechanism and manufacturing costs, and also depends on the processing conditions involved in the manufacturing product and the end use of the product.

Table 1.1. Methods of encapsulation, particle size and applications of different methods [1].

Encapsulation Method	Particle Size (μm)	Applications
Coacervation	1-500	carbonless paper, fragrance
Co-extrusion	1-5 000	drugs, vitamins
Spray drying	6-600	pharmaceuticals, flavourings
Fluid bed coating	20-1500	pharmaceuticals, flavourings
Interfacial polymerization	2-2 000	pesticides, carbonless paper
In situ Polymerization	1-500	fragrances, adhesives, carbonless paper

The patents on the microencapsulation of fragrances refer coacervation [2-4], interfacial polymerization and in situ polymerization [5-7] as the main technologies used.

The first application of a microencapsulation process was developed by L. Schleicher and B. Green the of U.S. Company National Cash Register (NCR) for the production of carbonless copy paper (1953). The commercialization of the product began in 1968 with a production of 110 tons of microcapsules in the U.S.A. In recent years, it was observed an increase in the number of functional products using microencapsulation, as shown by the number of patent filings and publications (Figure 1.1).

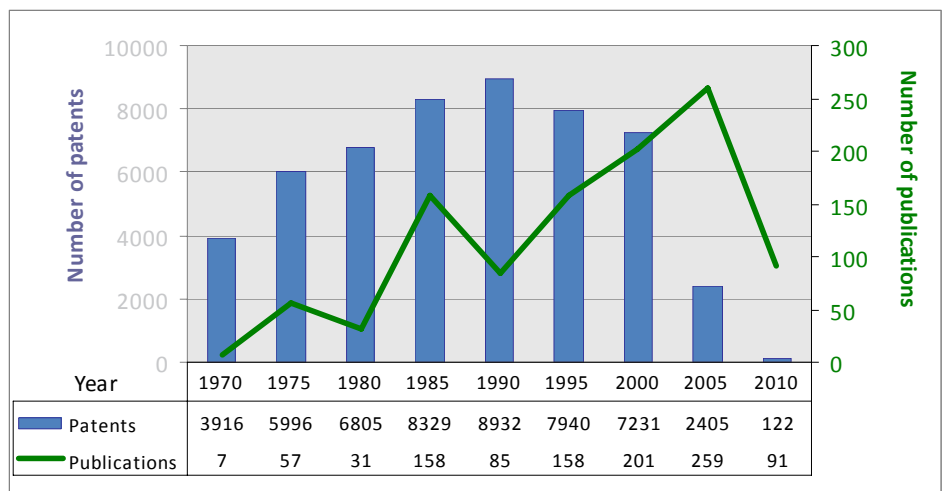


Figure 1.1. Number of patents and publications in the period from 1970 to 2010 (obtained on free patents online database and ISI web of knowledge, April 2010; keyword: microencapsulation).

Figure 1.2 shows the evolution of the number of patents considering microencapsulation, fragrances and textiles simultaneously.

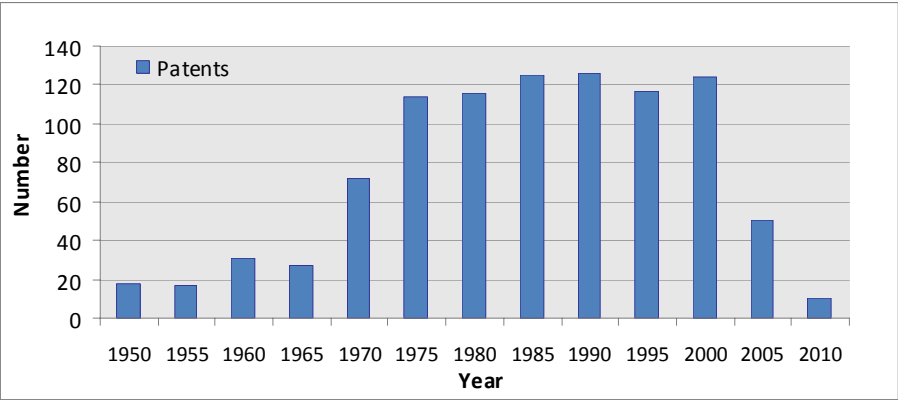


Figure 1.2. Number of patents registered in the period from 1950 to 2010 (obtained on free patents online database, April 2010; keywords: microencapsulation, fragrances and textiles).

Currently, there are several companies involved in microencapsulation processes such as 3M and Elf (pesticides), BASF, Ciba, Abbott and Pfizer (pharmaceuticals), Appleton and Mead Corporation (carbonless paper), Collaborative Laboratories (personal hygiene products), H&R , F&C and Balch Corporation (flavourings), Bayer, Mikiriken, Matsui FOLCOScent (flavours) and Ronald T. Dodge Company (cosmetic & personal care products and scented products).

The application of microcapsules in the textile industry emerged only in the 90th decade and it is targeted for some niche markets like "functional textiles", which goes beyond the simple use of textiles as just clothing.

Table 1.2 lists some examples of microcapsules applications in textiles. Microencapsulation enables the application of some active principals in textile material, preventing its lost or release during washing and thus lasting its function and durability.

Table 1.2. Functional fabrics commercially available

Function	Active agent	Applications	References
Anti-bacterial	Triclosan	Underwear Bed sheets	[8-9]
UV Protection	Ceramic Fibers Pigments	sport clothing Children's garment	[10]
Body temperature regulation	PCM (phase change materials)	Jacket (Damart)	[11]
Decontamination	Hypochlorite Amine	Decontamination of clothing	[12]
Repellence	Fluorinated Resins	T-shirts Children's garment	[13-15]
Perfume Release	Perfumes	Lingerie (Neyret)	[16-21]

The majority of the available commercial microencapsulated fragrance systems for textile applications are based on phenol-formaldehyde or melamine-formaldehyde resins, which are facing several restrictions under the present environmental policies. In such context, polyurethane urea (PUU) systems appear a more attractive and environmental friendly solution. Moreover, they are known as versatile polymer systems which can be tailor-made from a wide range of raw materials in order to achieve the desired physical, chemical and mechanical properties. They are also gaining extreme importance due to their thermal and chemical stability and easiness of preparation.

Microcapsules can be applied to textiles by stamping techniques, exhaustion, impregnation, spraying and coating or by incorporation into the fiber without modifying its sensation and colour. Several kinds of fabrics can be impregnated with microcapsules, e.g., silk, cotton and synthetic fibres (polyamide or polyester).

As it was referred above, microencapsulation technology is gaining wide acceptance in a broad range of industrial applications in markets such as textiles, cosmetics, drug delivery systems, pesticides and agrochemicals, consumer care and adhesives. In textile industry the higher interests in microencapsulation are specially directed to the application of durable fragrances to obtain added value products.

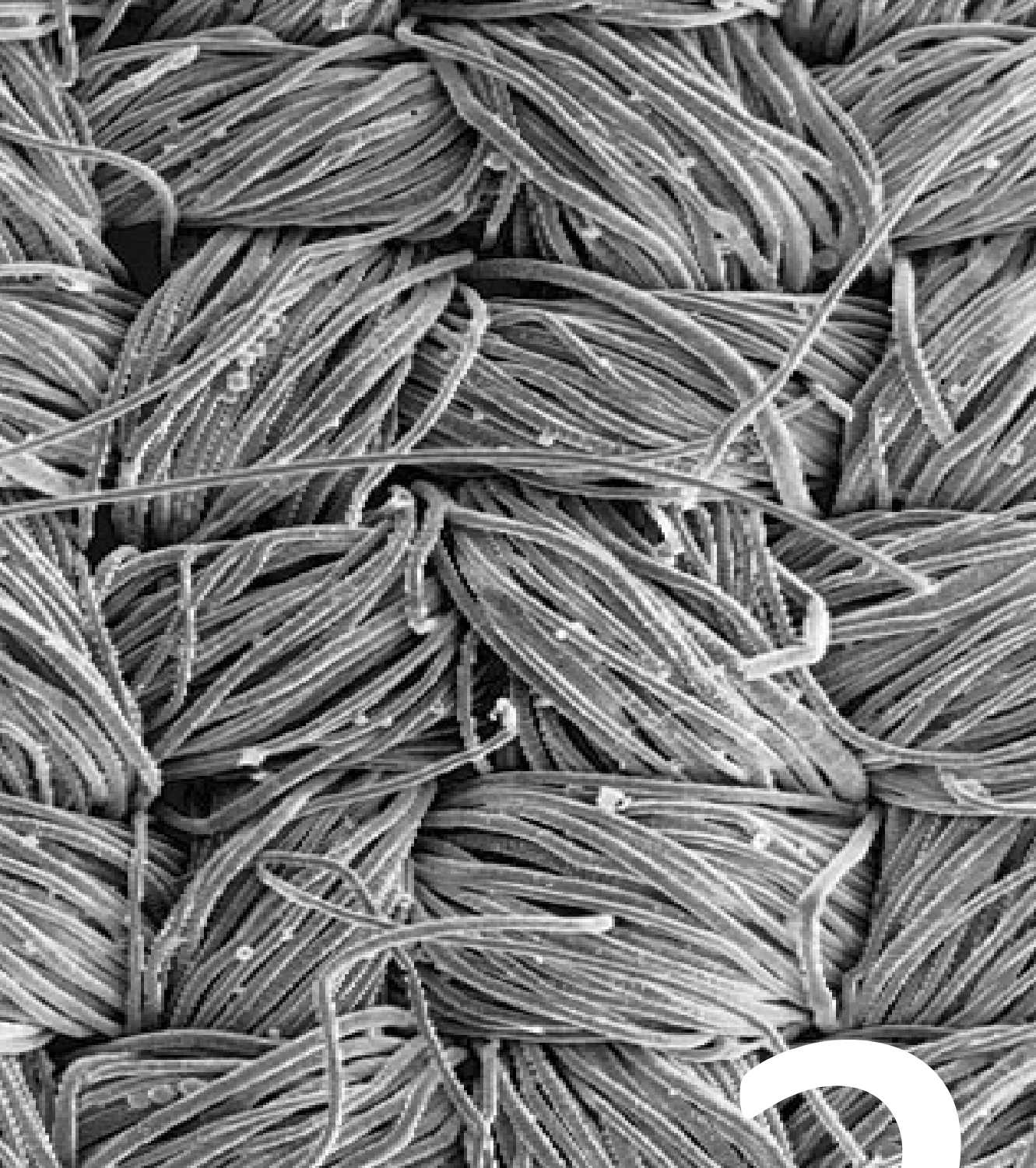
This work was developed in the framework of the “Scentfashion” project funded by ADI (Agência de Inovação, nº 13-02-03-FDR-01291) in partnership with CITEVE-Centro Tecnológico das Indústrias Têxtil e do Vestuário de Portugal and company A Penteadora, S.A.

1.2 Objectives and outline

The aim of this thesis was the encapsulation of fragrances and perfumes into polyurethane-urea microcapsules by interfacial polymerization to be applied in the

production of perfumed textiles. The goal is to achieve microcapsules able to meet required specifications defined as: (i) resistance to dry cleaning (5 cycles) and (ii) resistance to abrasion (9000 cycles). The overall objective is to contribute to the development of emergent technologies in the textile sector (microencapsulation) and generate added value products.

This thesis is organized as follows. In Chapter 1, "Introduction", the relevance and motivation are described and the objectives and outline of the thesis are presented. In Chapter 2 the state of the art regarding microencapsulation of essentials oils and perfumes and its application in the textile industry is presented. Materials used for the synthesis of microcapsules, equipments and procedures will be presented in Chapter 3, "Materials and methods". In Chapter 4 the study of commercial microcapsules for textiles application is presented. Chapter 5, "Microencapsulation of limonene", presents the results of the performed studies concerning the production of polyurethane-urea limonene microcapsules by interfacial polymerization. Its characterization and application in textiles is also presented. In Chapter 6, "Microencapsulation of perfumes", the technology developed and described herein was applied to produce microcapsules containing a masculine perfume, intended for a specific industrial application: manufacture of man perfumed suits. Finally, in Chapter 7 the main conclusions are referred and suggestions for future work are presented.



State of the art

2

2.1 Introduction

Chemical Product Engineering (CPE) is becoming a new paradigm in Chemical Engineering in response to the changes occurring in job structure [22]. Chemical Product Design (CPD) is just a part of CPE and evolves from identification of customer needs, generation and selection of ideas up to product manufacture satisfying target specifications and performance [22-26]. Various books have been published recently [23-25] in response to the need of adapting ChE – Chemical Engineers curricula to the new times in line with the book on Product Design and Development of Ulrich and Eppinger [27] used largely in management schools.

In the beginning of the 1990s, a few commercial applications of microencapsulation in textiles appeared. Today the number of commercial applications of microencapsulation in textile keeps on growing. Developed countries have shown interest in textiles with new properties and high added value, such as functional textiles and medical textiles. This need is therefore leading textile industries to take action by investing in cutting-edge technology such as microencapsulation, in order to achieve the desired finishes on textiles with the required properties, that would not be possible using another technology [28].

Nowadays, scientific advance is being used for the development of innovative textile products. Insect repellents [29], anti-cellulite treatments, long-lasting fragrances and skin softeners [30-32], medical applications such as antibiotics, hormones and other drugs [33-35] and antimicrobial agents for medical textiles [36-37] are some applications for which clothing manufacturers are applying to add value to the products. In particular, finishing a textiles with fragrances is an important commercial target and engineering challenge [38]. Developing new products with high-added value increases the competitiveness, improves market dynamics and may lead to economic growth of the industry [25]. «Cosmeto-textiles» is a new generation under garments and describe high-tech fabrics that

incorporate personal care ingredients, which can impart skincare benefits, combating ageing and promoting feeling of wellness or wellbeing, such as slimming, perfume or moisturizing. Cosmeto-textiles contain microscopic capsules of such ingredients. The core substance contained in the microcapsule is released instantaneously on textile by mechanical action such as abrasion, deformation, and friction and, consequently, the active agents are released on the skin (Figure 2.1).



Figure 2.1. Schematic representation of the release of the active agent on the skin.
1. Textile fibre; 2.Release of the active agent on the skin; 3.Binder.

2.2 Microencapsulation and techniques

Microencapsulation includes a number of different techniques that aim to involve small solid, liquid or gas particles with size between 50 nm and 2 mm (active agent) [39] with a natural or synthetic polymeric membrane [40]. The encapsulated material is also called internal phase, core material or fill, and the capsule wall is referred as coating, shell or membrane. Several materials are used in the coating: natural or modified polysaccharides, gums, lipids, protein materials and a large number of synthetic polymers. The structure of the microcapsules depends on the materials (core and capsule) and methods involved in its preparation. Figure 2.2 represents some of the possible morphologies.

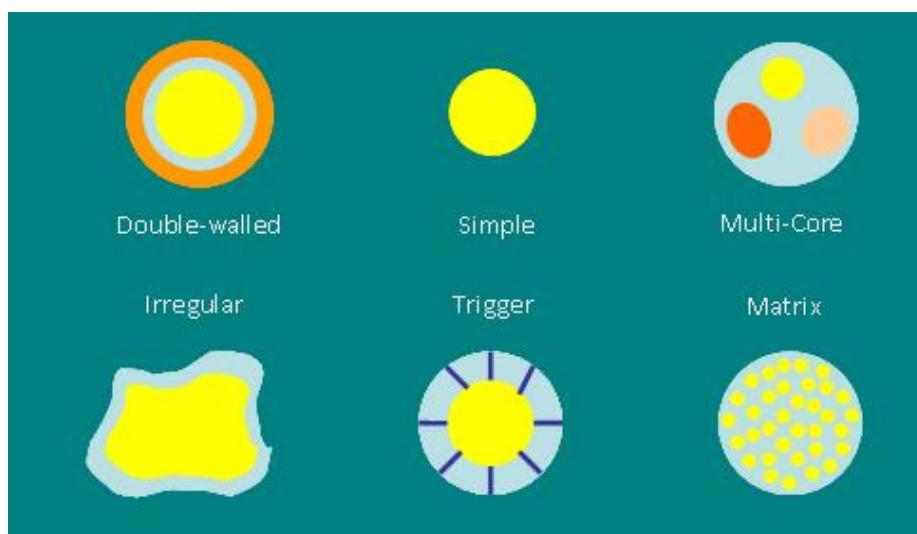


Figure 2.2. Microcapsules basic structures. (Courtesy of Ronald T. Dodge 2009)

The encapsulation is used to protect active agents, such as fragrances or anti-oxidizing materials, from oxidation caused by heat, light, moisture and exposure to other substances over their lifetime. It has been also used to prevent evaporation of volatile compounds and to control the release rate. The encapsulated agent can be released by many actions, such as: mechanical, temperature, diffusion, pH, biodegradation and dissolution [28, 41].

There are several techniques used for the production of microcapsules. The production method and shell material selection depend on product final application, considering physical and chemical stability, concentration, desired particle size, release mechanism and manufacturing costs.

Nowadays, microcapsules are widely spread and the production techniques vary from chemical, physicochemical to mechanical methods (Table 2.1). A brief description of some techniques is given below.

Table 2.1. Several techniques used for the production of microcapsules.

TECHNOLOGY	
Chemical/Physicochemical Processes	Mechanical Processes
Interfacial polymerization In situ polymerization Suspension polymerization Emulsion crosslinking Molecular encapsulation with Cyclodextrins Coacervation Processes based on supercritical fluids	Spray drying Fluid bed coating Extrusion

2.2.1 In situ polymerization

In situ polymerization is a chemical microencapsulation process in which the capsule shell formation occurs due to a polymerization process involving specific monomers/pre-polymers added to a stable emulsion formed between a continuous solution and an immiscible core material. The relevance of this technology is that no reagents are added to the core material. The polymerization occurs exclusively in the continuous phase (not miscible with the core material). Figure 2.3 shows the morphology of the microcapsules formed by in situ polymerization.

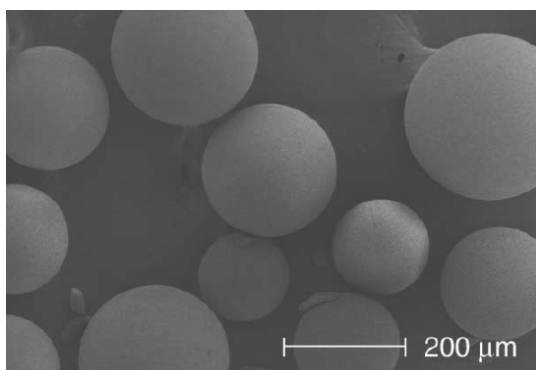


Figure 2.3. ESEM image of urea-formaldehyde microcapsules containing dicyclopentadiene core [42].

In situ polymerisation is used extensively to produce small capsules loaded with carbonless paper inks or perfume for scented strips. Examples of this method include urea-formaldehyde and melamine formaldehyde encapsulation systems and phase change materials [40, 42-49].

2.2.2 Emulsion crosslinking

Emulsion based preparation, also called emulsion stabilisation, or “emulsion crosslinking”, is a frequently used method for the preparation of protein- and polysaccharide-based microcapsules and microspheres [50-52].

This technology may be used for microencapsulate solid agents, as well as, soluble or insoluble liquids. The emulsions can be of two types: single and double emulsions. Particularizing, when using a biopolymer (usually water-soluble) to produce microspheres, the emulsions are of single type if the core material is water-soluble; and double if the core material is hydrophobic. Figure 2.4 represents a scheme of double emulsion technique.

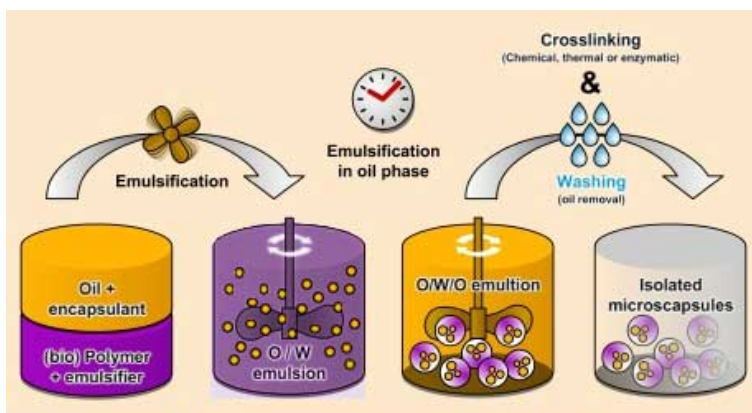


Figure 2.4. Process scheme for based emulsion technique [53].

Several biopolymers can be used in the production of microcapsules with this technique. Chitosan and polysaccharides in general are often used because they are biodegradable, abundant and therefore commercially interesting. Using this microencapsulating method it is possible to obtain small particles with controlled size.

The release of the active agents occurs mainly by diffusion, erosion or dissolution [51-52, 54].

2.2.3 Suspension polymerization

Suspension polymerization is a technique where polymerization is carried out in an aqueous phase. In suspension polymerisation the initiator is soluble in the monomer phase, which is dispersed into the dispersion medium by strong stirring and by the addition of stabilizers to initiate chain-growth polymerization and therefore occurring the formation of droplets [40, 55-59]. The polymer is obtained in the form of granules or beads, which may be dried and packed. Figure 2.5 shows SEM micrographs of a batch of microcapsules containing PRS® paraffin wax.

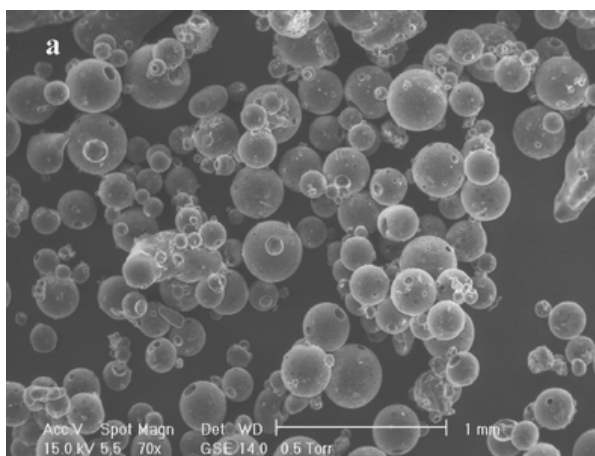


Figure 2.5. SEM micrographs of a batch of microcapsules containing PRS® paraffin wax [55].

2.2.4 Molecular encapsulation using cyclodextrins

Cyclodextrins are molecules with a ring structure and an internal cavity that makes them able to include guest molecules and therefore confer them new physicochemical properties [60-66].

Molecular microencapsulation alters the properties of incorporated molecules in many ways, concerning their solubilities, thermodynamics and transport properties. Furthermore, this technology can be valuable to isolate some compounds from natural products, enabling its use in different applications that need to enhance the drug bioavailability and drug formulation stability. Cyclodextrins are compounds made with sugar molecules organized in a ring and have a molecular form like a cone. They develop a hydrophobic cavity which is able to incorporate small or medium molecules. The size and molecular properties of cyclodextrins, influence the stability and properties of the incorporated molecules.

Microencapsulation with cyclodextrins has been used for several years in industry, such as pharmaceutical, chemical and textile and also in environmental research [66-68]. An example of this application is the incorporation of cyclodextrins in a textile fabric in order to remove the odour [69]. Because of the hydrophobicity of odour molecules they are sequestered in the cyclodextrins cavities and are thereafter removed during laundering. Figure 2.6 represents a scheme of the odor molecules being wrapped up in the cavities of the cyclodextrins and thereafter being removed during laundering.

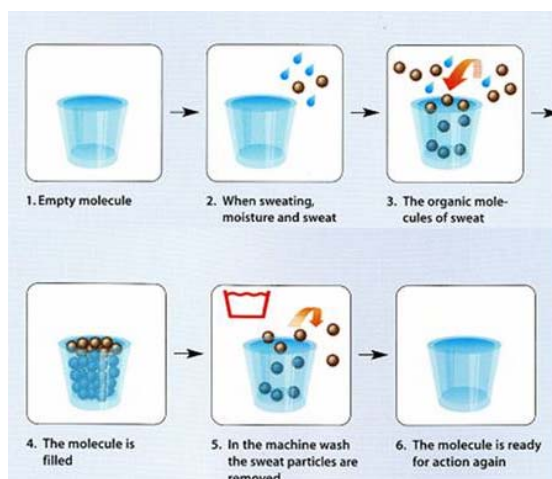


Figure 2.6. Scheme of odor molecules capture using cyclodextrins [70].

2.2.5 Processes based on supercritical fluids

Supercritical fluids, especially supercritical carbon dioxide (sc CO₂), have been used to develop new microencapsulation processes with the intention of entirely remove or minimize organic solvents use. They have been used at industrial scale, for example, in extractions and reactions. This technology has enormous advantages regarding microencapsulation, as it works in very mild process conditions, while other methods operate in more drastic conditions such as temperature, pH and require the use of solvent [71-75]. Carbon dioxide (CO₂) has

two important characteristics which are, the low critical temperature (31 °C) and the critical pressure (74 bar) (Figure 2.7). Due to its low critical temperature, CO₂ is the most common used supercritical fluid. The use of supercritical CO₂ has several advantages: CO₂ is abundant, non-flammable, colourless, odourless, non-toxic, and inexpensive. Therefore it can be applied in a broad range of industrial sectors. In addition, CO₂ has a unique behaviour that makes it very attractive for microencapsulation processes substituting the used organic solvents since its solvent power varies by changing conditions of temperature and pressure used [71]. The principal disadvantages of this technology are the high equipment and operation costs.

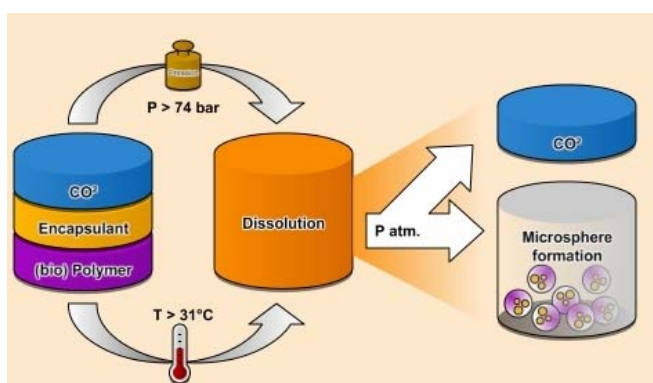


Figure 2.7. Scheme of encapsulation and microsphere formation using supercritical fluids [76].

2.2.6 Coacervation

Coacervation is a physicochemical process for microencapsulation and the most frequently used. It is also called phase separation. This technology appears in the 1950s by National Cash Register Company, USA, and was used to produce a two-component ink system for carbon less copy paper [77]. The concept is based on

the capacity of cationic and anionic water soluble polymers to interact in water thus forming a liquid polymer rich phase, called complex coacervate [78-89].

Two types of coacervation exist, simple and complex, depending of the type of separation mechanism in the aqueous phase. In the first case, the polymer is formed by changing temperature, by electrolytes action, or by desolvation by addition of a water miscible nonsolvent. In the second case, the polymer is formed by combination of oppositely charged polyelectrolytes in aqueous media. Coacervation is affected by pH, ionic strength, temperature, molecular weight, and concentration. Figure 2.8 shows the spherical shape of polylactide (PLA) microcapsules with thyme oil by optical microscopy.

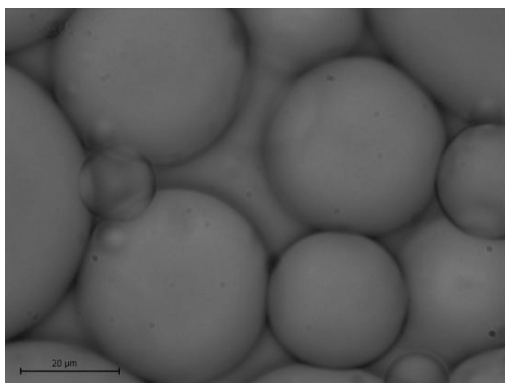


Figure 2.8. Microcapsules containing thyme oil obtained by coacervation (optical microscopy with magnification of 1000x) [90].

There are various patents where coacervation is used for the microencapsulation of fragrances and perfumes [3-4, 78-80, 90-95]. The polymeric structures generally used in coacervation have low molecular mass, and the resulting microcapsules have weak mechanical resistance.

2.2.7 Spray drying

Spray drying is a mechanical microencapsulation method developed in the 1930s, specially popular within the food industry as it is economical, fast and produces good-quality material at bulk scale [96]. The spray-drying encapsulation process is simple and similar to a one stage drying process. Firstly, an emulsion is prepared by dispersing the core material, usually an oil or active ingredient immiscible in water into a concentrated solution of wall material until the desired size of oil droplets are attained. The resultant emulsion is atomized into a spray of droplets by pumping the slurry through a rotating disc into the heated compartment of a spray drier. Then the water portion of the emulsion evaporates, yielding dried capsules of variable shape containing scattered drops of core material. A spray dryer layout is shown on Figure 2.9. The capsules are collected through continuous discharge from the spray drying chamber [97-98].



Figure 2.9. A spray dryer layout from Gea Process Engineering Inc [99].

Together with the fact that it represents a rather cheap alternative since production of beads is not necessary, the major advantage of spray-drying is that heat-labile substances can be encapsulated due to the relatively low core temperatures reached.

2.2.8 Fluid bed coating

Another example of mechanical microencapsulation method is fluid bed coating, which can only be applied when the core material is a solid, or a liquid absorbed into porous solids. This technique is used extensively to encapsulate pharmaceuticals. With the increasing number of pharmaceutical sustained release products on the world market, there is also an increasing need for reliable processing equipment, warranting perfect reproducibility of the process parameters and therewith of the film morphology [100-102].

This technology is well-known, and it owes to its optimal heat and mass exchange that enables a rapid and efficient evaporation of the liquid. The liquid transports the coating material to the surface of the substrate, if the latter is a powder, a granule, a pellet or a tablet. Whenever a solid particle to be encapsulated passes through the coating zone, small patches of coating material are applied, until the entire surface has been covered. Droplet formation, spreading, and evaporation occur almost simultaneously during the process. Below on Figure 2.10 is a scheme of the fluidized bed principle.

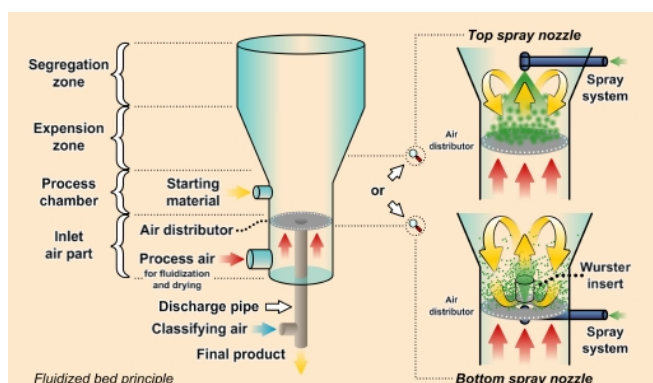


Figure 2.10. Scheme of the fluidized bed principle [103].

The process of suspending, spraying, and cooling is repeated until the capsules walls reached the desired thickness.

Usually, air atomized spray nozzles are used for all fluid bed film coating options, as the atomization air allows better control of droplet size compared with airless nozzles. Common target of each option is also to minimize droplet travel distance for uniform and optimal spreadability.

2.2.9 Extrusion technology

Industrial applications of extrusion process appeared in 1930. In subsequent years this technology has been developed mainly focusing the plastics processing industry. Extrusion was also applied to other fields, for example, to produce controlled release formulations (Figure 2.11). The principle of encapsulation using extrusion is that the active agent dissolved in the extruded material will be entrapped after cooling [104-109].

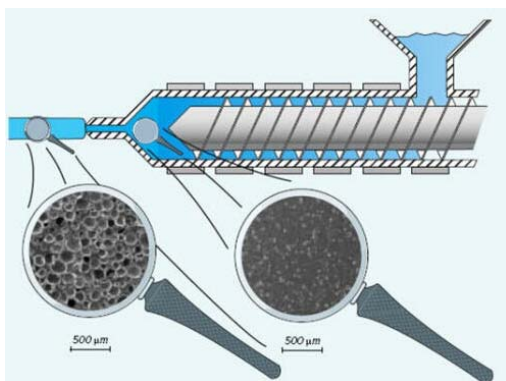


Figure 2.11. Schematic representation of an extruder for microencapsulation [110].

The extrusion process is effective for a wide range of encapsulated products such as pharmaceuticals. The control release of the active agent can be obtained using the right formulation.

2.2.10 Interfacial polymerization

The interfacial polymerization technique is described more detailed since it was the technique adopted in this study.

Interfacial polymerization is based on a polycondensation reaction and is usually assumed as a simple technique to obtain the capsule wall. It consists in making an emulsion of two non-miscible phases, each one containing a dissolved monomer(s) able to react with the monomer(s) present in the other phase. After the initial formation of the wall, the polycondensation reaction is diffusion controlled. As a consequence, the polymer formation is the result of an interfacial reaction between the monomers, leading to the formation of capsules-like particles. The size of the formed microcapsules (Figure 2.12) depends on the initial emulsion droplets size [29-30, 111-123].

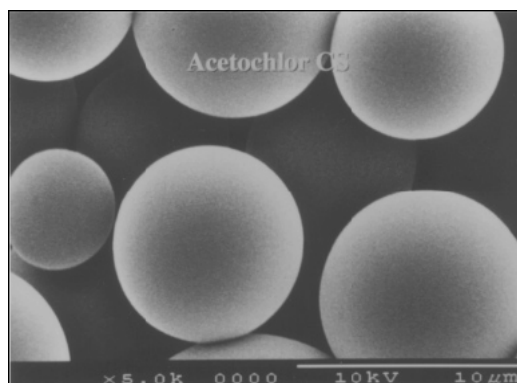


Figure 2.12. SEM photographs of microcapsules produced by Interfacial Polymerisation [124]

Depending upon the type of the primary emulsion (o/w or w/o), hydrophobic and hydrophilic agents could be encapsulated, respectively. The size of these capsules ranges from 2 to 2000 μm . Nanocapsules can also be obtained by interfacial polymerization [125].

Technology

Interfacial polymerization uses two sets of monomers which are able to react with each other. Before the emulsifying step of the encapsulation process one of the monomers is solubilised in the dispersed phase (oil or water phase, depending on the type of encapsulated active substance). Then, a co-monomer (soluble in the continuous phase) is added to the emulsion and the proper reaction conditions are settled in order to promote the wall formation until the total (or almost total) depletion of the monomer putted inside the droplets (dispersed phase).

A general outline of the process, for the case where an oil active substance is encapsulated, is shown in Figure 2.13 and can be described as consisting on three steps:

Step I: formation of an oil-in-water (o/w) emulsion;

Step II: formation of the coating (interfacial reaction between the added monomers),

Step III: stabilization of the coating – maturation.

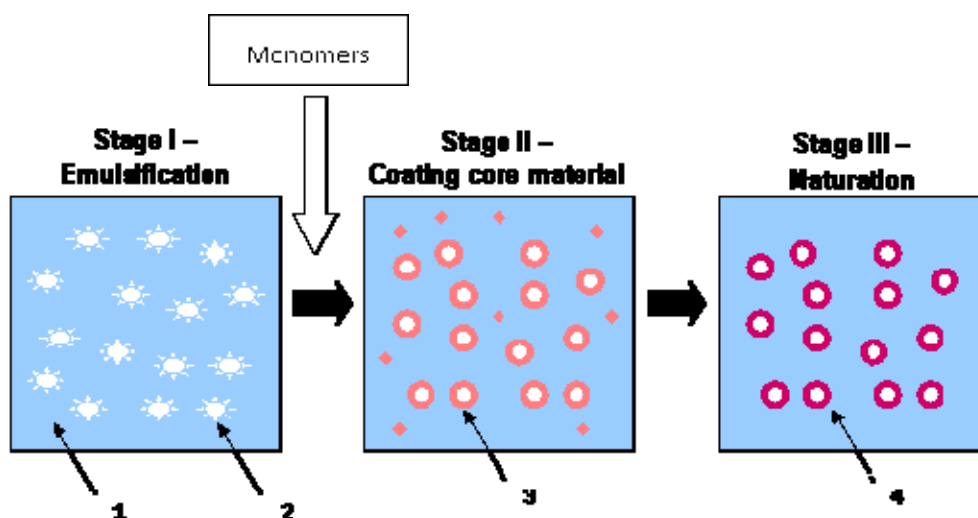


Figure 2.13. General process scheme for microcapsules preparation by interfacial polymerisation. 1) Aqueous phase with a protective colloid, 2) oil active principal with monomer A; 3) formation of the wall material at the interface due to the reaction of monomer A with monomer B (added to the continuous phase); 4) formed microcapsules.

Limitations and application

Depending on the technique used to produce the emulsion, interfacial polymerization could generate a heterogeneous mixture of microcapsules in terms of size. This is particularly valid if an ultraturax system is used. Interfacial polymerization should also be used with criterion, since any reaction of the

monomers with the functional groups present in the active principal should be avoided.

Interfacial polymerization is used to encapsulate different active agents, such as vitamins, UV filters, perfume, oils, insoluble, water-soluble, oil-soluble compounds and ingredients for drug delivery (cosmetic, dermocosmetic, pharmaceutical agents, etc).

Polymers

Various monomers can be used in this process to promote the wall formation and generate polymers like polyesters, polyamides, polycarbonates, polyureas and polyurethanes. The large number of polymer possibilities that can be used, allows the diversification of microcapsule wall properties (permeability, resistance and adhesion onto substrates).

The majority of the available commercial microencapsulated fragrance systems for textile applications are based on formaldehyde systems (phenol-formaldehyde or melamine-formaldehyde resins), which are facing several restrictions under the present environmental policies. In such context, polyurethane-urea systems appear as a more attractive environmental friendly solution [126-131]. Moreover, they are known as versatile polymer systems which can be tailor-made from a wide range of raw materials in order to achieve the desired physical chemical and mechanical properties. However, polyurethane-urea systems must be designed and optimized taking into consideration the particularities of the active principle to be encapsulated.

Polyurethanes have been used in a variety of applications since they are one of the most versatile materials in the world today. Those polymers represent an important class of thermoplastics and thermoset polymers. Due to the excellent physical properties and good compatibility polyurethanes are used in many industrial applications (coatings, adhesives, sealants and elastomers used on floors

and automotive interiors) and also for the development of biomedical devices or drug delivery systems [59, 111, 129-135].

Polyurethanes result from the reaction between isocyanates and alcohols. If we use di-functional monomers, linear polyurethanes will be formed as shown in the example below. Poly-functional monomers will give rise to reticulated structures. Figure 2.14 shows the reaction scheme for urethane formation.



Figure 2.14. Reaction scheme for urethane formation.

During polyurethanes polymerization, amines can be introduced, resulting on ureas or polyurethanes/ureas as shown in Figure 2.15:



Figure 2.15. Reaction scheme for ureas or polyurethanes/ureas formation

Isocyanates also react strongly with water. This could be a parasite reaction or induced in order to origin ureas as represented in Figure 2.16:

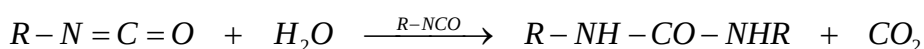


Figure 2.16. Reaction scheme for ureas formation.

Polyurethanes are a large family of products due to the different types of isocyanates and polyols that can be chosen. Isocyanates can be classified in two major families (aromatic and aliphatic) while the majority of the polyols are of polyester or polyether type. Figure 2.17 shows examples of isocyanates and Figure 2.18 examples of polyols.

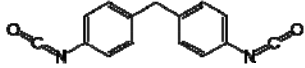
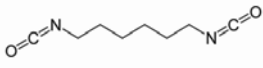
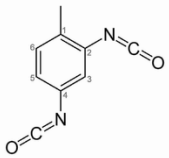
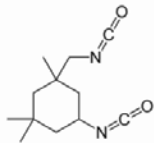
AROMATIC	ALIPHATIC
 MDI 4,4'-methylene diphenyl diisocyanate	 HMDI Hexamethylene-diisocyanate
 TDI Toluene diisocyanate	 IPDI Isophorone diisocyanate

Figure 2.17. Chemical structure of aromatic and aliphatic isocyanates.

Aliphatic isocyanates are used predominately in coating applications because they produce polyurethanes with excellent UV resistance and exterior durability. In comparison to aromatic isocyanates the aliphatic isocyanates are less reactive towards polyols.

Aromatic isocyanates, like toluenediisocyanate (TDI) and methylenediphenyl diisocyanate (MDI) represent the largest market for diisocyanate monomers. These isocyanates give rise to polyurethanes with better mechanical properties and are used in polyurethane foams, elastomers, adhesives and coatings.

For microencapsulation purposes aliphatic isocyanates are generally preferable since they are less reactive, including with the surrounding water phase. To favour the reaction with the polyol (urethane formation) a catalyst is usually added.

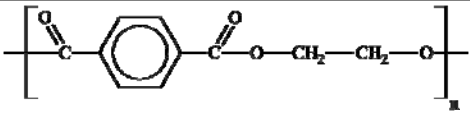
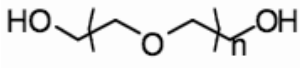
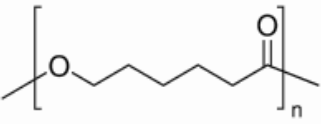
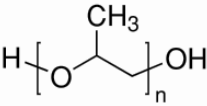
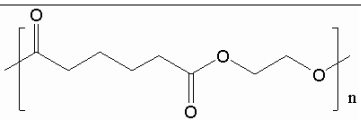
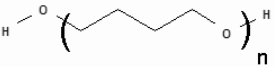
POLYESTHER	POLYETHER
 PET Polyethylene terephthalate	 PEO Poly(ethylene oxide)
 PCL Polycaprolactones	 PPO poly(propylene oxide)
 PA Polyadipates	 PTMO poly(tetramethylene oxide)

Figure 2.18. Chemical structure of polyester and polyether polyols.

Polyol is a compound with a high molecular weight comprising two or more hydroxyl groups. The most widely used polyols are of polyester and polyether type. Poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO) and poly(tetramethylene oxide) (PTMO) are examples of polyether polyols.

Polycaprolactones (PCL), polyadipates (PA) and polyethylene terephthalate (PET) belong to polyester type.

The chain extenders are used to extend the size of the hard segments and increase the density of hydrogen bonds. The most important commercial chain extenders include 1,4-butanediol (BD), ethyleneglycol (EG) and 1,6-hexanediol (HD).

2.3 Selection of “target perfumes” for encapsulation

The complexity of perfumes microencapsulation derives from the fact that fragrances and perfumes, in general, possess terminal groups such as -OH, -NH, -C=O, -CHO or -COOH. Its partial solubility in water, as described in some patents [136-139], leads to great instability in the microencapsulation process by interfacial polymerization. These chemical groups surround the wall of the microcapsule, modifying the hydrolytic stability of the particle and destabilizing the polymerization reaction. Moreover, several of these reactive groups can react with the monomers during the interfacial polymerization, leading to microcapsules formation that might modify the properties of the fragrances and perfumes. Microencapsulation systems using interfacial polymerization, in spite of its versatility and strengths, need to be designed taking into account the above mentioned restrictions. The chemical system might be defined trying to avoid or minimize these undesirable secondary reactions.

Essential oils are oily substances which are not soluble in water, with a complex and rather variable composition. They are obtained from natural products through extraction (with solvents), distillation, squeezing. The essential oils are the base of the manufacture of natural aromas.

2.3.1 Perfumes structure – Fragrances pyramid

The perfume ingredients are classified in three types of perfumed notes according to their volatility (Table 2.2):

- (i) Top Notes: more volatile components; they are noticed after the application of the perfume and last for a short time (30 seconds to some minutes). Examples are: Lemon, mint, grass;
- (ii) Middle Notes: these fragrances give the main character to a perfume; they are detected soon after the disappearance of top notes and can last some hours. Examples include flower and fruity odours;
- (iii) Base Notes: these fragrances can last for many hours and are used as fixative of the whole perfume, since they lower the volatility of top and middle notes. Examples are woody, musk, vanilla aromas.

Table 2.2. Classification of perfume notes according to their volatility

NOTE	CHARACTERISTIC	COMPOSITION	DURATION
Top	1 st impression	15-20%	minutes
Middle	recognition (heart)	30-40%	4-6 hours
Base	fixative and reminiscent odour	45-65%	+ 8 hours

The pyramid structure of perfume (Figure 2.19) suggested by Carles [139] is divided in three parts; each one representing top, middle and base notes. The recommended Carles ratios for each fragrant note are: top, 15-20%; middle, 30-40%; and base, 45-55% [140-141].



Figure 2.19. Classical perfume pyramid structure.

2.3.2 Fragrance family – Types of perfumes

There are several classifications of perfumes based on household characteristics. Figure 2.20 represents one of these classifications, men's fragrance, produced by the company Dragoco.

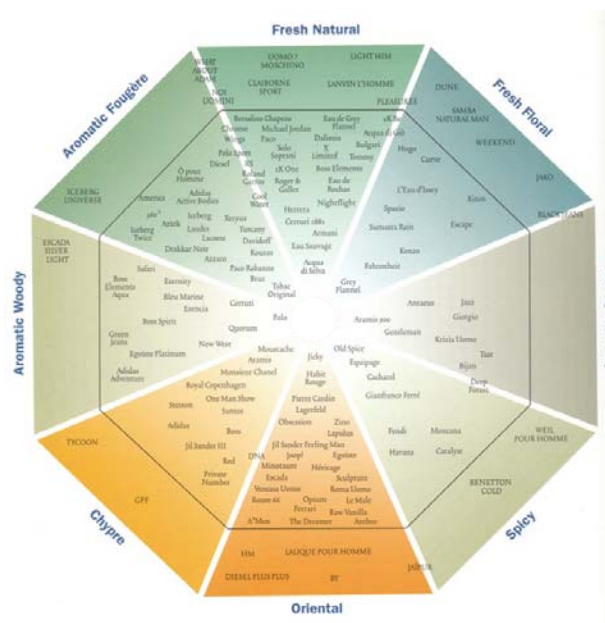


Figure 2.20. Example of classification methodology in men's fragrance families

2.4 Encapsulation techniques in textile industry

2.4.1 Patent review

Encapsulation techniques allow an opportunity for variable fragrant finishing that can favour the durability [94]. This innovative technology makes use of microcapsules which act as small containers of liquids to be released from the inner core under controlled conditions to address a specific purpose.

There are a number of patents relative to microencapsulation of flavours and fragrances with different applications. Table 2.3 presents a summary of the patents related to textile applications.

Table 2.3. Patented processes for microencapsulation of flavours and fragrances and applications in textile industry.

PATENT ASSIGNEE	PROCESSES SUMMARY
Arcade, Inc (1991) [94]	Methods for preparing microcapsules with perfume oil. Microcapsule wall is made of polymeric material of ethyl cellulose.
Aero, Kemicna, Graficna in Papirna Industrija, D.O.O. (1996) [7]	Preparation of microcapsule (melamine-formaldehyde or urea-formaldehyde) emulsion, coating and impregnation of carrier with microencapsulated scents.
Givaudan Roure (International) SA (2000) [78]	A coacervation procedure for encapsulation of an amphiphilic flavour or fragrance using a hydrogel shell and an oil core.

(Cont.)

(Cont.).

PATENT ASSIGNEE	PROCESSES SUMMARY
3M Innovative Properties Company (2001) [142]	Methods for producing microbeads of hydrogel (polysaccharides or synthetic polymers) to immobilize water soluble and water insoluble active principles (oils, fragrances and agricultural chemicals such as pheromones and insecticides).
Sara Lee Corporation (2002) [142]	Processes for applying microcapsules to textile materials and textile materials containing microcapsules. Provides techniques for treating a textile material with microcapsules, particularly interest for applying microcapsules to textile material such as fine denier hosiery, including hosiery comprising nylon.
Bayer Corporation (2002) [143]	Method for production leather or textile substrates with scent-containing microcapsules. The microcapsule wall contains reaction products of guanidine, polyamides and polyisocyanates.
Firmenich SA (2003) [144]	Method for the preparation of extruded delivery systems advantageous for the controlled released of an active hydrophobic principle such as flavours or perfumes.
Centre National De La Recherche Scientifique (CNRS) (2004) [145]	Microencapsulation techniques to encapsulate oil substances or sugars. The microcapsules can be used in therapeutics or in cosmetics.

(Cont.)

(Cont.).

PATENT ASSIGNEE	PROCESSES SUMMARY
The Hong Kong Polytechnic University (2004) [146]	Microencapsulation of phase-change paraffins using melamine-formaldehyde shell. The microcapsules were coated on textile fabrics to improve thermal regulation function.
BASF Aktiengesellschaft (2006) [146]	Production of microcapsules dispersion; the capsule core comprises a water soluble organic substance, such as water soluble dyes and the capsule wall is composed basically of polyureas.
Firmenich (2006) [119]	Method for producing microcapsules of 40-1000 nm containing fragrances: the shell is formed from the reaction between isocyanates, diols and diamines.
Firmenich (2007)[147]	Perfuming ingredient in microcapsules with a guanidine based poly-urea or poly-urea/polyurethane wall.
Universidad de Castilla-la-Mancha (2007) [148]	Microencapsulation process of phase change paraffins based on free radical polymerization. The wall materials are polystyrene and poly(styrene-co-methyl methacrylate)
Acciona Infraestructuras, S.A. (2009) [149]	A process for producing microcapsules containing phase-change materials by spraydrying. Paraffins are microencapsulated using polyethylene, and ethyl vinyl acetate (EVA) as encapsulating agents.

Adding fragrances to textiles has been carried out for long time in the form of fabric conditioners in the wash and during tumble-drying. However, no matter the quality of the technique used to integrate the fragrance its effect is relatively short-lived, only surviving one or two wash cycles. Microencapsulation offers the possibility to overcome this constraint prolonged the durability of the applied fragrance. The encapsulated fragrance is released from the textile by breaking the microcapsule shell. When the size of microcapsules is higher, easier is the release of fragrance.

2.4.2 Application of microcapsules on textile industry

The microcapsules can be applied by stamping works, exhaustion, impregnation, spraying, coating or by incorporation in the fiber without modifying its sensation and colour [33]. In this work, microcapsules were impregnated into the fabrics on the finishing process using a foulard as represented on Figure 2.21 followed by drying and curing steps.

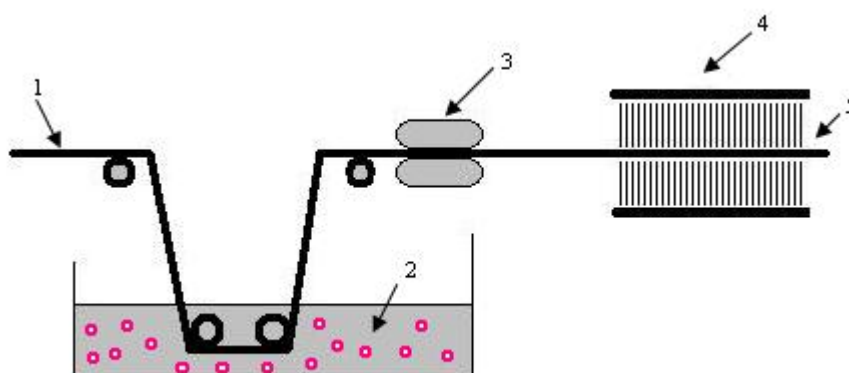


Figure 2.21. Schematic representation of the microcapsules application in fabrics using a Foulard. 1. Untreated fabric; 2. Microcapsules bath; 3.Squeezing; 4.Drying and curing; 5. Fabric treated containing microcapsules.

A crosslinking agent is required for the impregnation of microcapsules into the fabrics. This is the component that forms the continuous film, adherent to the substrate, and holds the microcapsules in the fabric [29, 150]. Crosslinking agents can be acrylic, polyurethane, silica, etc. Its function is to fix the microcapsules in the tissue and to keep them fixed during laundering. Several kinds of fabrics can be impregnated with microcapsules as silk, cotton or synthetic fibres (polyamide or polyester).

The processes for applying microcapsules to textile materials can be described as follows: (1) microcapsules are initially introduced in the textile material (without crosslinking agent) by means of using a dispersant to disperse the microcapsules around and through the textile material followed by the addition of a crosslinking agent to promote adhesion of the microcapsules to the textile material or (2) the microcapsules are applied during the finishing process of textiles fabrication using a foulard, in which the textile to be treated is impregnated using a finishing bath containing microcapsules, a softener and a self-crosslinking agent [32]. Taking into account the type of application the microcapsules have to fulfil specific requirements, such as resistance to abrasion and dry cleaning wash cycles [28].

Resistance of the microcapsules to washings

The use of fragrance microcapsules on textiles has been carried out for many years. However, no matter the type or quality of the technology used to impart the fragrance, the effect is relatively short. Numerous attempts have been made on processes but microcapsules still don't remain on textiles after a few washes. During the washing, the chemical action, the mechanical action and the temperature can cause a dramatic reduction of the microcapsules on textiles and consequentially a reduction in the desired effect.

Several externalities limitations are responsible for the shelf life of fragrance effect and they can be divided in two important groups. The first one is the group that encloses the factors that are responsible for the durability of the effect, and they can vary from water (hardness, quality), light exposure, organic solvents used in washing. The second one is the group that encloses the factors with limitative character, such as mechanical resistance or ironing.

Figure 2.22 represents some of the critical factors raised by the new product development and that may prolonged the life cycle:

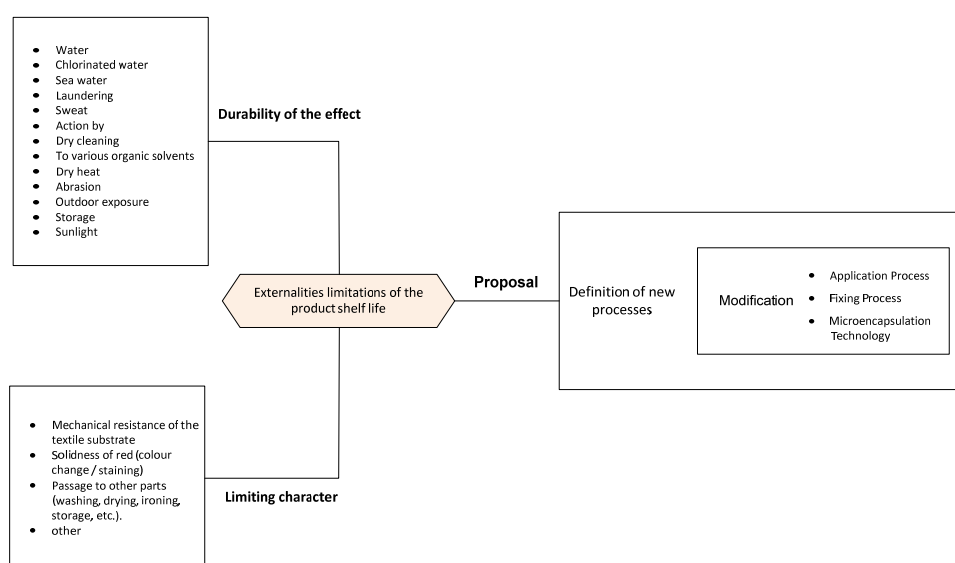


Figure 2.22. Critical factors of new product development (adapted from Scentfashion project report [151]).

It should also be mentioned other constraints for the application of fragrances microcapsules to textile substrates (Figure 2.23), raised by the production process: The microencapsulation process must consider more carefully the desired products of textile industry and specifically design microcapsules that overcome these limitations.

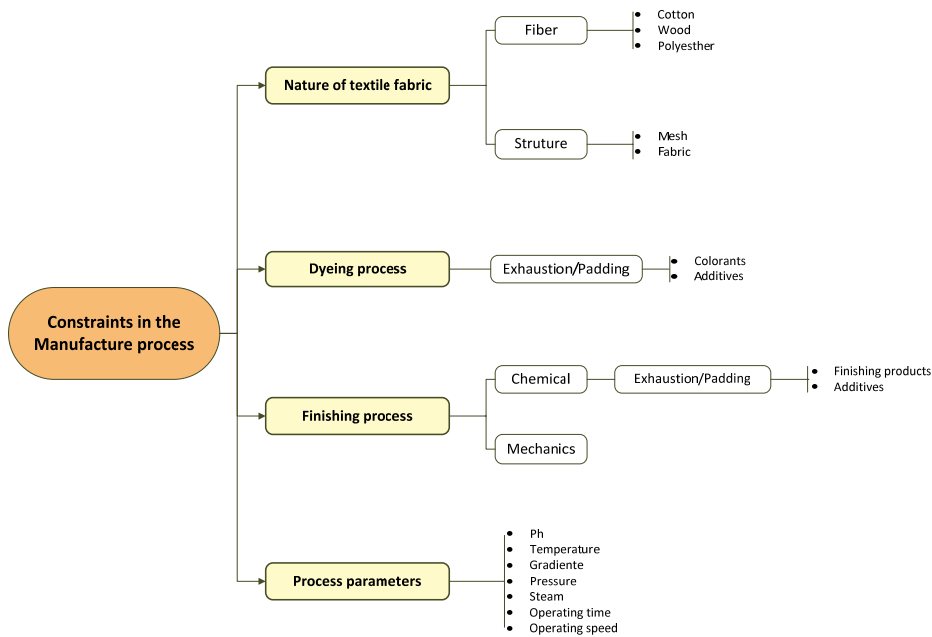
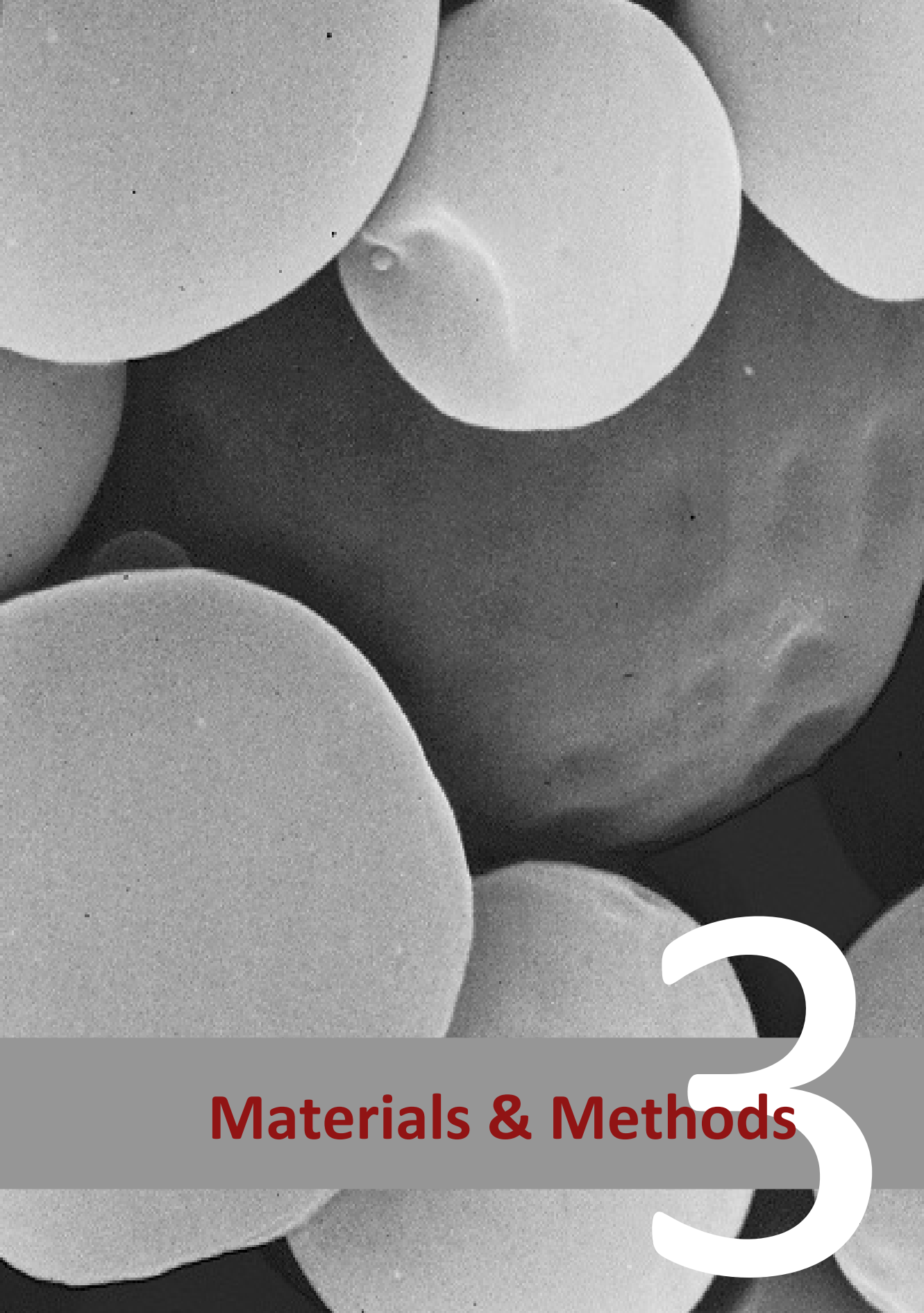


Figure 2.23. Fragrances microcapsules application conditioning factors on textile substrates (adapted from Scentfashion project report [151]).

The microencapsulation process must consider more carefully the desired products of textile industry and specifically design microcapsules that overcome these limitations.

In this thesis the preparation via interfacial polymerization of polyurethane/urea microcapsules containing limonene and perfume and its application on fabrics is addressed. It is an example of Product Engineering [23-27, 152] approach starting from market *needs* (perfumed suits for man) up to the *manufacture* of microcapsules after *selection* of a microencapsulation technique and shell material among various possibilities.

The target of this research is the production of perfumed textiles which have to meet required specifications. Various steps are involved: fabrication of microcapsules with the active agent, impregnation of the textile with microcapsules and binder and testing the final product.



Materials & Methods

3

In this chapter the encapsulated active agents and chemicals used for the production of the microcapsule wall are listed. The experimental facilities to produce polyurethane-urea microcapsules and impregnate textile substrates are described. The experimental techniques for the characterization of microcapsules and fabrics are reviewed.

3.1 Chemical compounds and reagents

Two kinds of active agents have been encapsulated:

- Limonene (lemon scent - LMN) (Sigma Aldrich, ref. 183164)
- Perfume, Woody-Musk-White Flowers
 - o Limonene (lemon scent - LMN) (Sigma Aldrich, ref. 183164);
 - o Methyl cedryl ketone (vetiver scent – MCK) (Sigma Aldrich, ref. W522805);
 - o Methyl dihydrojasmonate (jasmine scent - MJD) (Sigma Aldrich, ref. W340804);
 - o 1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]-2-enopyran solution (galaxolide); 50% in diethyl phthalate (dep) (musk scent) (Sigma Aldrich, ref. W520608).

Polyurethane-urea capsule wall:

- Isocyanate: Hexamethylene-1,6-diisocyanate isocyanate (HMDI) (Bayer, Desmodur W)
- Polyol: polyethylene glycol 400 (PEG400) (Sigma-Aldrich, Ref. 81170)

- Amines: Etilenodiamine (EDA) (Panreac, Ref.121869) and hydrazine monohydrate purum (HYD) (Sigma-Aldrich, REF.53850)
- Catalyst: dibutyl tin dilaurate (DBDTL) (Sigma-Aldrich, Ref. 291234)
- Protective colloid: polyvinyl alcohol (PVA) (Celanese Chemicals, Celvol 840)
- Emulsifier: Tergitol 15-S-9 (Dow Company), Tergitol 15-S-20(Dow Company), Triton CA (Dow Company), Renex 95 (GAP Químicas Lda), Ultramina 200 (Oxitenó), Span 85 (Flurka, ref. 85549), Tween 20 (Sigma-Aldrich, Ref. P1379)
- Ethanol (Merck Schuchardt OHG, Ref. 1.00983.2511)
- Acetone (Panreac, Ref. 131007)

3.2 Experimental facilities

3.2.1 Microcapsules production

The microencapsulation reaction was performed using a IKA® LR-2.ST system (Figure 3.1). It is a modular miniplant reactor system planned and designed to simulate and optimize chemical reaction processes as well as mixing, dispersion and homogenization processes at a model scale with a maximum volume of 2l.

The medium in the reactor vessel can be heated up to 230 °C. Vacuum operation is possible up to 25 mbar.

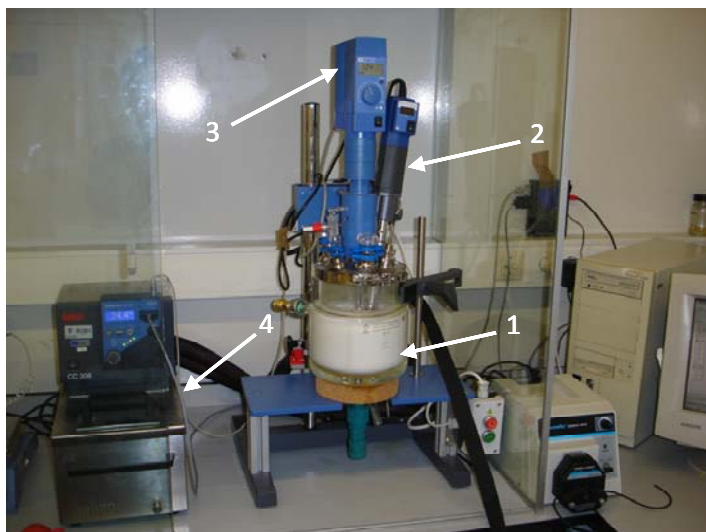


Figure 3.1. Experimental set-up for the production of microcapsules by interfacial polymerization: (1) reactor vessel; (2) ultraturrax; (3) overhead stirring drive and (4) thermostatic bath.

The reactive system is composed by the following components:

1. Reaction system:
 - 1.1. Reactor base of type LR-2.ST
 - 1.2. Reactor Vessel in double-walled glass with bottom outlet valve- Type LR 2000.2
2. Homogenization system:
 - 2.1. Ultra-Turrax type T25 digital
 - 2.2. Component of dispersion-type S 25 KV - 18 G
3. System for heating and temperature control:
 - 3.1. Thermostatic bath from Hubel type CC3-308
4. Data acquisition and control:
 - 4.1. Software LABWORDSOFT

3.2.2 Impregnation of microcapsules on textile substrate

Microcapsules were applied to textiles at laboratory scale - using a laboratory scale Foulard from CITEVE reproducing the industrial application conditions - and at industrial scale - using the industrial facilities of A PENTEADORA S.A. A Foulard system is an equipment generally used to perform finishing treatments to the textile substrates. Important substrates, such as: dyes, pigments and other finishing products, including microcapsules, can be applied using this methodology.

The textile to be treated is impregnated using a finishing bath containing microcapsules, a softener and a self-crosslinking substance, as represented on Figure 3.2 a), followed by drying at 100°C during 3 minutes and curing at 140°C during 3 minutes, as represented on Figure 3.2 b).

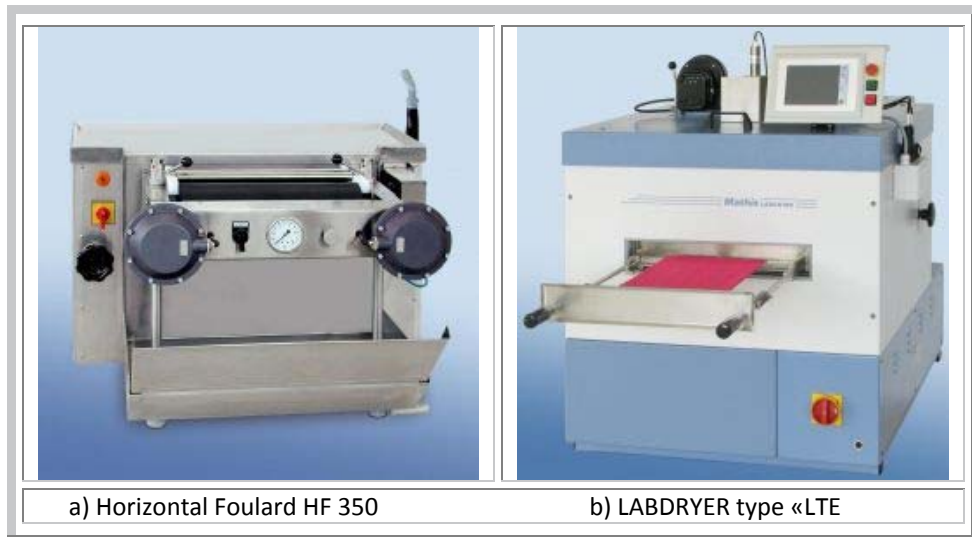


Figure 3.2. a) Laboratory horizontal foulard; b) Laboratory dryer [153].

The textile substrates used in the impregnation tests were supplied by A Penteadora S.A., and their composition is 60% wool, 38% polyester and 2% elastane.

Figure 3.3 shows some pictures of the industrial Foulard (from A Penteadora, S.A.) taken during the impregnation process of scented microcapsules. In Figure 3.3a) it is shown the whole foulard equipment. In green the bath container can be seen. In Figure 3.3b) it is visible the oven where the microcapsules are thermofixed and cured on textiles. Figure 3.3c) shows the finished impregnated textile.



Figure 3.3. Several views of the industrial Foulard during the impregnation process of scented microcapsules. a) Overview of the Foulard; b) View of the fabric entry in the oven for the thermofixing and curing steps. c) View of the output of the final fabric with impregnated microcapsules.

3.2.3 Binder selection

Textiles impregnation with microcapsules has been evaluated with two commercial binders: Primal ECO 934 TK (an acrylate emulsion, from Horquim) and Peripret Plus (a polyurethane emulsion, from Bayer). The tests were done with commercial microcapsules of mint (Horquim). Quantification of the flavour was done by GG-FID-Headspace and validated by a panellist created by CITEVE.

The solidness of the flavour, i.e. the strength of the aroma present in the impregnated textiles, was performed according to the number of dry washes and the number of abrasion cycles. Thus textile samples subjected to 0, 1, 2, 3, 4 and 5 dry washes were analyzed as well as samples subjected to 3000, 6000 and 9000 abrasion cycles.

The impregnation bath was prepared with 10 g/L of microcapsules, 10 g/L of softener (Perisoft SML) and 50 g/L of binder.

Acrylate binder (Primal ECO 934 TK)

Figure 3.4 shows the evolution of the mint odour as a function of the number of dry washes (0-5 washes). From the analysis of the FID chromatograms we can observe a more prominent peak that was identified as menthol, which is the main component of the mint aroma. As the number of dry washes increases, the presence of menthol in the textiles decreases.

In order to quantify the GC-FID-headspace analysis the relative weight of menthol present in the washed textiles, expressed as the amount of methanol present in the analysed textile (x_{mint}) relative to initial amount of menthol present in the textile without washing (x_{mint_0}), was determined. As it can be seen from Figure 3.5, a loss of menthol aroma is progressively noticed as a function of the number of washes. More precisely, after 5 dry washes only 35% of the initial mint aroma persists, i.e., a loss of 65% has been observed.

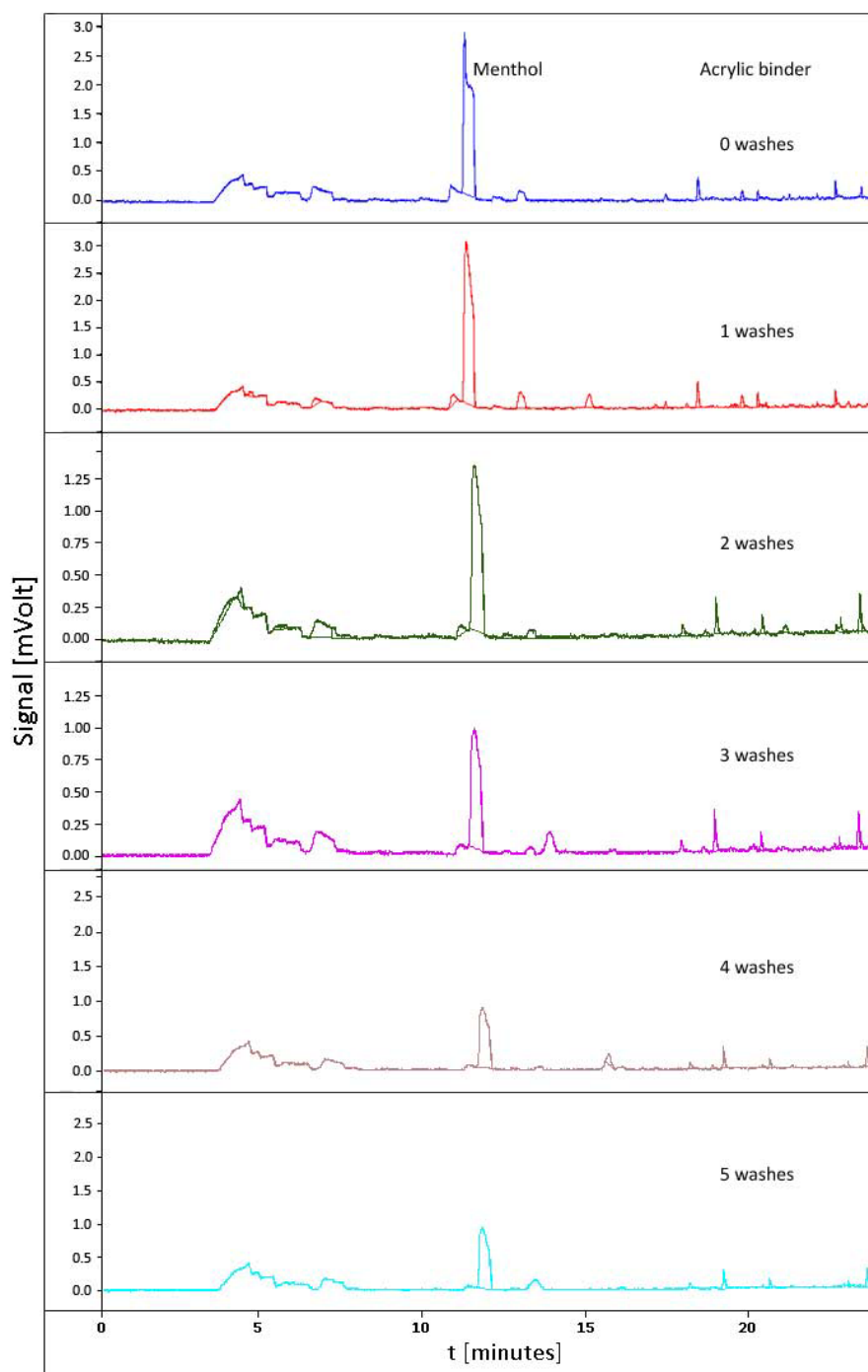


Figure 3.4. FID chromatograms of the textiles impregnated with mint microcapsules (Horquim) using the acrylic binder after 0, 1, 2, 3, 4 and 5 washes.

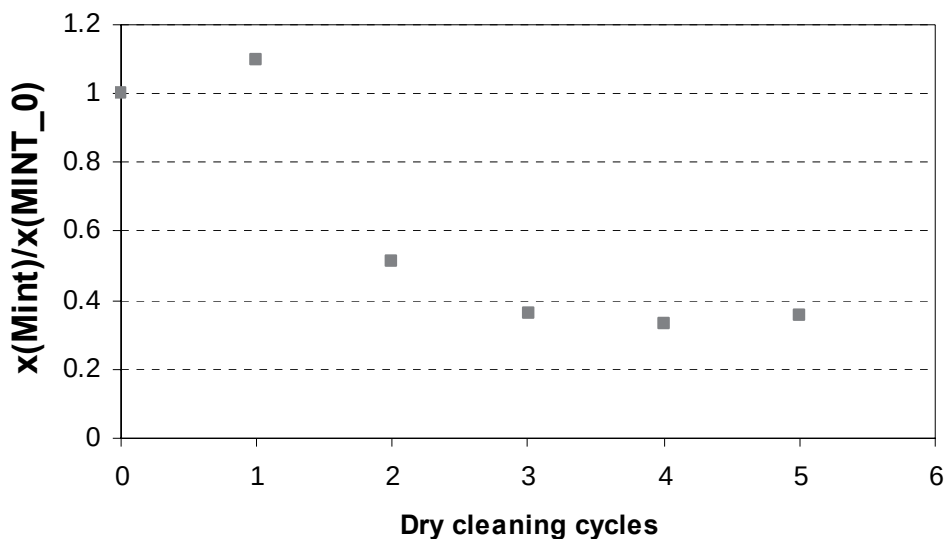


Figure 3.5. Relative weight of menthol present in the textiles impregnated with mint microcapsules using the acrylate binder, as a function of dry washes number.

Figure 3.6 shows the analysis performed with the impregnated textiles subjected to different number of abrasion cycles (3000, 6000 and 9000 cycles) as well as the analysis of the original impregnated textile. It can be observed that the presence of menthol remains almost constant up to 6000 cycles, nevertheless a sharp decrease was observed for 9000 cycles.

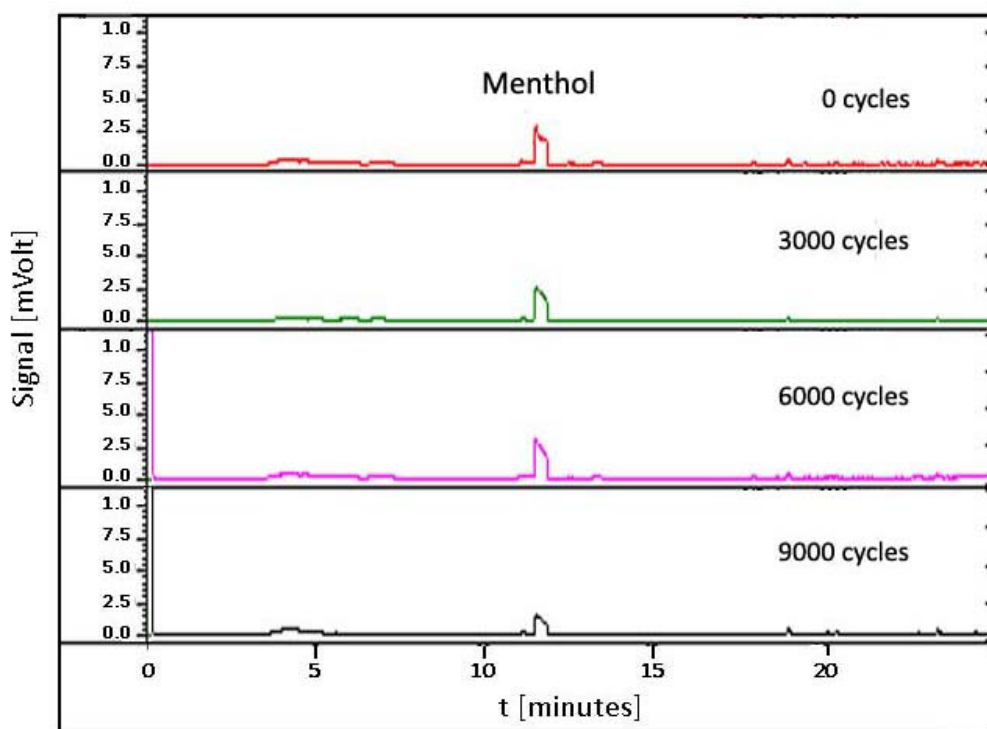


Figure 3.6. FID chromatograms of the textiles impregnated with mint microcapsules (Horquim) using the acrylate binder after 0, 3000, 6000 and 9000 abrasion cycles.

In order to quantify the headspace analysis the same methodology used before was applied, i.e., the relative weight of menthol as a function of the abrasion cycles number was calculated. The results obtained are presented in Figure 3.7. It can be noticed that the loss of odour is minimal after 3000 and 6000 abrasion cycles (only 1%) but it increases to 52% after 9000 cycles.

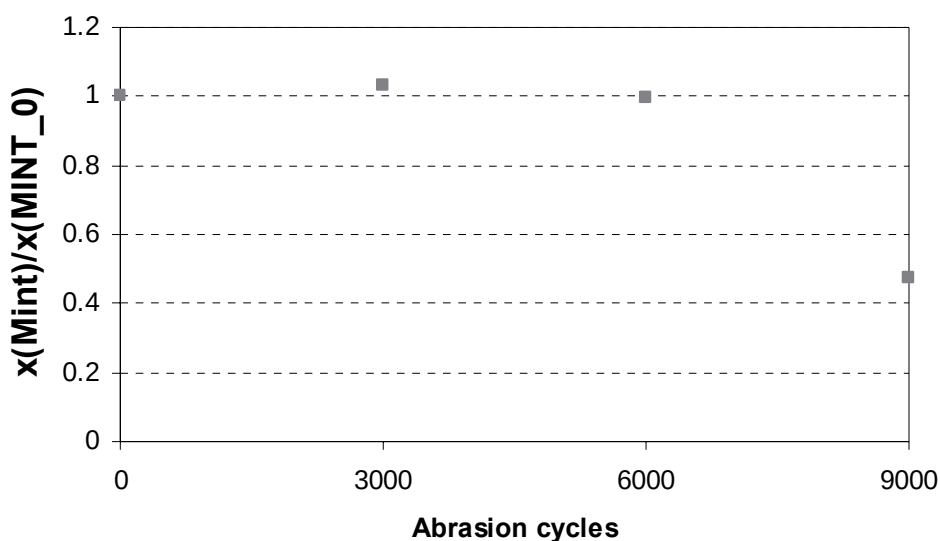


Figure 3.7. Relative weight of menthol present in textiles impregnated with mint microcapsules using the acrylate binder, as a function of abrasion cycles.

Polyurethane binder (Peripret Plus)

Figure 3.8 shows the chromatographic evolution of the mint odour of the impregnated textiles as a function of dry washes number (0-5 washes) and Figure 3.9 presents the results in terms of relative weight of methanol. It can be observed a loss of odour as the number of dry washes increases. More precisely, after 5 dry washes 90% of the odour persists, i.e., a 10% loss has occurred.

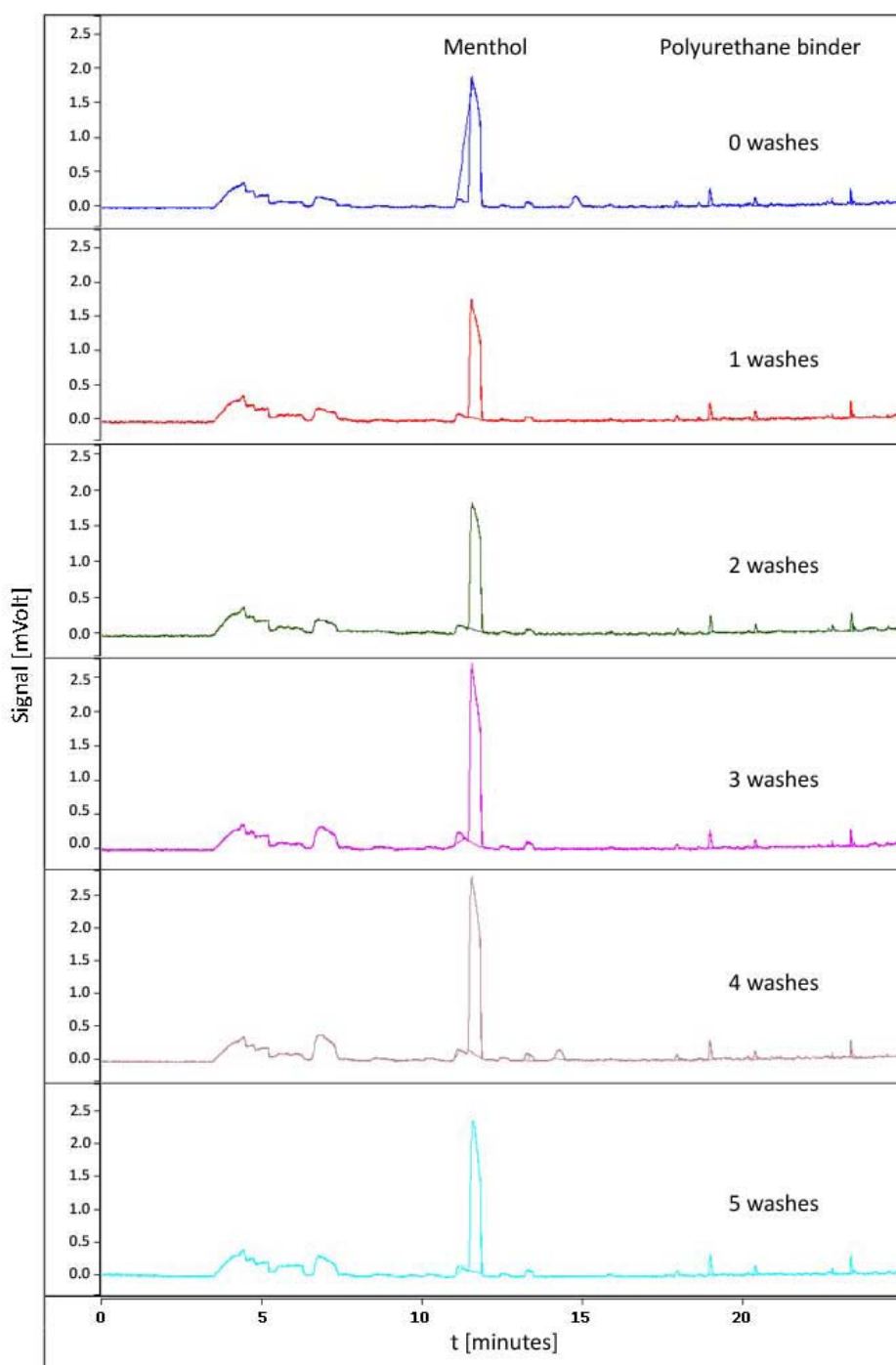


Figure 3.8. FID chromatograms of the textiles impregnated with mint microcapsules (Horquim) using the urethane binder after 0, 1, 2, 3, 4 and 5 washes.

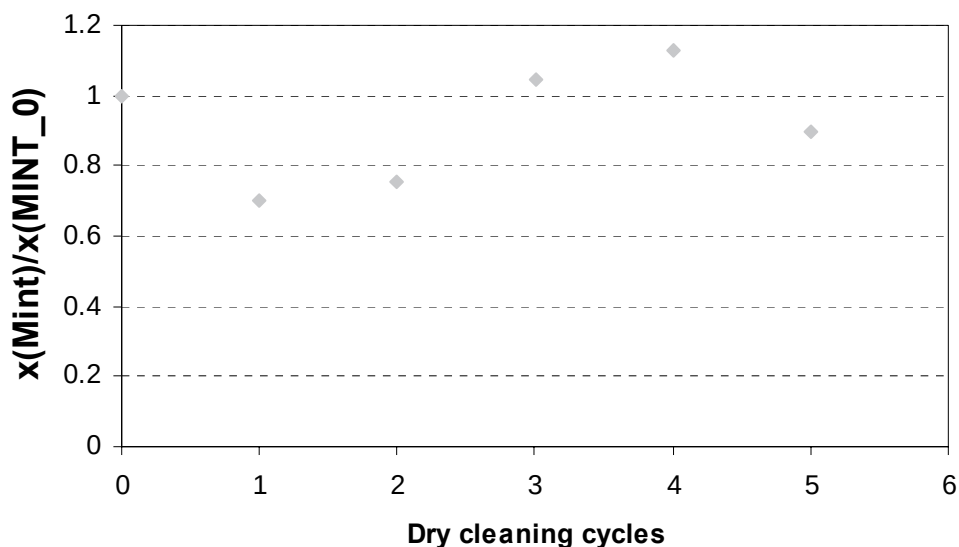


Figure 3.9. Relative weight of menthol present in the textiles impregnated with mint microcapsules using the polyurethane binder, as a function of dry washes number.

Comparison of binders

Using the acrylate binder it appears that increasing the number of dry washes decreases the presence of menthol in the textiles, and the loss of flavour is 65% after 5 cycles. For the polyurethane binder a loss of only 10% was observed.

Analyzing these chromatograms of textiles samples subjected to cycles of abrasion it can be observed that the presence of menthol remains constant up to 6000 cycles, with an evident decrease for 9000 cycles, with a loss of aroma of 52%.

In the case of impregnated textiles with polyurethane binder there is a smooth decrease of the presence of menthol aroma. The maximum loss observed in these samples is around 30%, and it is also visible a 12% increasing of the presence of aroma.

3.3 Techniques for microcapsules and fabrics characterization

3.3.1 Mean particle size and particle size distribution (Laser dispersion).

The particle size distribution of the produced microcapsules was determined by laser dispersion using a Coulter LS230 (Figure 3.10).

The LS uses reverse Fourier lens optics incorporated in a patented binocular lens system. This enables the LS to optimize light scattering across the widest dynamic range in a single scan. It uses low angle forward light scattering with optional patented PIDS technology and has a full implementation of both Fraunhofer and Mei theories of light scattering. The particle size analysis range is 0.04 μm to 2000 μm .



Figure 3.10. Laser Diffraction Particle Size Analyzer COULTER LS230.

3.3.2 Optical microscopy.

A Leica DM 2000 microscope (Figure 3.11) equipped with the software Leica Application Suite Interactive measurement was used to analyse microcapsules in solution. The samples were analysed using the transmitted light mode.



Figure 3.11. Optical microscope- Leica DM 2000.

3.3.3 Scanning electron microscopy (SEM).

SEM was used to analyse microcapsules in the impregnated textile substrates. Textile samples were coated with a thin layer of sputtered gold prior to examination. Samples were observed using a scanning electron microscope JEOL JSM-6301S at 15 kV (Figure 3.12).



Figure 3.12. Scanning electron microscope JEOL JSM-6301S.

3.3.4 Determination of solid content and pH

The solid content of the microcapsules solutions was determined according to the European Standard EN 827 - Determination of solids content in water based adhesives. This test allows the determination of solid content in microcapsules, through the difference between initial weight and final weight after the complete evaporation of water. Hereafter is the detailed procedure: firstly, weight 1g of microcapsules solution, put it onto a tare watch glass and let it dry in an oven at 100 °C. Remove from the oven after 30 minutes and let it cool in the desiccator for 15 minutes and then weight the residual mass (m_f). Repeat the drying step and reweigh at intervals of 30 minutes, until the difference between the weighted masses does not exceed 2mg. Finally, relate the residual mass (the last weight - m_f) with the initial mass (m_i) (Equation 3-1):

$$\% \text{ Solid Content} = \frac{m_f}{m_i} \times 100 \quad \text{Eq. 3-1}$$

The determination of pH was performed using a pH meter Crison, model Micro pH 2002 which had been previously standardized to pH 4 and pH 7.

3.3.5 Fourier Transform Infrared spectroscopy (FTIR).

FTIR spectra were collected on a FTIR BOMEN (model MB 104) (Figure 3.13) in transmittance mode using two techniques: (1) using a liquid cell (an Omnicell® from Specac) with NaCl crystals to record the perfume spectra, and (2) using KBr pellets with a sample concentration of 1% (w/w) to record the shell material spectra. Spectra were collected between 650 and 4000 cm^{-1} at a resolution of 4 cm^{-1} and co-adding forty eight scans.



Figure 3.13. FTIR BOMEN (model MB 104).

3.3.6 Gas chromatography GC-FID-Headspace and GC-MS.

Quantification of the limonene and perfume was performed by gas chromatography GC/FID and the corresponding composition determined by GC/MS. The analyses were carried out using a Varian CP-3800 instrument (Figure 3.14) equipped with a split/splitless injector, a CP-Wax 52 CB bonded fused silica polar column (50 m x 0.25 mm, 0.2 μ m film thickness) and a Varian flame ionization detector (FID) and a Varian Saturn 2000 ion-trap mass spectrometer (MS), both controlled by Saturn 2000 WS software. The carrier gas was helium He N60, at a constant flow rate of 1 mL/min. The oven temperature was programmed as follows: isothermal (50 °C) during 5 min, then increased from 50 °C to 200 °C at 2 °C/min and held isothermal (200 °C) during 25 min. The injectors were set at 240°C, with a split ratio of 1/50 for FID and 1/200 for MS. The FID detector was maintained at 250°C. For the headspace analysis, it was used a gastight syringe

(SGE, 1 ml). The sampling volume injected was 0.5 mL for FID-headspace and 1 mL for MS. The sample was injected manually into GC-FID-Headspace at a rate of 0.1 ml/s. The syringe was flushed with air after the sampling to prevent carryover of the sample between analyses.



Figure 3.14. GC-FID-Headspace equipment with an automatic sampler coupled.

A sample of headspace normally is prepared in a bottle containing the sample and headspace (Figure 3.15). The volatile components of the sample can be extracted and isolated in headspace or gas phase in the bottle. Once the sample is introduced in the bottle it is immediately closed. The volatile components spreads out in the gas phase until headspace reaches equilibrium. Volumes of 0.5 mL from the gas of headspace are collected and are injected in the system of GC for the separation and identification of all components.

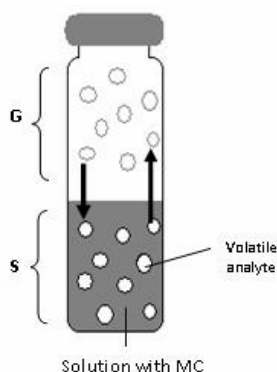


Figure 3.15. Vial of headspace analysis; Headspace phases: G = the gas phase (headspace); S = the sample phase; MC= Microcapsules.

For the headspace analyses of fabrics impregnated with microcapsules a procedure for the breakage of the microcapsules impregnated in the fabric was developed that consists of isolating a fabric sample impregnated (4x4 cm) with microcapsules in a plastic bag (12x23 cm) (Figure 3.16 a) and to break the microcapsules of the fabric without breaking the plastic bag (Figure 3.16 b). After balance of the gas phase overnight, 0.5 mL of the gas phase was removed from the bag, and the amount of perfume present in the samples was analyzed by chromatography.

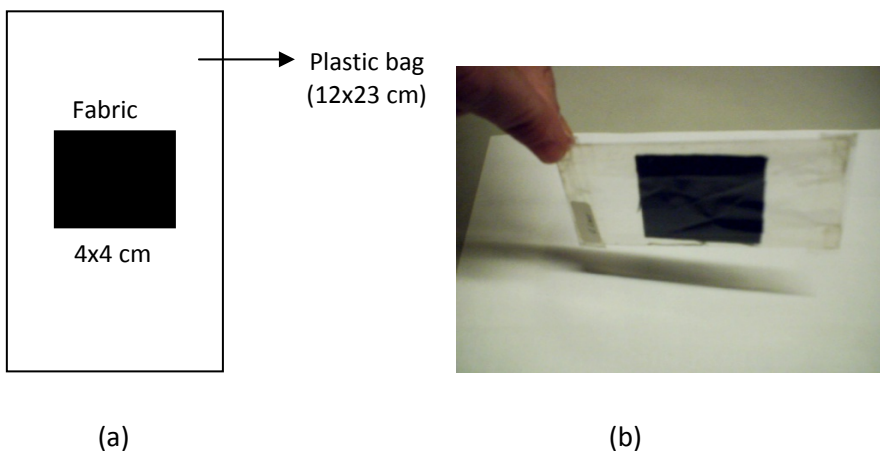


Figure 3.16. Impregnated fabric isolated on plastic bag (a) for GC headspace analyses (b).

3.3.7 Solidness of the aromas by abrasion, dry cleaning and washing tests

Abrasion tests were performed at CITEVE using a Martindale abrasion tester (Figure 3.17) to evaluate the resistance of textile substrates according to the European Standard EN ISO 12947-2: Determination of the abrasion resistance of fabrics by the Martindale method - Part 2: Determination of specimen breakdown. Fabrics of all types may be tested by this method, including woven, non-woven, and knit apparel fabrics, household fabrics and industrial fabrics. The principle of this test is to put the textile between two discs that are driven by a rotor along a zigzag course in a circular orbit so that it repeatedly impinges on the walls while at the same time being continually subjected to extremely rapid, high velocity impacts. The specimen is subjected to flexing, rubbing, shock, compression, stretching and other mechanical forces during the test. Each circular movement is a cycle.



Figure 3.17. Martindale abrasion tester [154].

Dry cleaning cycles were performed according to the European Standard EN 3175-2: Professional care, dry cleaning and wet cleaning of fabrics and garments - Part 2: Procedure for testing performance when cleaning and finishing using tetrachloroethene (perchloroethylene). Dry cleaning of clothing and textiles is a process which uses an organic solvent (perchloroethylene). The washing time was

15 minutes followed by a rinsing procedure during 5 minutes. The general conditions are presented in Table 3.1.

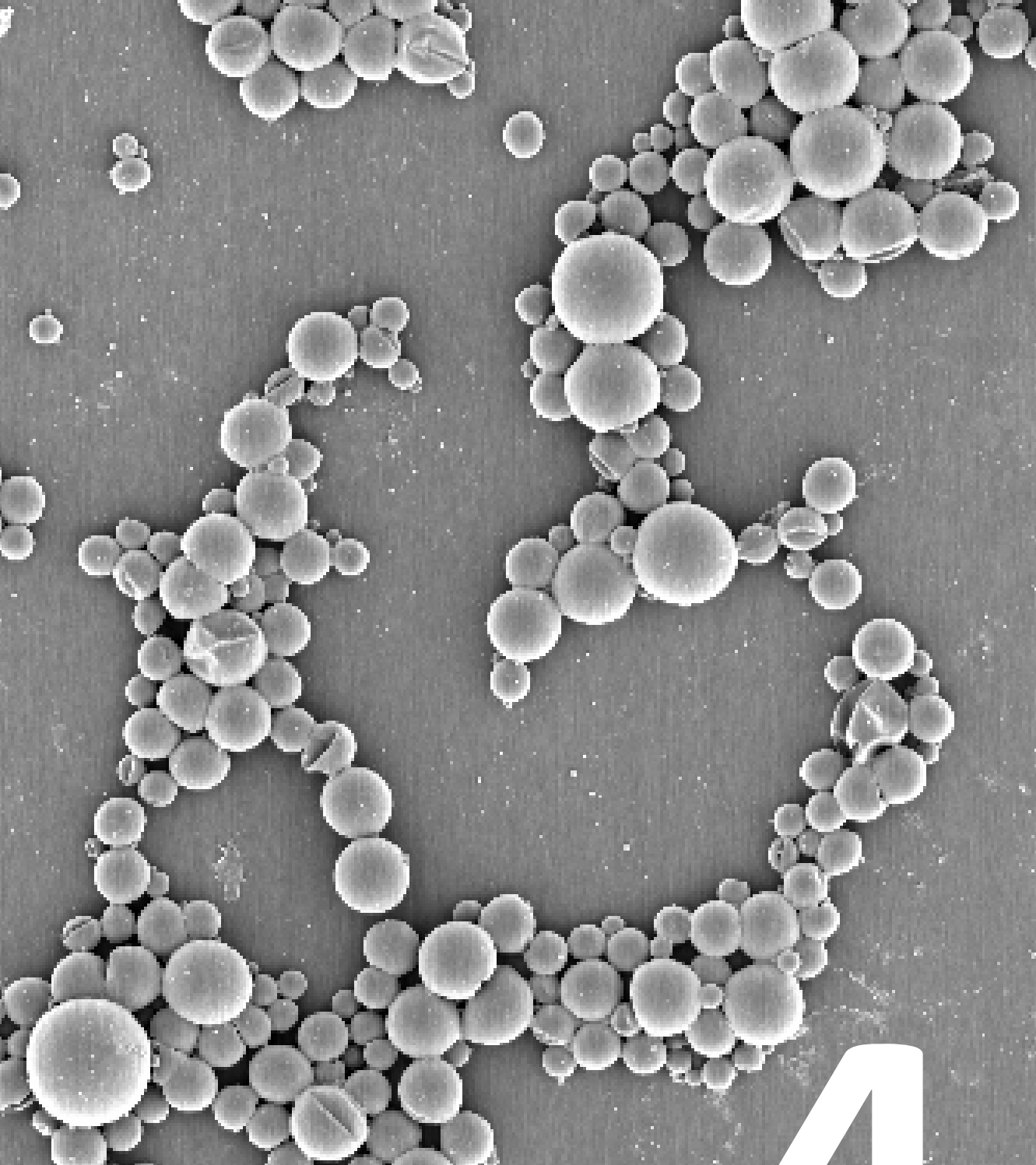
Table 3.1. Conditions of dry cleaning cycles.

European standard	En 3175- Part 2
Organic solvent	Perchloroethylene
Washing Time	15 min
Rinsing Time	5 min

The effect of washing by domestic laundering of impregnated textiles was evaluated in agreement with the European standard EN ISO 105-C10:2007: Tests for colour fastness - Part C10: Colour fastness to washing with soap or soap and soda. The washing time was 40 minutes. The general conditions are presented in Table 3.2.

Table 3.2. Washing conditions for domestic laundering.

European standard	EN ISO 105-C10:2007
Temperature	40°C
Bath volume	30 L
Centrifugation time	30 sec.
Soap	Without soap
Drying	Air



**Commercial samples
characterization**

4

In this chapter the fragrant commercial microcapsules for textile application are characterized as well as the impregnated textiles.

The commercial samples were characterized in order to determine particle size, morphology, chemical composition and fragrance intensity. The available samples were gently offered by companies.

4.1 Commercial microcapsules and impregnated textiles characterization

In Table 4.1 are described the fragrances and respectively suppliers of the commercial microcapsules.

Table 4.1. Fragrances and suppliers of the commercial microcapsules.

Fragrance	Suppliers
Lemon	Bayer
Lemon	Focor
Lemon	Horquim
Strawberry	Horquim
Jasmine	Focor
Lavender	Horquim
Mints	Horquim
Eucalyptus	Focor
Apple	Focor

4.1.1 Laser dispersion

Figure 4.1 shows the particle size distribution (in volume) for the samples Lemon (Bayer, Focor and Horquim), Jasmine (Focor) and Strawberry (Horquim). Figure 4.2 shows the corresponding distributions in number.

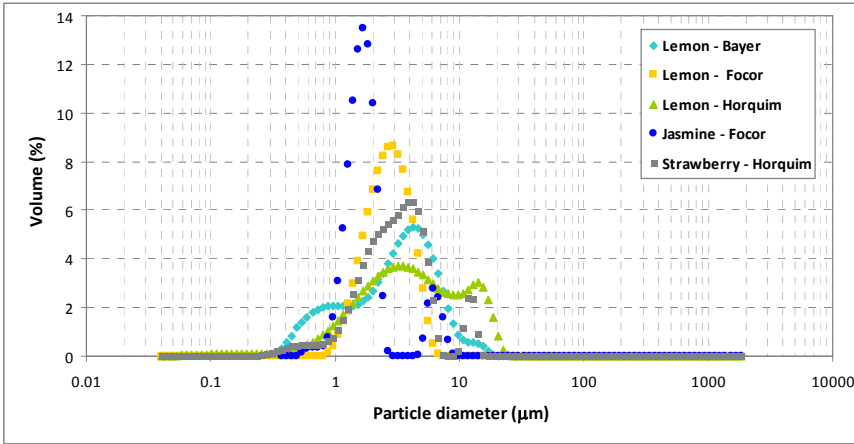


Figure 4.1. Particle size distribution (in volume) for the samples Lemon (Bayer, Focor and Horquim), Jasmine (Focor) and Strawberry (Horquim)

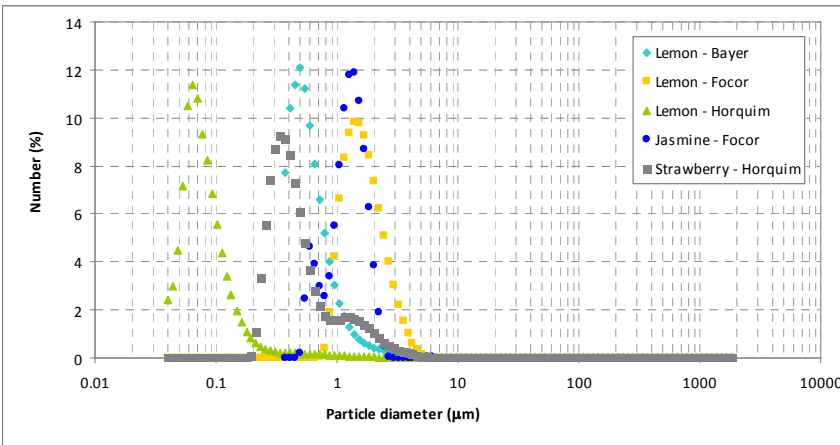


Figure 4.2. Particle size distribution (in number) for the samples Lemon (Bayer, Focor and Horquim), Jasmine (Focor) and Strawberry (Horquim)

With these analyses it was possible to conclude that the particle size distribution of commercial samples, in volume, was predominantly comprised between 1-10 μm . Analysing the corresponding results in number, it was possible to verify that most of the particles present small sizes. The microcapsules mean size (based on volume distribution) is presented on Table 4.2.

Table 4.2. Microcapsules mean size based on volume distribution

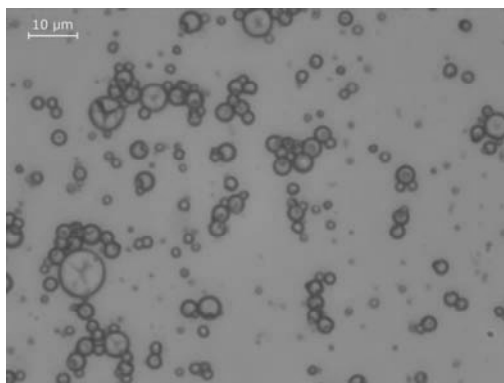
Fragrance	Supplier	Particle Diameter (μm)
Lemon	Bayer	3.88
Lemon	Focor	2.96
Lemon	Horquim	6.08
Strawberry	Horquim	3.90
Jasmine	Focor	2.23

The mean particle size (in volume) of the lemon commercial microcapsules from Horquim is the highest one (6.08 μm) and the jasmine microcapsules from Focor the lowest one (2.23 μm).

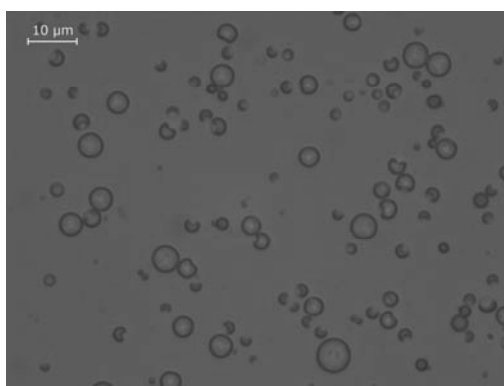
4.1.2 Optical microscopy

Microcapsules morphology was observed by optical microscopy for the case where its size was larger than 1 μm . For SEM analysis, samples should be prepared, air dried (without forced drying technique) and prior analyzed by optical microscopy to verify the quality of the sample (optimize microcapsules concentration and verify the absence of impurities) that could change the results in electron microscopy. The commercial microcapsules were analysed in bright field with

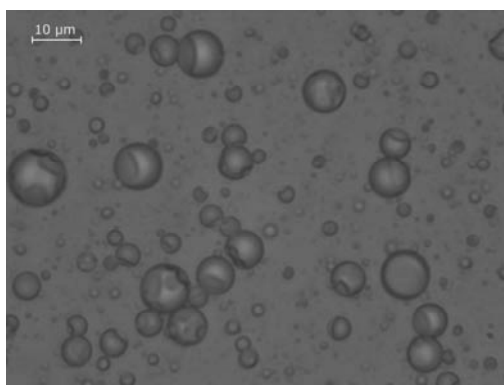
1000x magnification. Below are presented the photographs of different commercial samples (Figure 4.3a to Figure 4.3e).



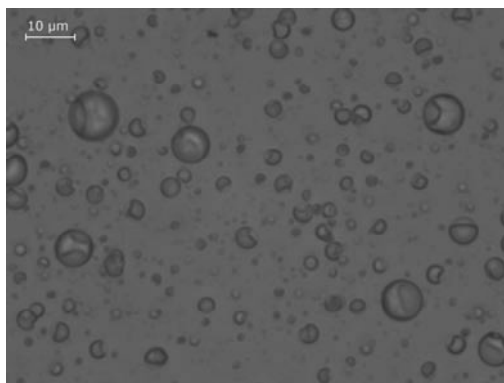
a) Microcapsules with lemon from Bayer



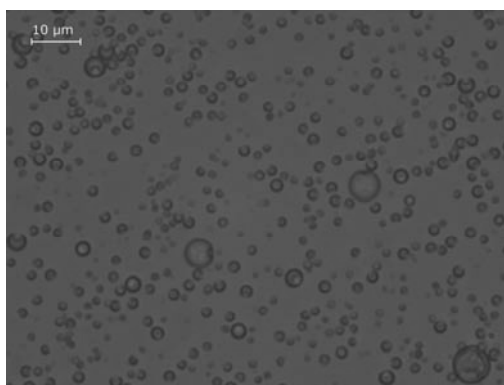
b) Microcapsules with lemon from Focor



c) Microcapsules with lemon from Horquim



d) Microcapsules with strawberry from Horquim



e) Microcapsules with jasmine from Focor

Figure 4.3. Optical micrographs with magnification of 1000x of commercial microcapsules.

Comparing the five micrographs obtained, Figure 4.3 a) to e), using the same magnification, it can be confirmed the size of the commercial products and their spherical shape. It is also visible that microcapsules from Horquim are larger than others, and they also present some deformations.

4.1.3 Scanning Electron Microscopy (SEM) and Environmental Scanning Electron microscopy (ESEM)

The results obtained by scanning electron microscopy (SEM) show the spherical structure of microcapsules. Commercial products from Horquim have a clear spherical shape as shown in Figure 4.4 and Figure 4.5.

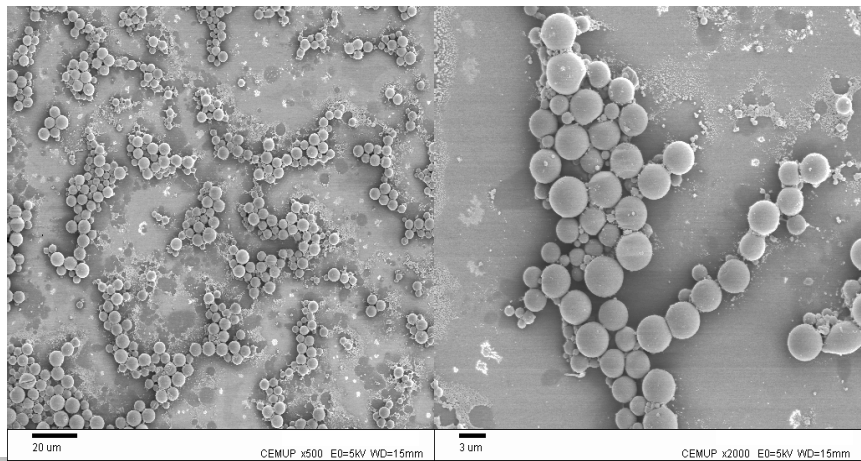


Figure 4.4. SEM micrographs of strawberry microcapsules from Horquim with magnification of 500x and 2000x.

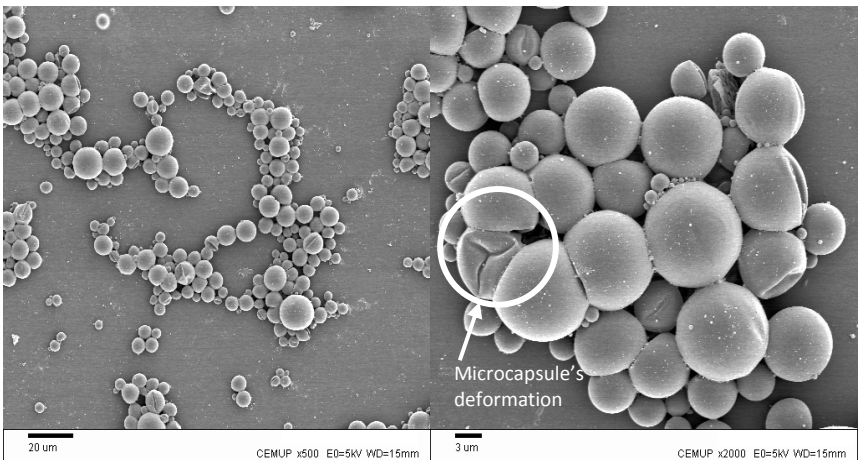


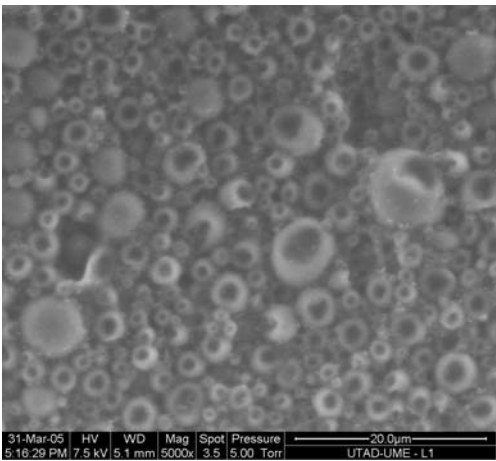
Figure 4.5. SEM micrographs of lemon microcapsules from Horquim with magnification of 500x and 2000x.

The observation of these two groups of micrographs revealed the presence of a salt that was identified as NaCl by elemental analysis (Energy Dispersive X-ray Spectroscopy-EDS). To perform this analysis it was necessary to eliminate the presence of the glass elements and also the gold that covered the sample for SEM analysis. It is visible on these micrographs the microcapsules aggregation. This phenomenon can occur because of the presence of excessive concentration of NaCl.

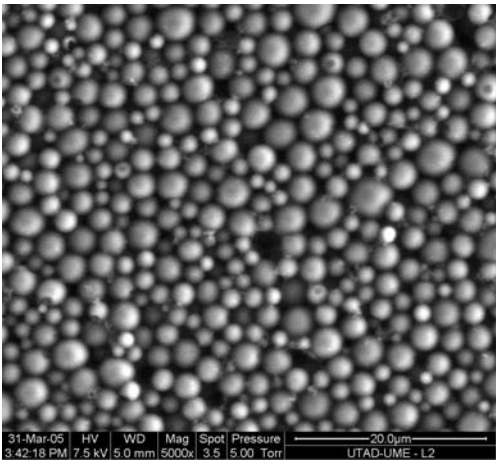
Comparing similar magnifications on Figure 4.4 and Figure 4.5, it can be concluded that lemon microcapsules have larger dimensions than strawberry microcapsules. Figure 4.5, particularly the micrograph with 2000x of magnification, shows some deformed microcapsules. This might have occurred due the vacuum conditions that were applied to the sample.

Analyses of the commercial microcapsules dried at room temperature by ESEM were also performed. This method requires some care but avoids the need to completely dry the sample, as in SEM. In these tests the samples had a moisture content of about 40%. The samples were analyzed without any specific preparation or coating. In fact, without the gold coating, the obtained images were dark images.

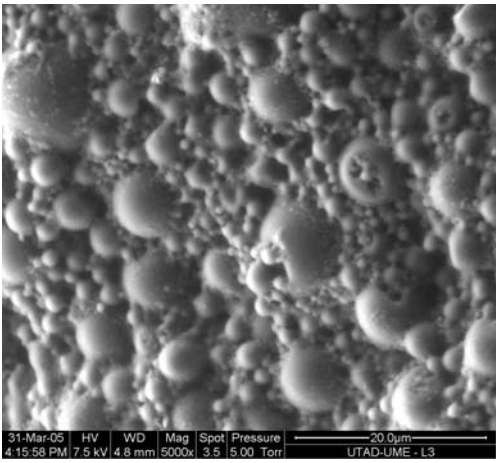
On Figure 4.6 a) to e) are presented the micrographs of higher magnification, 5000x, and it is possible to see the morphology of these commercial microcapsules.



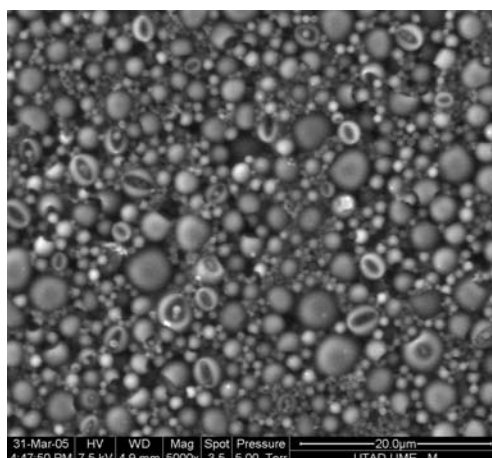
a) Microcapsules with lemon from Bayer.



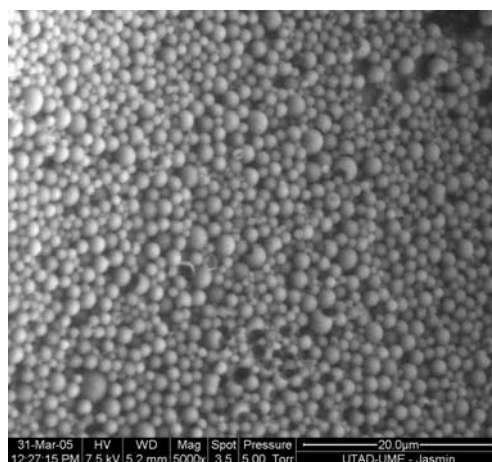
b) Microcapsules with lemon from Focor.



c) Microcapsules with lemon from Horquim.



d) Microcapsules with strawberry from Horquim.



e) Microcapsules with jasmine from Focor.

Figure 4.6. ESEM micrographs of commercial microcapsules. a) Lemon from Bayer, b) Lemon from Focor, c) Lemon from Horquim, d) Strawberry from Horquim, e) Jasmine from Focor.

It was visible the collapse of the microcapsules during the analysis. One explanation might be the incidence of electron beams during analysis. As the magnification increases the incidence of electrons is concentrated in an area of the sample, sometimes in a single microcapsule. When it is focused in a higher radiation in order to obtain a better image, the sample may not be able to absorb

all this energy without degrading. That is what happened when commercial microcapsules were observed since they have collapsed in seconds.

4.1.4 FTIR

The commercial samples listed in Table 4.3 were characterized by FTIR for reference standards. In the case of lavender and mint samples, material data sheets were available thus enabling the comparison between experimental and tabulated values.

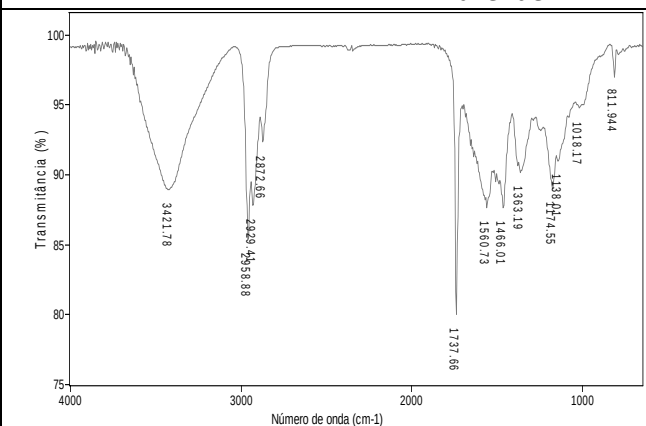
Table 4.3. Data relating to commercial microcapsule of lavender and mints.

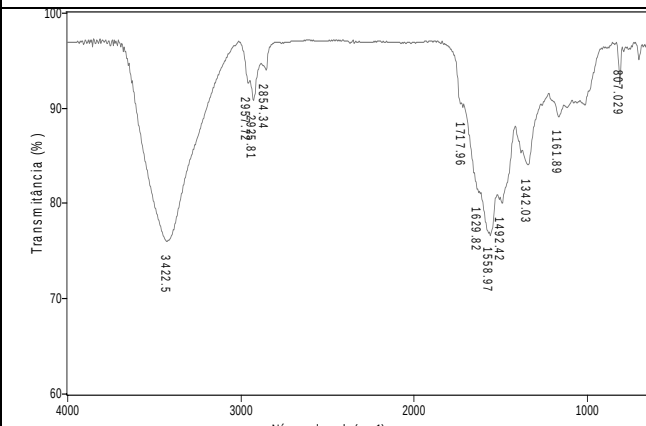
Fragrance	Supplier	Specifications
Lavender	Horquim	Material: Melamine-formaldehyde Solids content: Approx. 50% pH: 6-7
Mints	Horquim	<u>Material</u> : Copolymer Melamine <u>pH</u> : 6

Using FTIR analyses it is possible to identify the functional groups responsible for the vibrations pointed out in the spectrum. As it is documented in the material data sheet lavender microcapsules wall are made of melamine-formaldehyde and mints microcapsules wall are made of a copolymer of melamine (the other block is unknown). Using these two spectra as reference it was possible, to infer the material of the other analysed microcapsules wall. In Table 4.4 are presented the spectra of commercial microcapsules analysed and also the main vibrations identified. Material data sheet of this sample (lavender) refers the presence of free

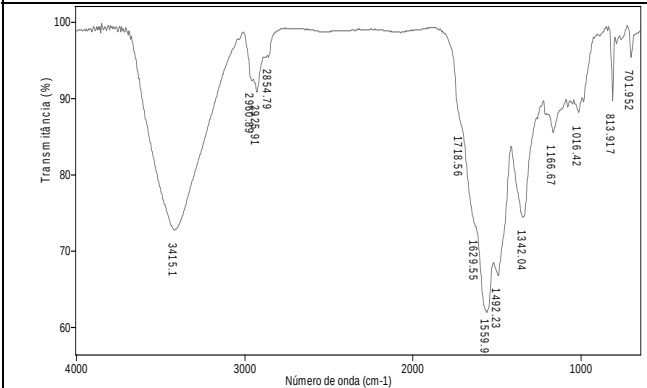
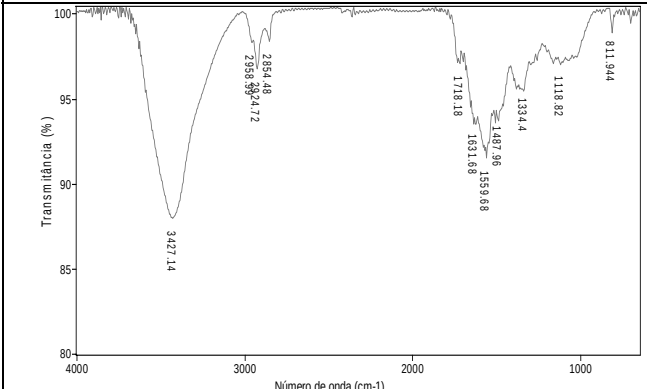
formaldehyde and this component is the responsible for the strong vibration assigned at 1737 cm^{-1} identified as the stretch vibration of $\text{C}=\text{O}$ group of formaldehyde. Microcapsules of eucalyptus and apple, supplied by Focor, presented spectra very similar to the one obtained for mints, so it is possible to conclude that the chemical composition of these microcapsules are identical: copolymer of melamine.

Table 4.4. FTIR analyses of commercial microcapsules.

FTIR Spectra		Vibrations	
Lavender			
	Wavenumber (cm ⁻¹)	Characteristic group	
	3421.78	N-H e O-H	
	2958.88 2929.41 2872.66	C-H	
	1737.66	C=O	
	1560.73	C=C	
	1466.01	N-H e CH ₃	
	1363.19	C-N	
	1174.55	C-O	
	811.94	CH ₂ of long chain	

Mints			
	wavenumber (cm ⁻¹)	Characteristic group	
	3422.5	N-H e O-H	
	2957.72 2925.81 2854.34	C-H	
	1717.96	C=O	
	1558.97	C=C	
	1492.42	N-H e CH ₃	
	1342.03	C-N	
	1161.89	C-O	
	807.029	CH ₂ of long chain	

(Cont.)

Eucalyptus		
	wavenumber (cm ⁻¹)	Characteristic group
	3415.1	N-H e O-H
	2957.6 2925.91 2854.79	C-H
	1718.56	C=O
	1559.9	C=C
	1492.23	N-H e CH ₃
	1342.04	C-N
	1166.67	C-O
	813.917	CH ₂ da cadeia longa
FTIR Spectra		Vibrations
Apple		
	wavenumber (cm ⁻¹)	Characteristic group
	3427.14	N-H e O-H
	2958.99 2924.72 2854.48	C-H
	1718.18	C=O
	1559.68	C=C
	1487.96	N-H e CH ₃
	1334.4	C-N
	1118.82	C-O
	811.94	CH ₂ of long chain

4.1.5 Solid Content and pH

The solid content and pH were determined using the procedures described in section 3.3.4.. Horquim provided datasheets of lavender and mints microcapsules and therefore the comparison between experimental values and some available reference values were in good agreement, being also an indication that the adopted experimental procedures were adequate and provided reliable measures.. The values measured experimentally and available from datasheets are listed in Table 4.5.

Table 4.5. Solid content and pH of samples of commercial microcapsules.

SAMPLE	EXPERIMENTAL VALUES		REFERENCE VALUES	
	Solid Content (%)	pH	Solid Content (%)	pH
Lavender (a)	50.01	6.45	~50	6 -7
Mints (a)	27.0	6.03	n.a.	6
Lemon (a)	45.0	5.87	n.a.	n.a.
Strawberry (a)	49.4	6.09	n.a.	n.a.
Eucalyptus (b)	27.7	5.94	n.a.	n.a.
Apple (b)	28.4	6.10	n.a.	n.a.
Lemon (c)	38.5	6.01	n.a.	n.a.

Na – not available; (a) Horquim; (b) Focor; (c) Bayer;

Lavender and strawberry microcapsules from Horquim present a higher value of solid content (~50%). According to the corresponding datasheet these microcapsules are suitable for fabrics printing processes. Mint microcapsules (Horquim) have a lower value of solid content (27%) and, according to the corresponding datasheet, are appropriate to apply to finished fabrics. The pH of all the analysed microcapsules is around 6.

4.1.6 SEM of impregnated textiles with lemon microcapsules

Textiles were impregnated with lemon microcapsules supplied by Horquim at laboratory scale in the conditions detailed in Table 4.6.

Table 4.6. Application conditions of microcapsules on textiles

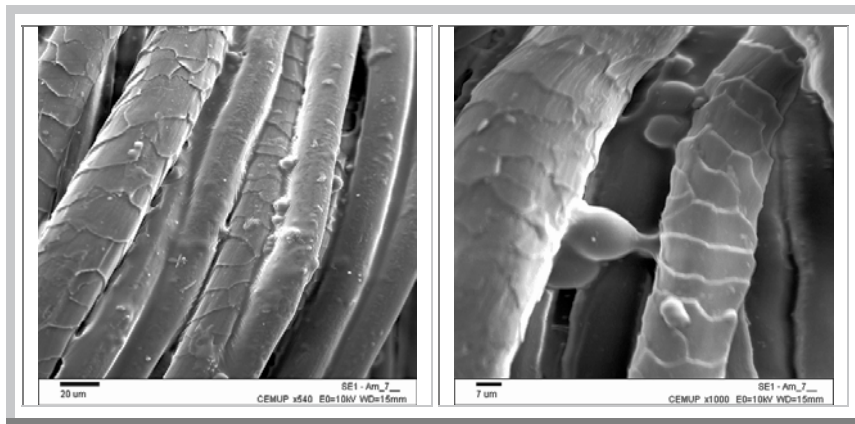
Products	Characteristics	Concentration (g/L)
Aroma	Lemon Horquim	10
Softener	Perisoft SML	10
Crosslinking (polyacrylate)	Primal ECO 934 TK	50

The washing conditions were the previously mentioned in table VI. Impregnation and washing were performed by CITEVE. Below are presented several SEM micrographs Figure 4.7 (a-f) of the impregnated textiles with lemon microcapsules from Horquim and subjected to domestic washing processes. In Figure 4.7 a), microcapsules are quite visible and adherent to the textile fibers.

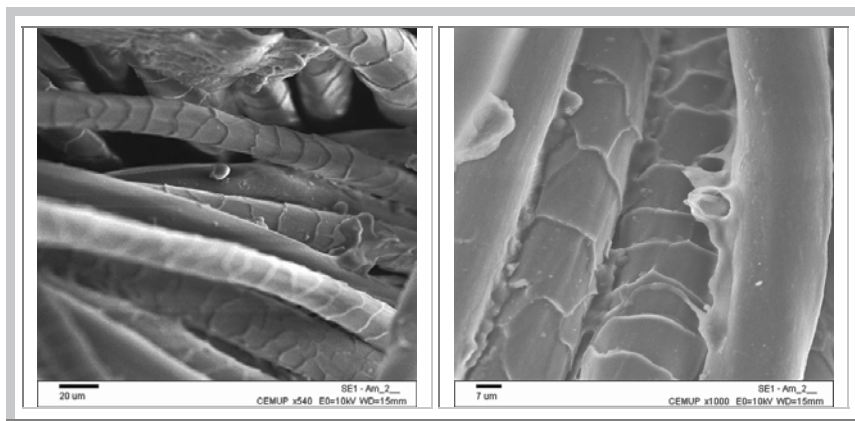
When the washing cycles begin, the micrographs show a decrease in the presence of the microcapsules on textiles as it can be seen with only one washing cycle (Figure 4.7 b)

Observing the impregnated textiles with only 2 washes it is clearly that few microcapsules are presented (Figure 4.7 c).

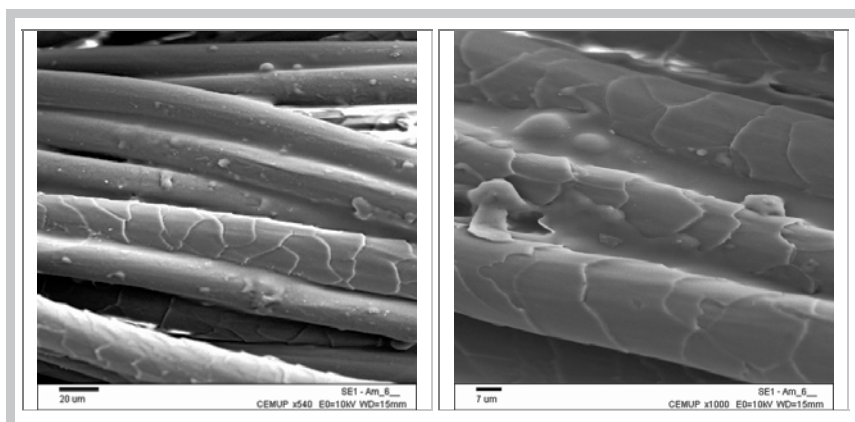
When impregnated textiles are subject to more washing cycles the presence of microcapsules is substantially diminished, and looking to the micrographs of impregnated textiles with 20 washes (Figure 4.7 f) no microcapsules were found.



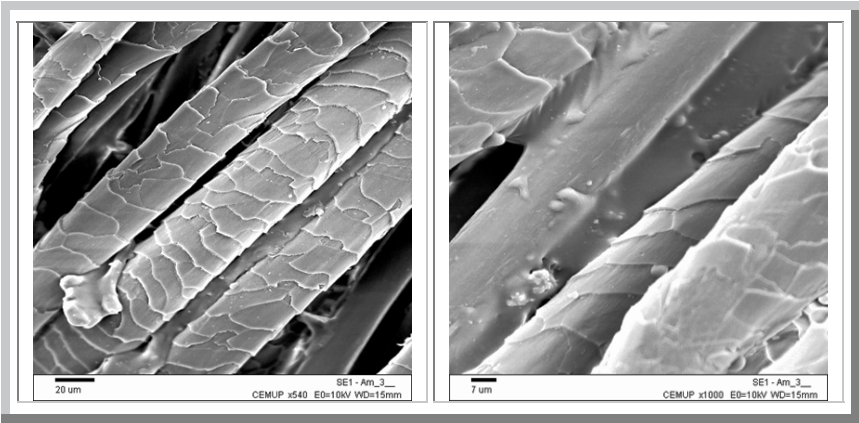
a) unwashed



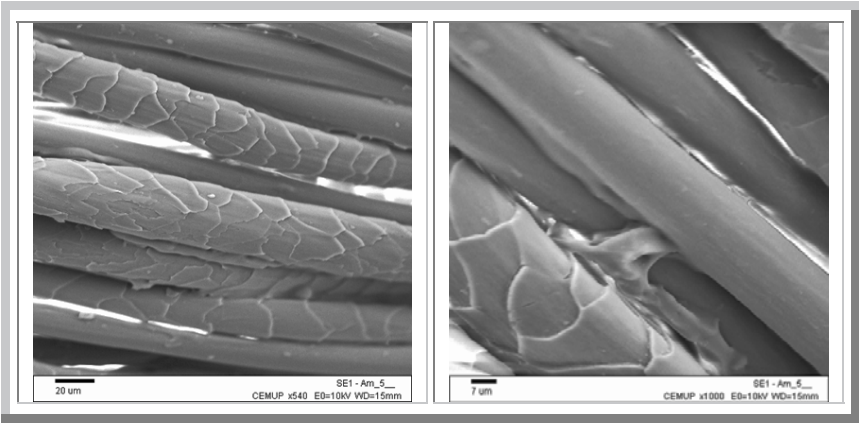
b) 1 wash



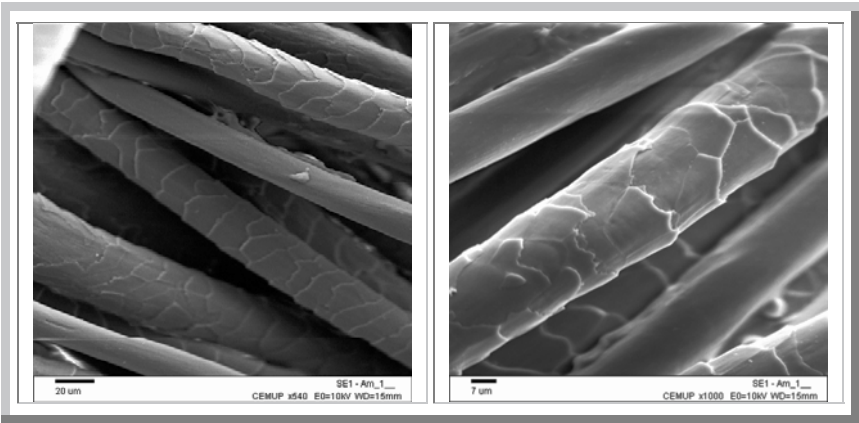
c) 2 washes



d) 5 washes



e) 10 washes



f) 20 washes

Figure 4.7. SEM micrographs after domestic washing process of impregnated textiles with commercial lemon microcapsules from Horquim.

4.1.7 GC-headspace analyses of commercial lemon microcapsules

Headspace analyses were performed with commercial samples of lemon microcapsules and also with lemon essential oil. This last one was used as standard to identify the retention time of limonene peak.

Three commercial lemon samples were analyzed: Bayer, Focor and Horquim. It can be observed through the MS chromatograms they are essentially composed of limonene (Figure 4.8). The first chromatogram corresponds to the Bayer sample and is the most complex of all, with other compounds in addition to limonene. The other two analysed samples (Focor and Horquim) are practically composed of limonene, which is the main component of lemon flavour.

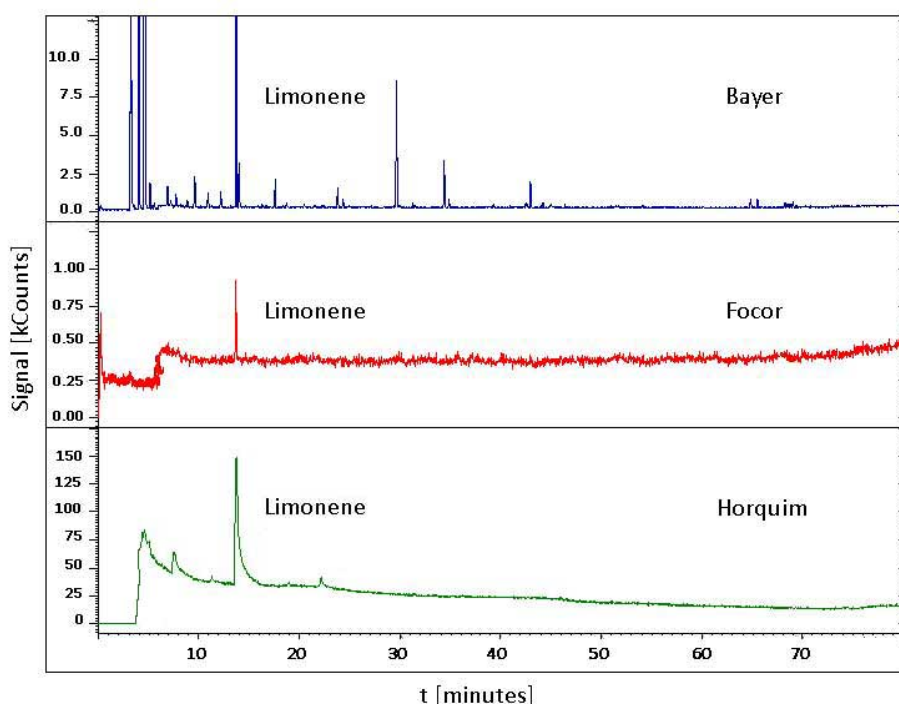


Figure 4.8. MS Chromatograms of lemon commercial samples.

Comparing the chromatograms of Horquim and lemon essential oil (Figure 4.9), it can be observed that the chromatogram of Horquim sample presents essentially

the limonene component thus confirming the simplicity of the used active principle of these microcapsules.

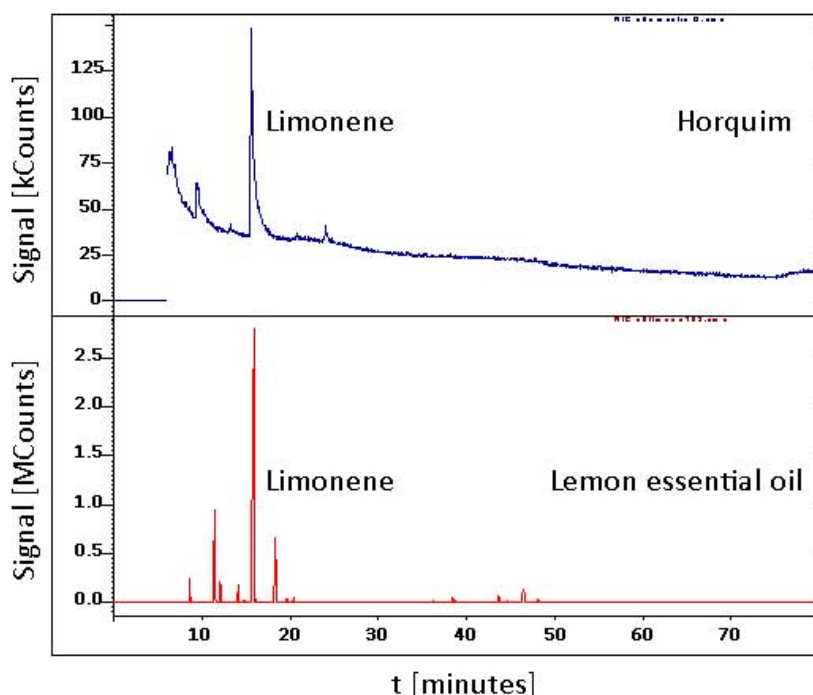


Figure 4.9. Comparison of MS chromatograms of the commercial sample of lemon from Horquim and essential oil of lemon.

4.1.8 Headspace Analysis of impregnated textiles with commercial microcapsules

Figure 4.10 shows the GC-FID-Headspace chromatograms of limonene and samples of impregnated textiles with lemon microcapsules from Horquim after 0, 1 and 20 domestic washes. It is noticeable the decrease of the peak area of limonene peak with the increasing number of washes.

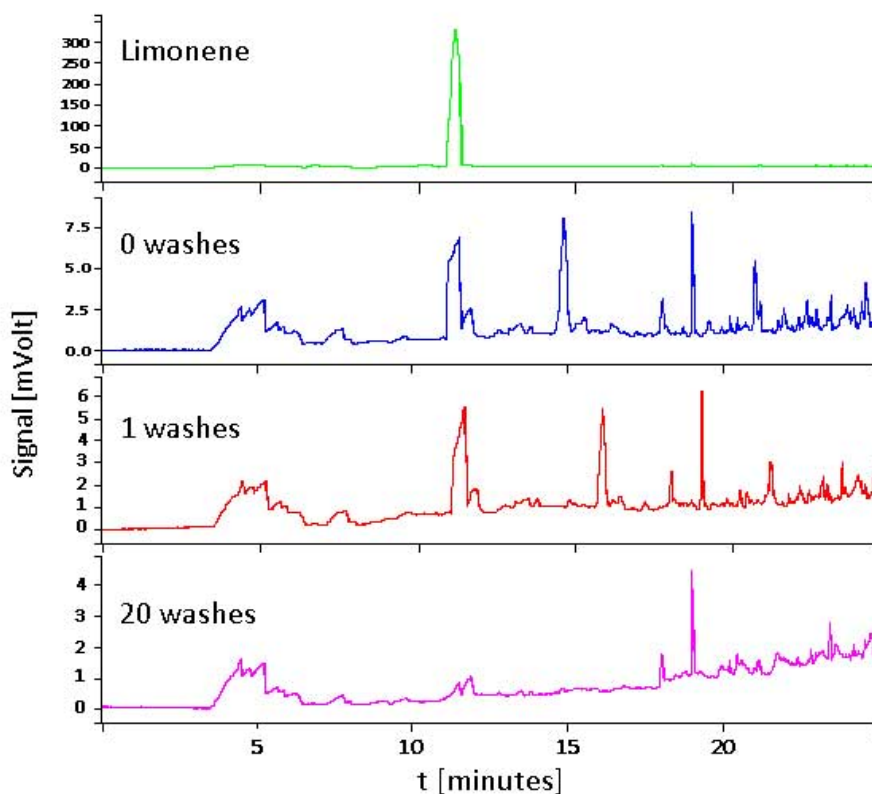


Figure 4.10. FID chromatograms of limonene and impregnated textiles samples with microcapsules of Horquim after 0, 1 and 20 washes.

In order to quantify the analysis of headspace it was determined the amount of mass of limonene-based on the calibration curve of limonene (Figure 4.11). It is in evidence on Figure 4.12 the decrease between the amount of mass present in the impregnated textiles with 0 washes ($3.2\text{E-}05$ mg) and the quantity of mass present in the impregnated textiles with 20 washes ($8.14\text{ E-}07$ mg) and it can also be observed that there is a loss of 46% at the first wash cycle and a loss of 97% after 20 washes.

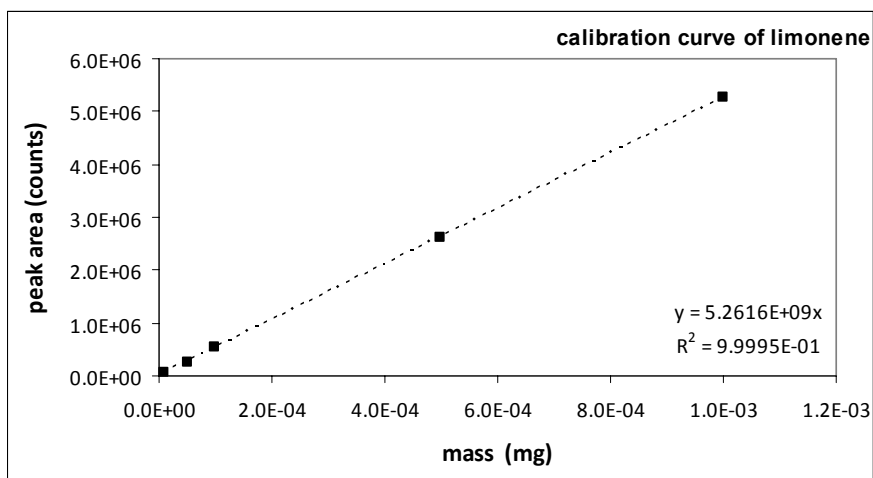


Figure 4.11. Calibration curve of limonene.

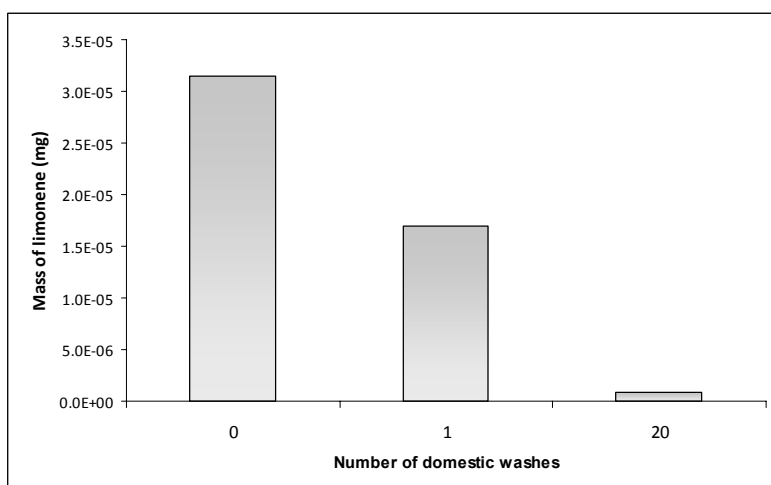


Figure 4.12. Values of the mass of limonene-based on calibration curve of limonene.

The evaluation of fragrance presented in impregnated textiles was performed also by a panel list select by CITEVE. The results obtained by GC-FID-Headspace were in accordance with the results obtained by the panel list. The panel list was constituted by 10 persons [151]. Figure 4.13 shows the results of the panel list

using the impregnated textiles with commercial samples of lemon microcapsules of Horquim after being subjected to 1 and 20 washes.

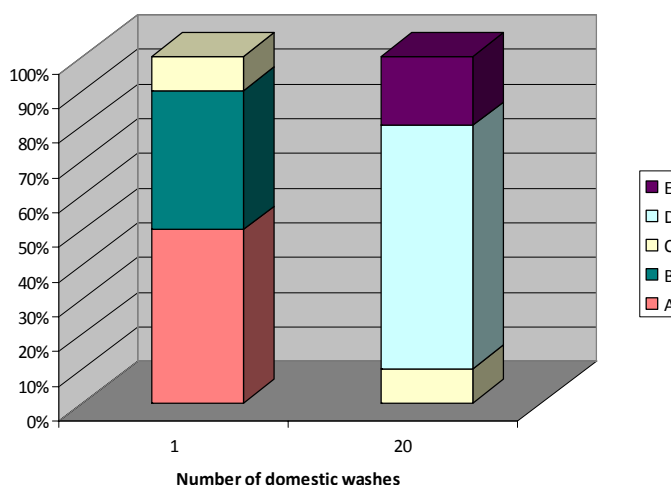


Figure 4.13. Panel list evaluation of impregnated textiles subjected to domestic washes. Where: A – Intense aroma, B - Slightly less intense aroma, C - Aroma exists but with low intensity, D - Aroma exists but with very low intensity, E - Do not smell the aroma.

4.2 Conclusions

In this chapter a review of Materials and Methods used throughout the thesis was presented and several techniques were applied for the characterization of commercial microcapsules.

It was possible to obtain information about their particle size, morphology, solid content and pH, chemical composition and quantify the encapsulated fragrance.

With laser dispersion it was possible to conclude that the mean particle size distribution (in volume) of commercial samples were predominantly between 2.23 μm and 6.08 μm .

Using optical microscopy it can be confirmed the size of the commercial products and their spherical shape.

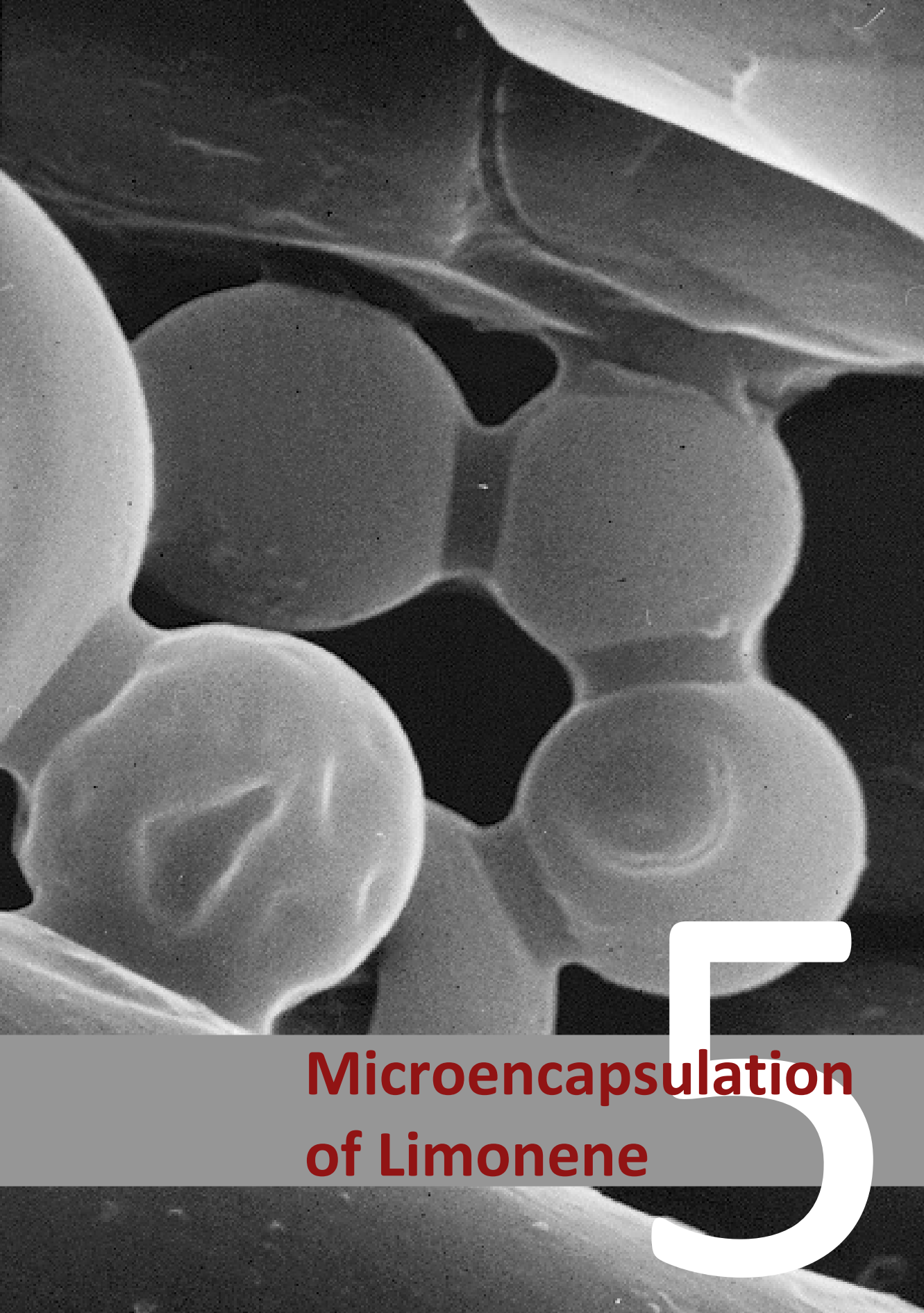
The results obtained by SEM/ESEM showed the spherical structure of microcapsules and also showed that in some cases the microcapsules are deformed looking like a bowl.

Using FTIR analyses it was possible to identify the functional groups responsible for the vibrations pointed out in the spectra and thus get information about the wall material. By comparing the spectra obtained, it was possible to conclude that the wall of the eucalyptus and apple microcapsules are made of a melamine copolymer since the spectra of these samples are very similar to the spectrum obtained for mint commercial microcapsules.

The determinations of the solid content of the analysed commercial microcapsules are between 27.0% and 50.0% and the pH is between 5.87 and 6.45.

As lemon is one of the most widely fragrances used in perfumery, commercial microcapsules of lemon were analysed by GC-FID and GC-MS. Three commercial lemon samples were analyzed: Bayer, Focor and Horquim. It can be observed through the MS chromatograms of the samples that they are essentially composed of limonene.

Lemon microcapsules from Horquim were impregnated on textiles substrates and after that the textiles were subjected to domestic washing in order to evaluate the permanence of microcapsules on textiles. Using GC-FID-Headspace several samples were analysed: limonene and impregnated textiles with lemon microcapsules from Horquim after 0, 1 and 20 domestic washes. There was a loss of limonene of 46% after the first wash cycle and a loss of 97% after 20 washes. The results obtained by the panel list were in agreement with the results obtained with GC-FID-headspace technique.



Microencapsulation of Limonene

Encapsulation is useful to protect fragrances from oxidation caused by heat, light, moisture, and exposure to detrimental substances over their lifetime. Moreover, it can be used to prevent evaporation of volatile compounds. The encapsulated agent will be released by mechanical action (mechanical breakage of the capsule wall).

The selection of the used technique and shell material depends on the envisaged final product application, i.e., must take into consideration: physical and chemical stability, concentration, desired particle size, release mechanism and manufacturing costs.

In this chapter the studies considering limonene microencapsulation using a polyurethane-urea material wall obtained by interfacial polymerization are presented. These studies represent a start point aiming at evolving to more complex systems: perfumes microencapsulation (to be presented in next chapter). Produced microcapsules suitability for textile applications will be evaluated.

The work presented in this chapter involves several steps: fabrication of microcapsules with the active agent, impregnation of the textile substrates with microcapsules and binder and testing of the final product having in view a future industrial application of the developed product. Considering the type of textile substrate used, the main requirements for industrial application were defined as: (i) resistance to dry cleaning (5 cycles) and (ii) resistance to abrasion (9000 cycles).

Formulation evolution till the improved one (final formulation) will be presented sequentially from the first approach (Formulation A).

This chapter is based on the following publication:

S. N. Rodrigues, et al. "Microencapsulation of limonene for textile application". *Industrial & Engineering Chemistry Research* **2008**, 47, 4142.

5.1 Formulation A

The methodology for microcapsules production by interfacial polymerization using formulation A can be described in three steps:

- Preparation of an organic solution comprising the isocyanate, the active agent and a lipophilic surfactant mixed in a solvent miscible with water.
- Preparation of an aqueous phase formed by water, a diol and a hidrofilic surfactant.
- Emulsification of the organic phase with the aqueous phase under stirring. A membrane wall is immediately formed. Stirring is maintained for a certain time period to avoid microcapsules aggregation thus ensuring the growth of the microcapsules wall.
- After the wall formation, the organic solvent dissolved in the water phase is removed by evaporation under reduced pressure.

Table 5.1 shows the formulation (type of materials and amount used) and operating conditions.

Table 5.2 presents the experimental steps used in the preparation of these microcapsules.

Table 5.1. Base formulation (type of materials and amount used) and operating conditions used in the production of limonene microcapsules according to formulation A.

Material type	Polyurethane
Isocyanate	HMDI (0.38 mL)
Diol	Ethylene glycol (1.12 mL)
Active agent	Limonene (2.4 mL)
Organic solvent	Acetone (80 mL)

(Cont.)

Lipophilic surfactant	Span 85 (172 mg)
Hydrophilic surfactant	Tween 20 (272 mg)
Water	Deionised water (160 mL)
Reaction Temperature	25°C
Reaction time	3 hours
Stirring rate	8.000 rpm
Evaporation conditions	40°C during 45 min

Table 5.2. Experimental steps used in the preparation of limonene microcapsules according to formulation A.

STEP 1	Preparation of the organic solution: Acetone + HMDI + limonene + Span 85
STEP 2	Preparation of the aqueous solution: water + ethylene glycol (EG) + Tween 20
STEP 3	Preparation of the emulsion: Mixing of the organic solution with aqueous solution under stirring
STEP 4	Acetone evaporation under reduced pressure

Starting with the base-formulation, the following variables have been tested: (1) the amount of limonene was increased from 1% to 5% and (2) the organic solvent (acetone) was decreased from 80 mL to 40 mL.

5.1.1 Characterization of produced microcapsules using formulation A

LASER Dispersion

The produced microcapsules using formulation A were analyzed by laser dispersion using a Coulter LS230 to determine the particle size distribution in volume (Figure 5.1) and in number (Figure 5.2). The obtained microcapsules mean particle size (in volume) was $2.4\ \mu\text{m}$ which is in close to the lower limit of the values obtained for the characterized commercial samples (between $2.23\ \mu\text{m}$ and $6.08\ \mu\text{m}$). The obtained distribution is unimodal. A more detailed analysis reveal that, in volume, 89% of the particles have diameters higher than $1\ \mu\text{m}$ ($11\% < 1\ \mu\text{m}$), but this represents, in number, 33% ($67\% < 1\ \mu\text{m}$). This means that, even if a large number of microcapsules have small size; most of the limonene was encapsulated in particles with dimensions larger than $1\ \mu\text{m}$.

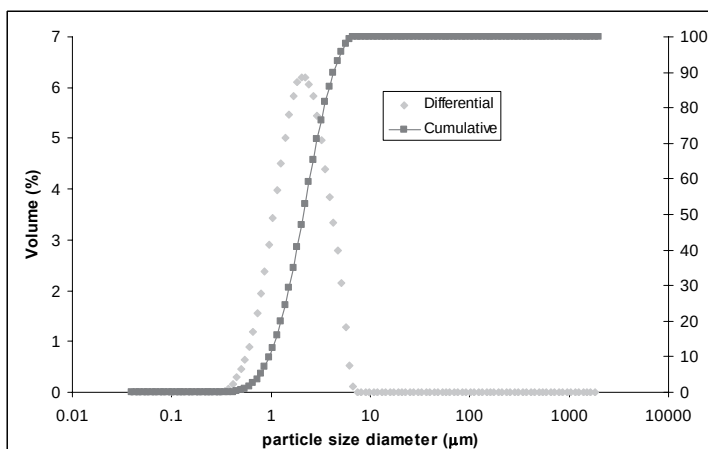


Figure 5.1. Differential and cumulative particle size distribution in volume of limonene microcapsules obtained with formulation A.

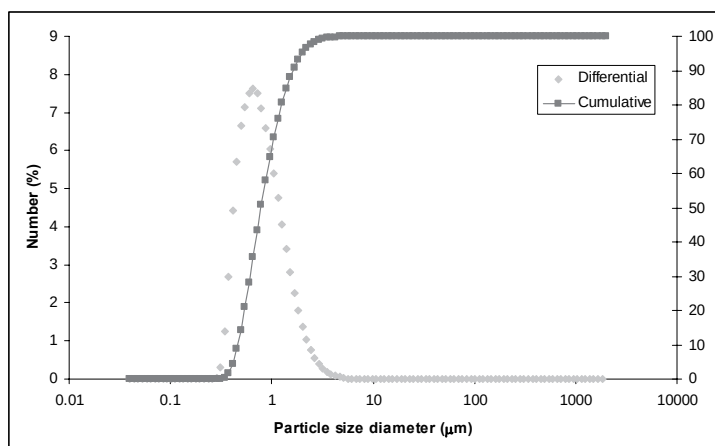


Figure 5.2. Differential and cumulative particle size distribution in number of limonene microcapsules obtained with formulation A.

Optical microscopy

Optical microscopy was used to study the morphology of the produced microcapsules. Figure 5.3 shows the microcapsules obtained with the base formulation. It can be observed that microcapsules have a quite irregular shape with a wide distribution of sizes. Some agglomerates can be also noticed.

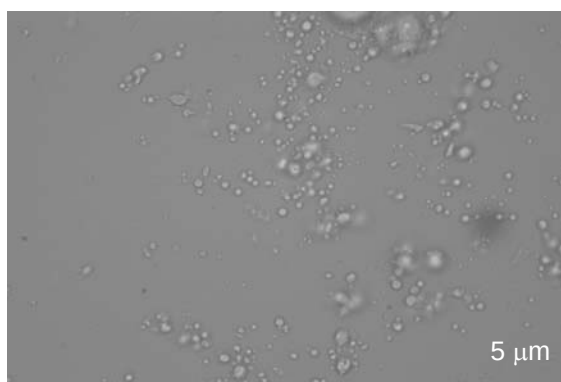


Figure 5.3. Optical microscopy in bright field with magnification 1000x. Formulation A-using the base formulation.

Figure 5.4 shows the morphology of the microcapsules produced after reducing the used amount of acetone. Comparatively to the base formulation, the microcapsules concentration decreased but, both shape and size distribution, are more regular.

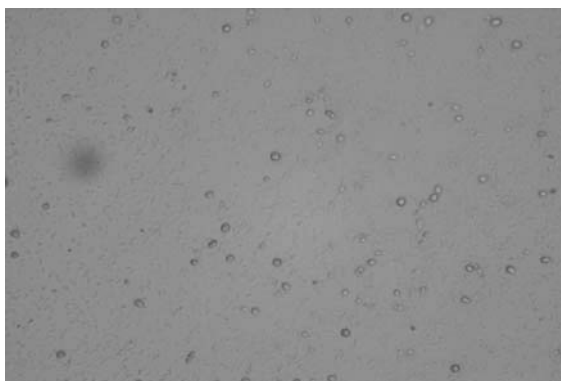


Figure 5.4. Optical microscopy in bright field with magnification 1000x. Formulation A after reduction of acetone content (50%).

SEM

Microcapsules produced with formulation A were analysed by SEM. Two samples were analysed: the original solution of microcapsules and the concentrated phase of microcapsules (after acetone evaporation). Figure 5.5 shows that microcapsules are organized in clusters and its morphology is not well defined.

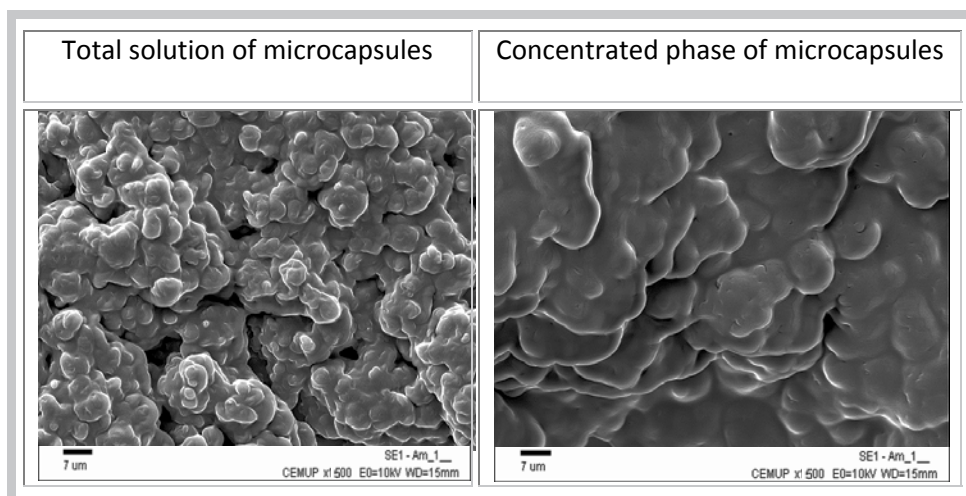


Figure 5.5. SEM micrographs of the whole microcapsules solution and concentrated phase solution obtained with formulation A (magnification of 1500X).

Following to the microcapsules production, textiles were impregnated at laboratory scale in the conditions detailed on Table 5.3. Since the solid content of the produced solution of microcapsules was very small (1.1%) a higher concentration of this solution was used to prepared the impregnation bath.

Table 5.3. Application conditions of microcapsules on textiles

Products	Characteristics	Concentration (g/L)
Aroma	Lemon using Formulation A (5%)	300
Softener	Perisoft SML	10
Crosslinking (polyacrylate)	Primal ECO 934 TK	50

After impregnation the textiles were analysed by SEM. In Figure 5.6 are presented two SEM micrographs at magnification of 1500x. Observing these micrographs it is evident the absence of microcapsules.

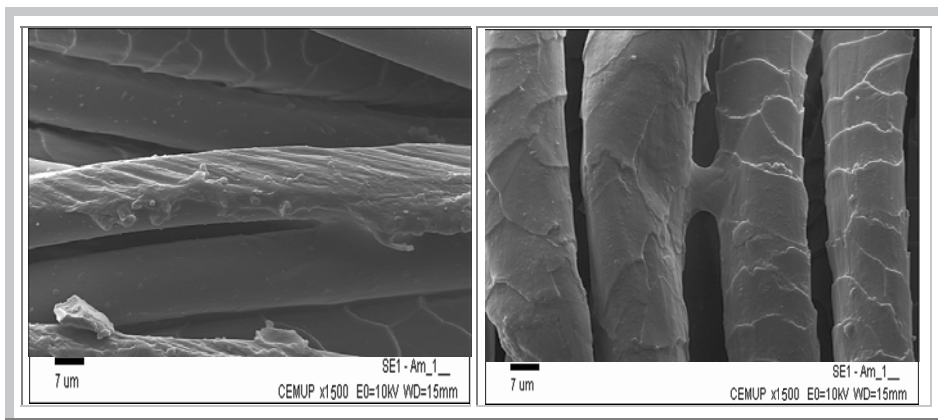


Figure 5.6. SEM micrographs of the impregnated textile with produced lemon microcapsules by formulation A with magnification of 1500x.

GC-HEADSPACE

The concentration of limonene present in the original solution of microcapsules was determined using the GC-FID-Headspace technique. The two samples with different concentrations of limonene, 1% and 5%, produced using formulation A, were analyzed.

It can be observed through the FID chromatograms that the samples are essentially composed of limonene, which is the main component of lemon flavour (Figure 5.7). The chromatogram in red refers to the sample with 1% of limonene and the chromatogram in green to the sample with 5% of limonene. As expected, an increase of the limonene peak was observed from sample with 1% to sample with 5%.

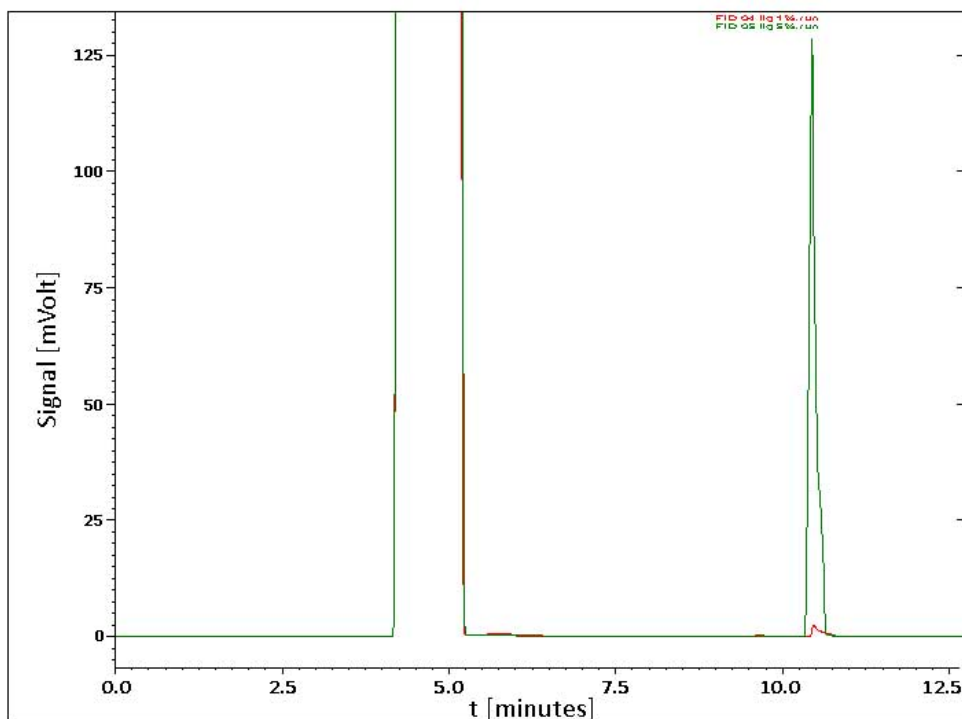


Figure 5.7. Comparison between the FID chromatograms obtained for the microcapsules solutions produced with 1% (red) and 5% (green) of limonene using formulation A.

Figure 5.8 shows the chromatograms of the headspace of a blank sample (white fabric not subjected to impregnation) and fabrics impregnated with microcapsules (samples with 1% and 5% of limonene) obtained using Formulation A. These textiles were prepared by covering the whole fabric with a solution of microcapsules but without using any conventional impregnation technique. It is visible the increasing of limonene as a function of the used limonene in the formulation (1 and 5%).

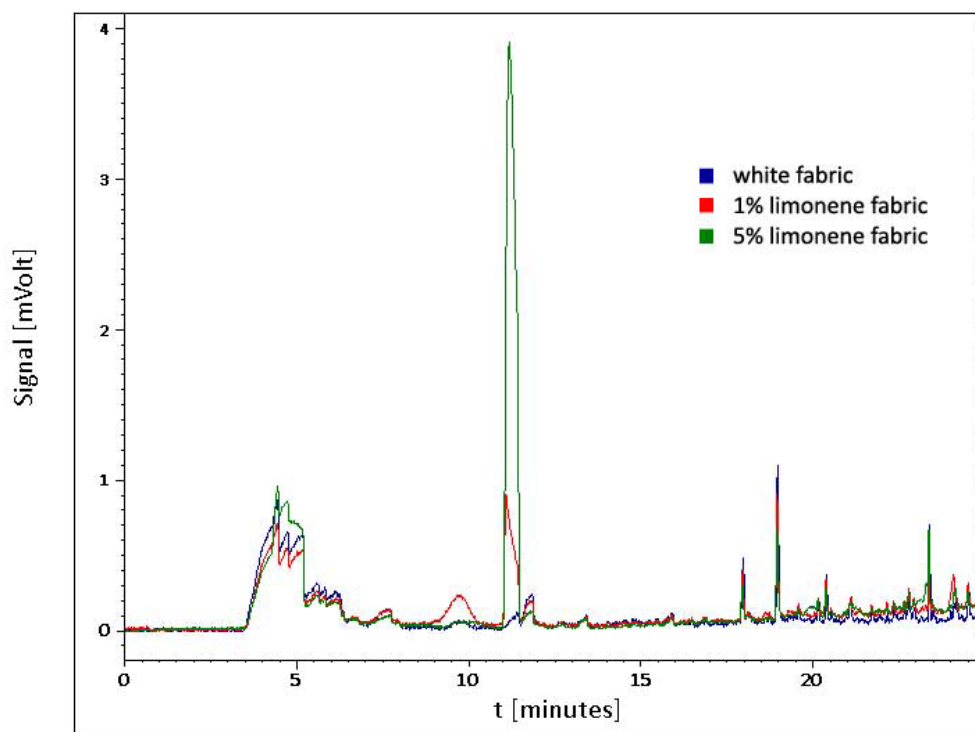


Figure 5.8. FID chromatograms of the blank sample (blue) and textiles impregnated with microcapsules solutions produced with 1% (red) and 5% (green) of limonene using formulation without washing.

Figure 5.9 shows the chromatograms of the headspace of the impregnated textiles, using a laboratory Foulard with microcapsules produced with formulation A with 5% of limonene after 0, 1, 2 and 3 dry cleaning washes. For the impregnation bath, it was used 300g/L of the produced microcapsules solutions, 50g/L of an acrylate crosslinking Primal ECO 934 TK and 10g/L of Perisoft SML softener.

It can be seen a decrease in the peak area of limonene with the increasing number of washes.

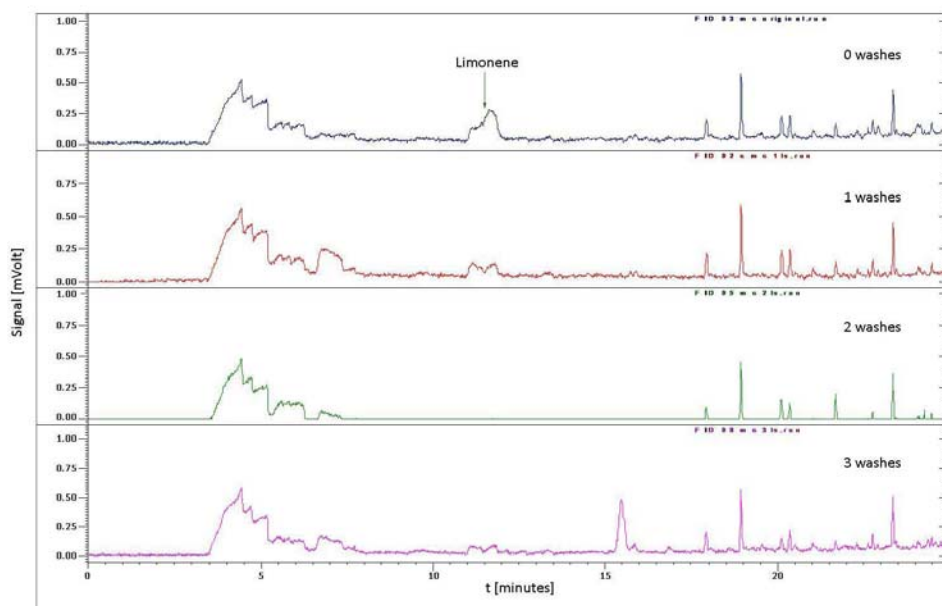


Figure 5.9. Chromatograms of the impregnated textiles with microcapsules of Formulation A after 0, 1, 2 and 3 dry cleaning cycles.

It is worth to mention that, the mass of limonene present in the unwashed textiles was already very small ($1.56\text{E-}06$ mg) thus posing problems of detection when using the CG-FID-Headspace technique.

To facilitate the interpretation of CG-FID-Headspace quantification the percentage of limonene present in the washed tissues (x_{lim}) relative to the amount of limonene present in the impregnated fabric without washing (x_{lim_0}), was calculated.

As it can be seen in Figure 5.10, it is visible the decrease of the amount of limonene flavour of the impregnated textile with the number of washing cycles. The mass present in the tissue after 3 washes represents 27% of the original impregnated fabric (before washing).

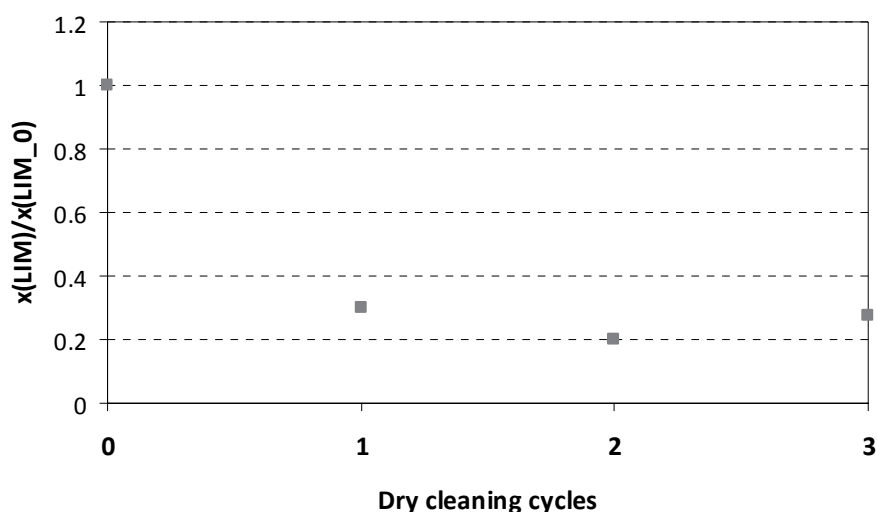


Figure 5.10. Mass of limonene remaining after 1, 2 and 3 dry cleaning cycles relative to the initial mass of limonene in the fabric.

Results and discussion

After characterizing microcapsules produced using formulation A it is possible to conclude that the methodology used to produce these microcapsules resulted in a unimodal distribution of microcapsules and fairly uniform, with an average diameter of 2.4 μm in volume as measured by the laser dispersion technology. It was observed that 89% by volume of particles have diameters higher than 1 μm (11% < 1 μm), but this represents 33% of the particles by number (67% < 1 μm). This means that, even if a large number of microcapsules have small size, most of the limonene was encapsulated in larger particles. The solid content obtained with this formulation was 1.1%.

The Optical microscopy allowed us to make a qualitative analysis simultaneously with the production of microcapsules. With this technique it was possible to

confirm the small size of the obtained products, the spherical shape as well the presence of small clusters. The reduction of solvent to 50% produces no change in the size of the microcapsules, although reducing the concentration of the solvent reduces the amount of microcapsules and clusters are not observed.

SEM micrographs of microcapsules solution confirmed the existence of clusters and showed that microcapsules have no defined morphology. Observing SEM micrographs of impregnated textiles with this formulation, it is evident the absence of microcapsules

The Headspace analysis confirmed the existence of limonene as the principal component of the produced microcapsules. It can be seen that increasing the concentration of limonene in the solution increases the quantity of limonene in these microcapsules.

However, when considering the impregnated textiles there is a significant decrease of the amount of limonene with the number of dry cleaning cycles.

It was also concluded that the amount of limonene released after GC-Headspace analysis of impregnated textiles with microcapsules obtained using the Formulation A is very small, needing to be improved by increasing the size of the microcapsules. For that purpose another formulation was used.

5.2 Formulation B

Face to the drawbacks observed with formulation A (low solid content, presence of agglomerates and rather poor impregnation results) a new interfacial polymerization method has been developed.

This method is divided into four main steps:

- Preparation of an emulsion, with the help of an ultraturrax system, consisting of an isocyanate, limonene, water and a protective colloid (PVA). This emulsion was thereafter completed to 500 mL with a solution of water with PVA and once more stirred.
- Addition of the polyol component and catalyst.
- Heating the reactive mixture to 90°C followed by the addition of the amine component. The reaction time was 1 hour.
- Finally, the solution of microcapsules was decanted and washed with a 30% ethanol aqueous solution. The microcapsules were dried at room temperature for 24h.

Table 5.4 shows the formulation (type of materials and amount used) and operating conditions. Table 5.5 present the experimental steps used in the preparation of these microcapsules.

Table 5.4. Base formulation (type of materials and amount used) and operating conditions used in the production of limonene microcapsules according to formulation B.

Material type	Polyurethane-urea
Isocyanate	HMDI (36 mL)
Polyol	Polyethyleneglycol (PEG 400) (40.8 mL)
Active agent	Limonene (42.6 mL)

(cont.)

(cont.)

Catalyst	Dibutyl tin dilaurate (DBDTL) (1mL)
Diamine	Ethylene diamine (EDA) (50 mL)
Protective colloid	Polyvinylalcohol (PVA) (2.1 g+ 2.1 g)
Water	Deionised water (250 mL + 172 mL)
Reaction temperature	90°C
Reaction time	1 hour
Stirring rate	1 st phase of the emulsion preparation: 8.000 rpm of during 1 minute 2 st phase of the emulsion preparation: 8.000 rpm during 5 minutes
Microcapsules washing	30% ethanol solution; 3 times

Table 5.5. Experimental steps used in the preparation of microcapsules– according to formulation B.

STEP 1	Preparation of the o/w emulsion: (1) HMDI + Limonene+ Water (250 mL)+ PVA (2.1 g) Stir with ultraturrax at 8000 rpm during 1 minute (2) Addition of water (172 mL) with PVA (2.1 g) Stir with ultraturrax at 8000 rpm during 5 minutes
STEP 2	Addition of PEG and DBTDL
STEP 3	Interfacial polymerization: Heating of the reactive mixture to 90°C. Addition of EDA followed by 1 hour reaction.
STEP 4	Solution decantation and washing: MC washing with a 30% ethanol solution followed by decantation (3 cycles) Storage at room temperature

5.2.1 Characterization of produced microcapsules using formulation B

LASER Dispersion

The produced microcapsules using formulation B were analyzed by laser dispersion using a Coulter LS230 to determine the particle size distribution in volume (Figure 5.11) and in number (Figure 5.12).

After production and storage, the same particle size distributions, both in volume and in number were obtained. The microcapsules mean size (based on volume distribution) is $14.1\ \mu\text{m}$ which means that these microcapsules are larger than the microcapsules obtained with formulation A. Moreover a bimodal distribution in volume was obtained. A more detailed analysis reveal that, in volume, 95% of the particles have diameters higher than $1\ \mu\text{m}$ ($5\% < 1\ \mu\text{m}$), but in number, 100% of the particles have a diameter lower than $1\ \mu\text{m}$. This means that, even if a large number of microcapsules have small size, most of the limonene was encapsulated in larger particles. This size heterogeneity is a direct consequence of the used dispersion technique (ultraturrax).

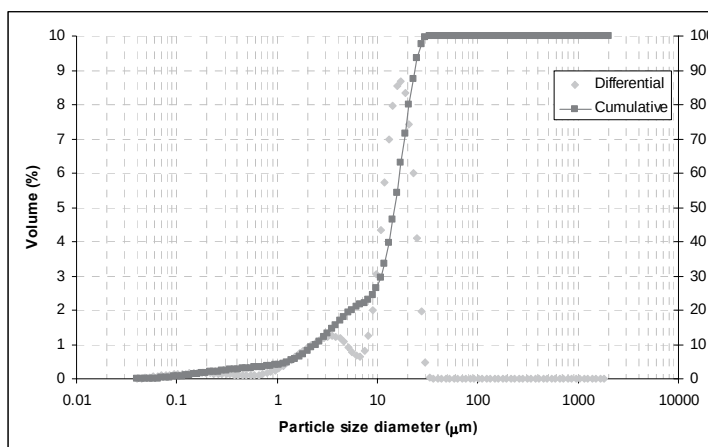


Figure 5.11. Differential and cumulative particle size distribution in volume of limonene microcapsules obtained with formulation B.

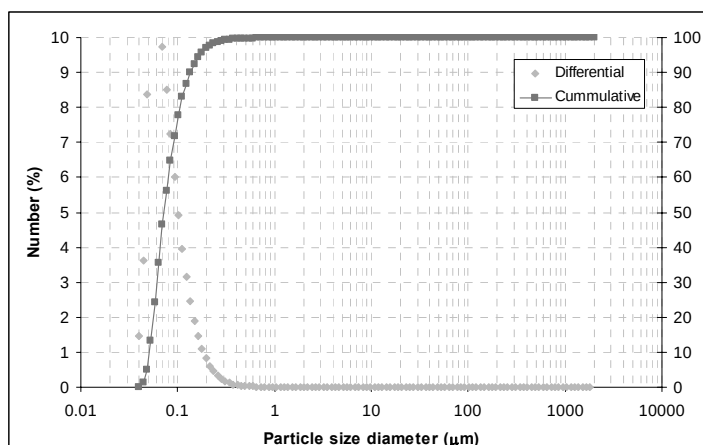


Figure 5.12. Differential and cumulative particle size distribution in number of limonene microcapsules obtained with formulation B.

Optical microscopy

The obtained images using a magnification of 400x and 1000x (Figure 5.13) puts clearly visible the existence of microcapsules. It can be concluded that Formulation B produces microcapsules with lemon scent, with well defined spherical morphology and no agglomerates have been detected.

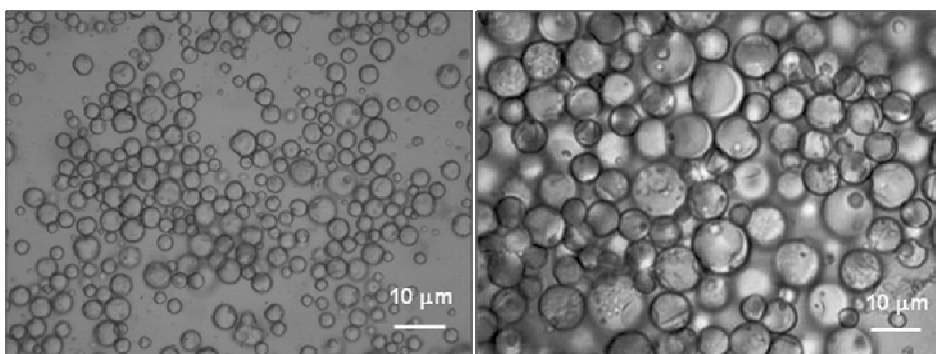


Figure 5.13. Photos of optical microscopy in bright field mode with magnifications of 400x (left) and 1000x (right) of the microcapsules produced using formulation B.

SEM

Microcapsules produced with formulation B were analysed by SEM. Textiles were covered with the microcapsules solution but without applying any impregnation technique. Two samples were analysed. In one case the textiles were dried at room temperature and in the second case the textiles were dried in an oven at 165°C in order to evaluate the resistance of microcapsules to high temperatures. Figure 5.14 shows SEM micrographs of the first case and Figure 5.15 shows SEM micrographs of the second case.

Observing these micrographs it can be seen the spherical morphology of microcapsules, some of them presenting deformations. It is also visible the existence of a residual material, like a film, covering the microcapsules.

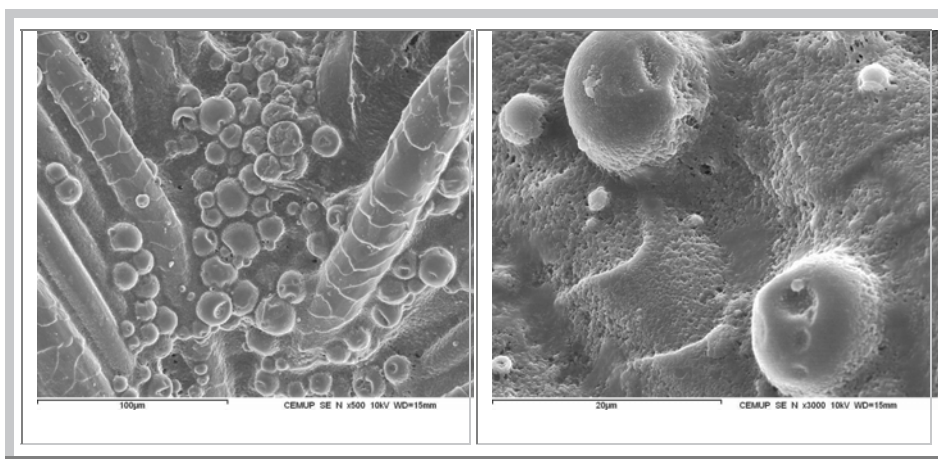


Figure 5.14. SEM micrographs of the textile covered with the produced lemon microcapsules according to formulation B dried at room temperature. Magnifications of 500x (left) and 3000x (right).

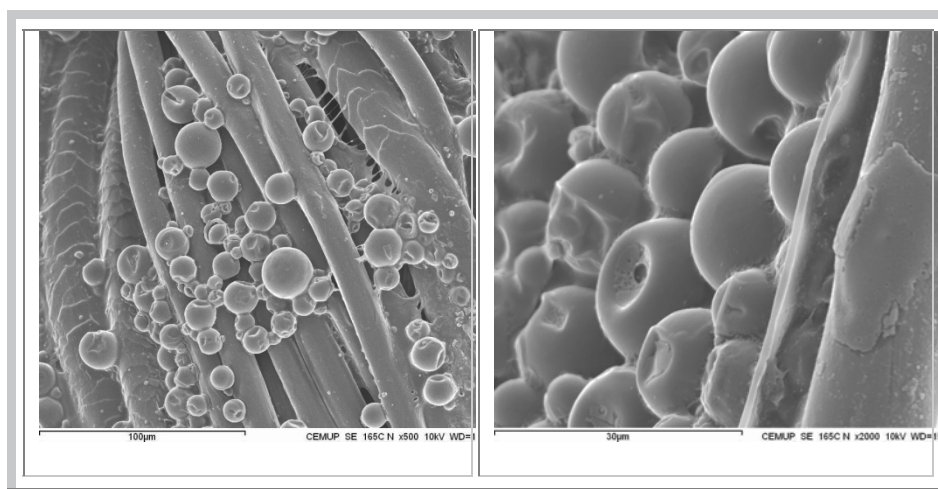


Figure 5.15. SEM micrographs of the textile covered with produced lemon microcapsules by formulation B and dried at 165°C with magnification of 500x (left) and 2000x (right).

SEM micrographs of dried microcapsules at 165°C showed that microcapsules have resistance at elevated temperatures. It is visible that the film disappeared, leaving microcapsules more visible, showing their spherical morphology, the smoothness of their surface and also the difference of particle size.

Textiles were impregnated with lemon microcapsules produced with formulation B at laboratory scale in the conditions detailed on Table 5.6 presented below. As the solid content was small (16%) the concentration of microcapsules was higher than the commonly recommended for commercial microcapsules. Two concentrations of microcapsules were used in this study and also the effect of the thermofixation process was analysed.

Table 5.6. Application conditions of microcapsules on textiles

Products	Characteristics	Concentration (g/L)
Aroma	Lemon Formulation B	20
		40
Softener	Perisoft Nano	10
Crosslinking (polyurethane)	Baypret USV	50

Textiles with lemon microcapsules impregnated with polyurethane binder were also analysed by SEM (Figure 5.16). These samples are textiles impregnated with 40g/L of lemon microcapsules.

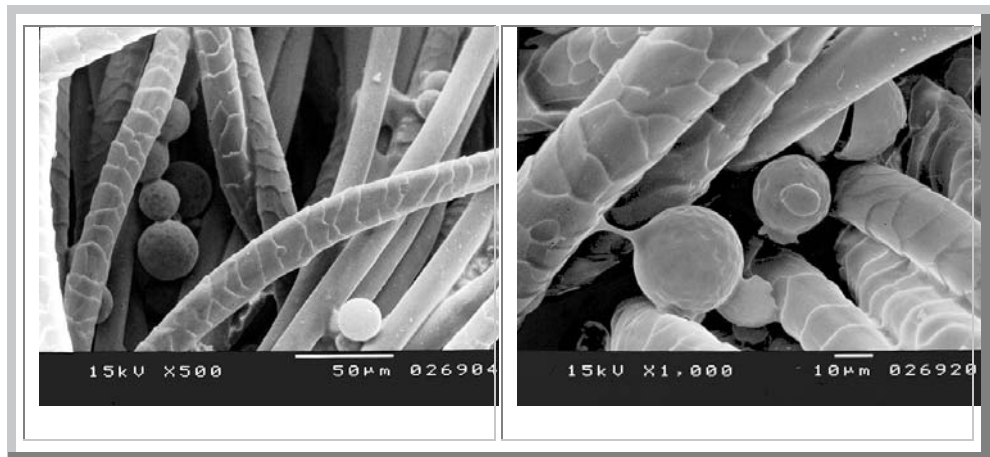


Figure 5.16. SEM micrographs of the impregnated textiles with lemon microcapsules (concentration 40 g/L) using a polyurethane binder (magnification of 500x (left) and 1000x (right)).

Observing these micrographs it is visible the spherical shape of the microcapsules and its rough surface. It can be also notice the good microcapsules adhesion to the textiles, although some of them are broken.

Textiles impregnation was studied with the produced PUU microcapsules and the polyurethane binder. The following experimental conditions have been used: (1) microcapsules concentration of 20 g/L with a thermofixation step (100 °C during 3 minutes), (2) microcapsules concentration of 40 g/L with a thermofixation step (same conditions as above) and (3) microcapsules concentration of 40g/L without the thermofixation step.

Figure 5.17 presented the obtained chromatograms with the limonene PUU microcapsules impregnated textiles using polyurethane binder and comparing the different concentrations used and the effect of the thermofixation process (with and without).

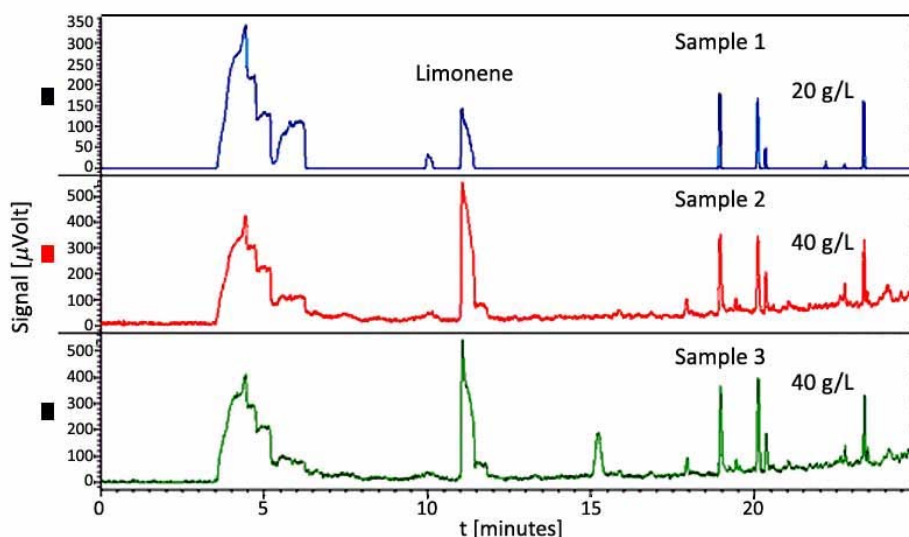


Figure 5.17. FID chromatograms of the limonene PUU microcapsules (Formulation B) impregnated textiles using different impregnation conditions (microcapsules concentration and the effect of presence and absence of a thermofixation process).

As it can be seen in Figure 5.18, there is a significant variation in relative weight of limonene present in impregnated textiles (sample 2), as a function of the number of washes. A loss of 72% was observed after the first dry cleaning cycle. For the same conditions the flavour wasn't detected by the panellist.

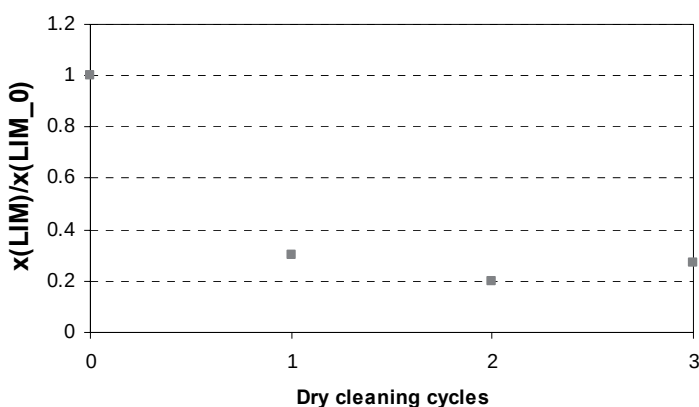


Figure 5.18. Relative weight of limonene present in the impregnated textiles with limonene microcapsules (sample 2) using the polyurethane binder, as a function of dry washes number.

Results and discussion

Lemon microcapsules produced using formulation B are larger than microcapsules obtained with formulation A, presenting a mean size, in volume, of 14.1 μm and a bimodal distribution. It was observed that 95% by volume of particles have diameters higher than 1 μm , but this represented 100% of the particles lower than 1 μm by number. This means that, even if a large number of microcapsules have small size; most of the limonene was encapsulated in larger particles. This size heterogeneity is a direct consequence of the used dispersion technique (ultraturrax). The solid content obtained with formulation B was also higher than the obtained with formulation A (16%).

The analysis performed with optical microscopy has shown well defined microcapsules with spherical shape and no agglomerates.

Microcapsules SEM analysis was firstly performed using the textile as substrate but without using any conventional impregnation technique. For this case, the results showed that textiles with microcapsules solution dried at room temperature presented a residual material- covering the microcapsules (like a film), although the microcapsules have spherical and well defined shape. Micrographs of dried microcapsules at 165°C showed that they have resistance at elevated temperatures and the previously formed film disappeared. Microcapsules showed a spherical morphology. The smoothness of their surface and also the difference of particle size are evidenced.

Although the microcapsules obtained by formulation B presented a well defined spherical shape, higher solid content, and good adhesion to textiles, the GC-FID-Headspace analysis showed a clear loss of odour (72%) only after the first dry cleaning wash.

To improve the performance of the microcapsules obtained using the methods described above; more specifically the microcapsules obtained using formulation B, other formulations have been developed.

- **Formulation C** – The PUU structure was maintained with the same reactants. The main modifications have been performed in terms of the used amounts.

- **Formulation D** - This formulation aimed at study the effect of producing only polyurethane microcapsules without the urea component resulting from the reaction of isocyanate with the introduced amine.

- **Formulation E** - This formulation aimed at study the effect of producing only polyurea microcapsules without the urethane component resulting from the reaction of isocyanate with the introduced polyol.

The reason that led to the choice of the systems described in formulations C, D and E, was based on the following considerations:

- Higher % Urethane -> Increased flexibility but lower thermal resistance;
- Higher % Urea -> Greater stiffness but higher thermal resistance.

5.3 Formulation C, D and E

The third method of producing microcapsules designated by formulation C is based on formulation B, using the same chemicals but changing the used amounts, and modifying the preparation procedure. The polyurethane-urea microcapsules are obtained by interfacial polymerization, as described below in five steps:

- Preparation of a homogeneous organic solution consisting of an isocyanate and limonene using magnetic stirring and a homogeneous aqueous phase formed by water and PVA with the help of an ultraturrax system.
- Preparation of an oil-in-water emulsion (o/w) by mixing the organic phase with the aqueous phase followed by stirring with an ultraturrax system
- Addition to the previously prepared emulsion of the polyol component and catalyst dissolved in water.
- Heating the reaction mixture to 80°C followed by 1 hour reaction before the addition of the amine component. The total reaction time was 2 hour.
- Decantation and washing with a 30% ethanol aqueous solution. The microcapsules were dried at room temperature for 24h.

Table 5.7 shows the formulation (type of materials and amount used) and operating conditions. Table 5.8 present the experimental steps used in the preparation of these microcapsules.

Table 5.7. Base formulation (type of materials and amount used) and operating conditions used in the production of limonene microcapsules according to formulation C.

Material type	Polyurethane-urea
Isocyanate	HMDI (15mL)
Polyol	Polyethyleneglycol (PEG 400) (23 mL)
Active agent	Limonene (50mL)
Catalyst	Dibutyl tin dilaurate (DBDTL) (0.5 mL)
Diamine	Ethylene diamine (EDA) (4 mL)
Protective colloid	Polyvinylalcohol (PVA) (4.2 g)
Water	Deionised water (250 mL + 100 mL+ 20 mL))
Reaction temperature	80°C
Reaction time	2 hours
Stirring rate	Preparation of the solutions: Organic: Magnetic stirring at 100rpm during 5 minutes Aqueous: Magnetic stirring at 100rpm during 5 minutes Preparation of the emulsion: 8.000 rpm during 5 minutes Interfacial polymerization: Magnetic stirring at 300 rpm till the end of the reaction
Microcapsules washing	30% ethanol solution; 3 times

Table 5.8. Experimental steps used in the preparation of these microcapsules– formulation C.

STEP 1	Preparation of the o/w emulsion: (1) Preparation of the organic solution: HMDI (15 mL) + Limonene (50mL) Magnetic stirring at 100rpm during 5 minutes
---------------	--

(Cont.)

STEP 1	(2) Preparation of the aqueous solution: Addition of water (250mL) with PVA (4.2 g) Magnetic stirring at 100rpm during 5 minutes (3) Mix organic solution with aqueous solution. Stir with ultraturrax at 8000 rpm during 5 minutes Magnetic stirring at 300 rpm till the end of the reaction
STEP 2	Addition of PEG and DBTDL previously dissolved in 100mL of water
STEP3	Interfacial polymerization: (1)Heating of the reactive mixture to 80°C followed by 1 hour reaction. (2) Addition of EDA dissolved in 20 mL of water followed by 1 hour reaction.
STEP 4	Solution decantation and washing: MC washing with a 30% ethanol solution followed by decantation (3 cycles) Storage at room temperature.

The fourth method of producing microcapsules designated by formulation D is based on formulation C, using almost the same reagents but without using the diamine in order to produce polyurethane microcapsules. The microcapsules are obtained by interfacial polymerization, as described below.

Table 5.9 shows the formulation (type of materials and amount used) and operating conditions. Table 5.10 present the experimental steps used in the preparation of these microcapsules.

Table 5.9. Base formulation (type of materials and amount used) and operating conditions used in the production of limonene microcapsules according to formulation D.

Material type	Polyurethane
Isocyanate	HMDI (15mL)
Polyol	Polyethyleneglycol (PEG 400) (46 mL)
Active agent	Limonene (50mL)
Catalyst	Dibutyl tin dilaurate (DBDTL) (0.5 mL)
Protective colloid	Polyvinylalcohol (PVA) (4.2 g)
Water	Deionised water (250 mL + 120 mL))
Reaction temperature	80°C
Reaction time	2 hour
Stirring rate	Preparation of the solutions: Organic: Magnetic stirring at 100rpm during 5 minutes Aqueous: Magnetic stirring at 100rpm during 5 minutes Preparation of the emulsion: 8.000 rpm during 5 minutes Interfacial polymerization: Magnetic stirring at 300 rpm till the end of the reaction
Microcapsules washing	30% ethanol solution; 3 times

Table 5.10. Materials and operating conditions used in the production of MC - formulation D.

STEP 1	Preparation of the o/w emulsion: (1) Preparation of the organic solution: HMDI (15 mL) + Limonene (50mL) Magnetic stirring at 100rpm during 5 minutes
---------------	--

(Cont.)

STEP 1	(2) Preparation of the aqueous solution: Addition of water (250mL) with PVA (4.2 g) Magnetic stirring at 100rpm during 5 minutes (3) Mix organic solution with aqueous solution. Stir with ultraturrax at 8000 rpm during 5 minutes Magnetic stirring at 300 rpm till the end of the reaction
STEP 2	Addition of PEG and DBTDL previously dissolved in 120mL of water
STEP3	Interfacial polymerization: Heating of the reactive mixture to 80°C followed by 2 hour reaction.
STEP 4	Solution decantation and washing: MC washing with a 30% ethanol solution followed by decantation (3 cycles) Storage at room temperature

The fifth method to produce microcapsules, designated by formulation E, is based on formulation C. But no polyol was introduced in the process. The amount of amine was recalculated in order to guarantee the excess of reactive groups towards isocyanates.

Table 5.11 shows the formulation (type of materials and amount used) and operating conditions. Table 5.12 present the experimental steps used in the preparation of these microcapsules.

Table 5.11. Base formulation (type of materials and amount used) and operating conditions used in the production of limonene microcapsules according to formulation E.

Material type	Polyurethane
Isocyanate	HMDI (15mL)
Diamine	Ethylene diamine (EDA) (8 mL)
Active agent	Limonene (50mL)
Protective colloid	Polyvinylalcohol (PVA) (4.2 g)
Water	Deionised water (250 mL + 120 mL))
Reaction temperature	40°C
Reaction time	2 hour
Stirring rate	Preparation of the solutions: Organic: Magnetic stirring at 100rpm during 5 minutes Aqueous: Magnetic stirring at 100rpm during 5 minutes Preparation of the emulsion: 8.000 rpm during 5 minutes Interfacial polymerization: Magnetic stirring at 300 rpm till the end of the reaction
Microcapsules washing	30% ethanol solution; 3 times

Table 5.12. Materials and operating conditions used in the production of MC - formulation E.

STEP 1	Preparation of the o/w emulsion: (1) Preparation of the organic solution: HMDI (15 mL) + Limonene (50mL) Magnetic stirring at 100rpm during 5 minutes
---------------	--

(Cont.)

STEP 1	(2) Preparation of the aqueous solution: Addition of water (250mL) with PVA (4.2 g) Magnetic stirring at 100rpm during 5 minutes (3) Mix organic solution with aqueous solution. Stir with ultraturrax at 8000 rpm during 5 minutes Magnetic stirring at 300 rpm till the end of the reaction
STEP 2	Addition of EDA (8 mL) previously dissolved in 120mL of water
STEP3	Interfacial polymerization: Heating of the reactive mixture to 40°C followed by 2 hour reaction.
STEP 4	Solution decantation and washing: MC washing with a 30% ethanol solution followed by decantation (3 cycles) Storage at room temperature

5.3.1 Characterization of produced microcapsules using formulation C, D and E

LASER Dispersion

The size distribution of the produced microcapsules was obtained after the reaction by laser dispersion. Figure 5.19 the comparison of the particle size distributions in volume for microcapsules produced using formulation C, D and E and Figure 5.20 shows the comparison in number.

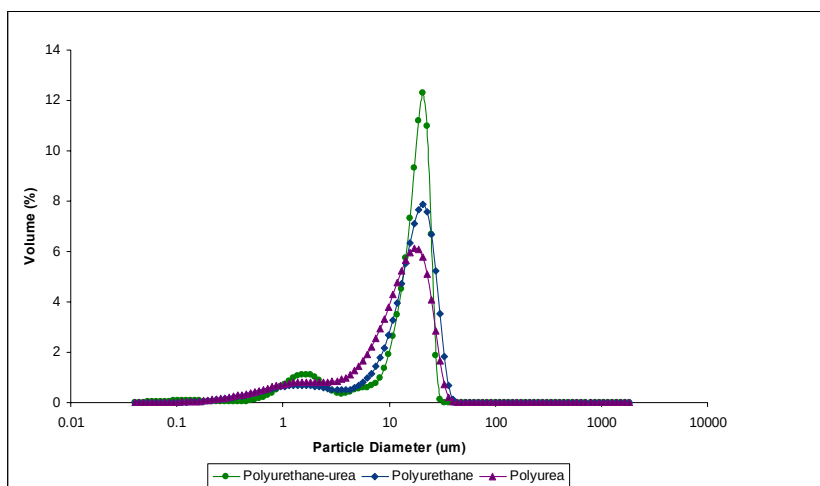


Figure 5.19. Particle Size distribution in volume for the limonene microcapsules produced by: a) Formulation C: Polyurethane-urea; b) Formulation D: Polyurethane; c) Formulation E: Polyurea.

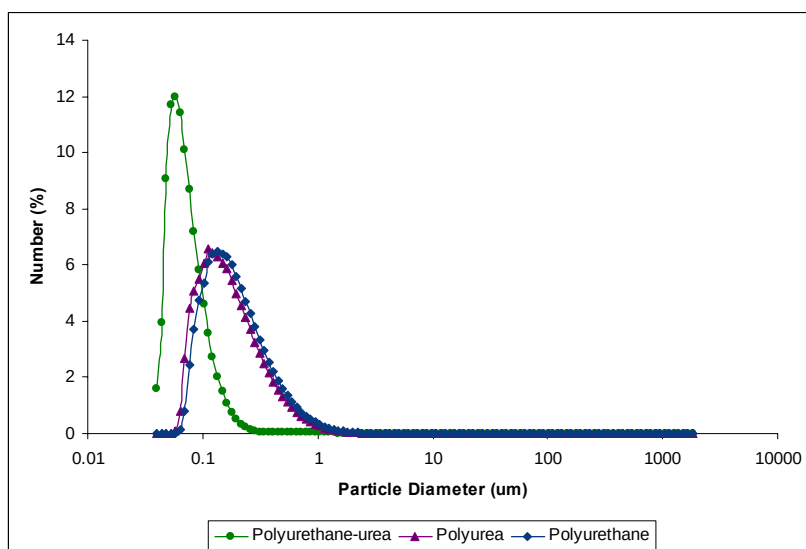


Figure 5.20. Particle Size distribution in volume for the limonene microcapsules produced by: a) Formulation C: Polyurethane-urea; b) Formulation D: Polyurethane; c) Formulation E: Polyurea.

For all the formulations (C, D and E) the particle size distribution in volume is bimodal and in number unimodal.

The mean particle size, in volume, of the produced microcapsules for the tested formulations (C, D and E) is presented in Table 5.13. As can be observed the higher mean size was obtained for the formulation D (polyurethane).

Table 5.13 Average size diameter of the microcapsules obtained using the formulations C, D and E.

Formulation	Average diameter (μm)
C	15.82
D	16.26
E	13.21

Optical microscopy

Analyzing in detail, using a magnification of 400x and 1000x (Figure 5.21), it is clearly visible the existence of microcapsules. It can be concluded that Formulations C, D and E produce lemon microcapsules with spherical and well defined shape.

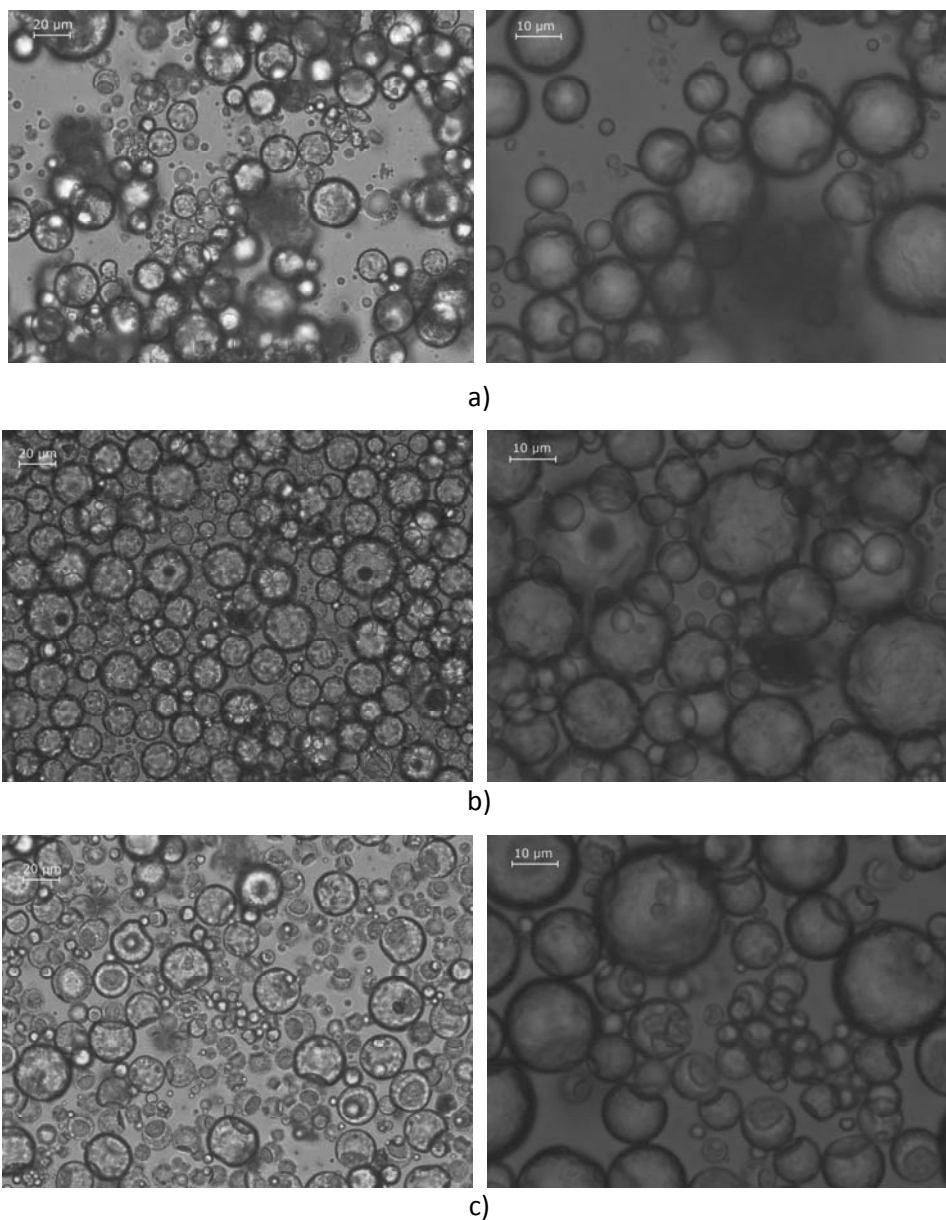
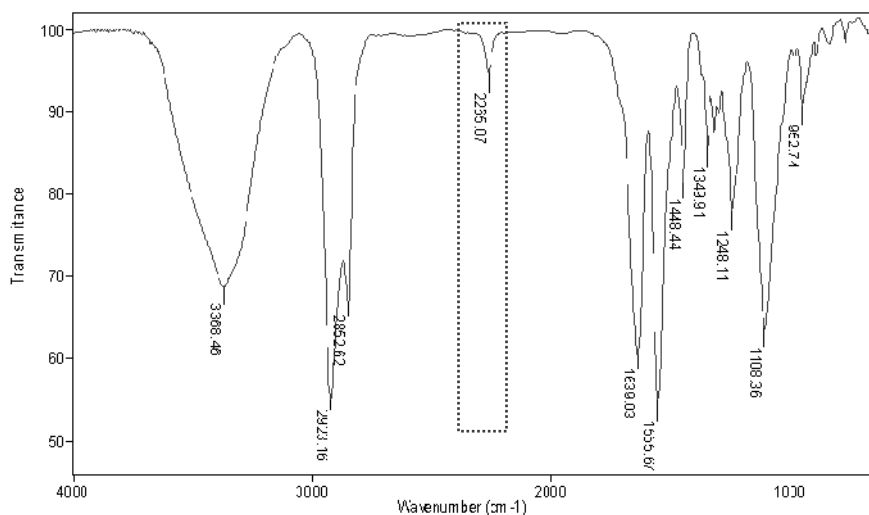


Figure 5.21. Photos of optical microscopy in bright field mode using a magnification of 400x (left) and 1000x (right) of microcapsules produced using: a) formulation C; b) formulation D; c) formulation E).

The microcapsules obtained using the formulation D, are larger than those obtained using the formulation C and E in accordance with the results obtained by laser dispersion.

FTIR

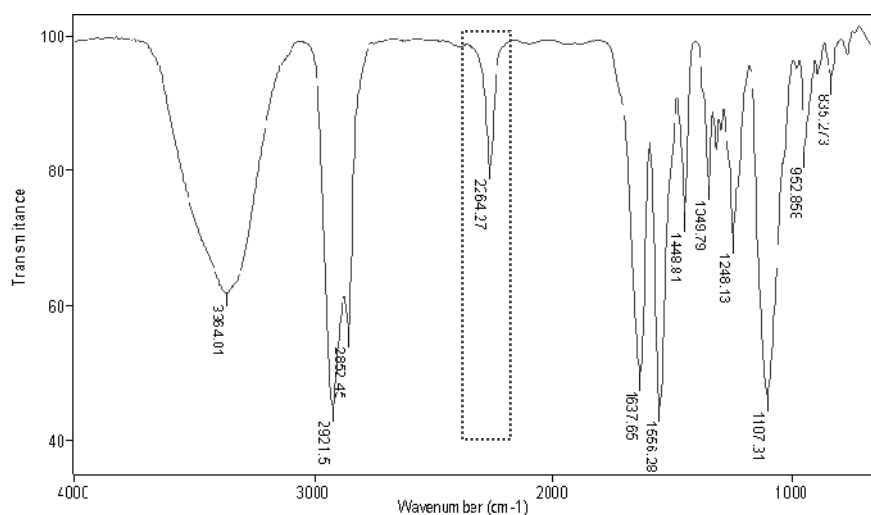
The evaluation of isocyanate groups consumption in the produced microcapsules was performed by infrared spectroscopy (FTIR) in transmittance mode. For all the formulations (Figure 5.22) the presence of residual isocyanates (peak assigned at 2270 cm^{-1}) was detected.



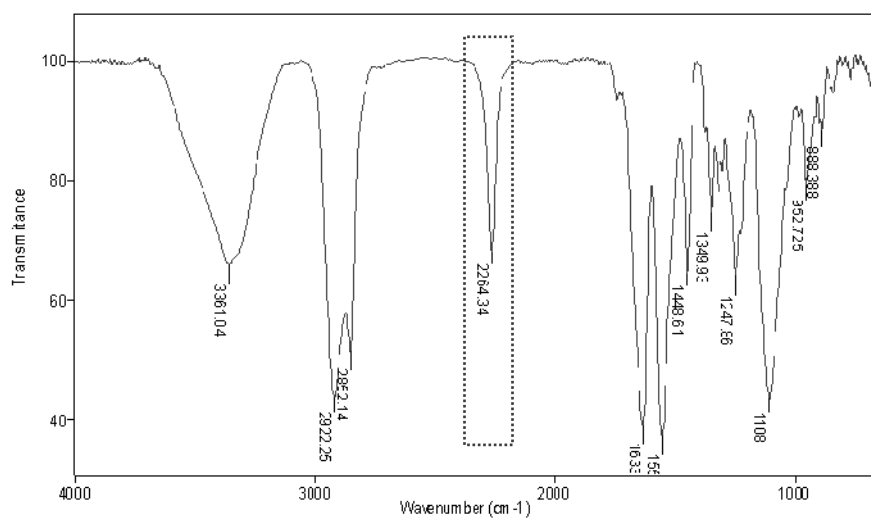
(a)

(Cont.)

(Cont.)



(b)



(c)

Figure 5.22. Infrared spectra (FTIR) of the microcapsules obtained using: (a) formulation C, (b) formulation D and (c) formulation E.

GC-FID-Headspace

The strength of the odour present in the impregnated textiles using formulations C, D and D was performed by GC-FID-Headspace analysis. Impregnated textiles were analysed according to the number of dry washes and the number of abrasion cycles. Thus textile samples subjected to 0, 1, 2, 3, 4 and 5 dry washes were analyzed as well as samples subjected to 3000, 6000 and 9000 abrasion cycles.

Textiles were impregnated with limonene microcapsules produced with formulation C, D and E at laboratory scale in the conditions detailed on Table 5.14 presented below. The solid content was 20.3% for formulation C, 18.9% for formulation D and 16.7% for formulation E.

Table 5.14. Application conditions of microcapsules on textiles

Products	Characteristics	Concentration (g/L)
Aroma	Lemon Formulation C, D, E	20
Softener	Perisoft Nano	10
Crosslinking (polyurethane)	Baypret USV	50

Figure 5.23 shows the obtained chromatograms for the impregnated textiles before being subject to washing (original samples).

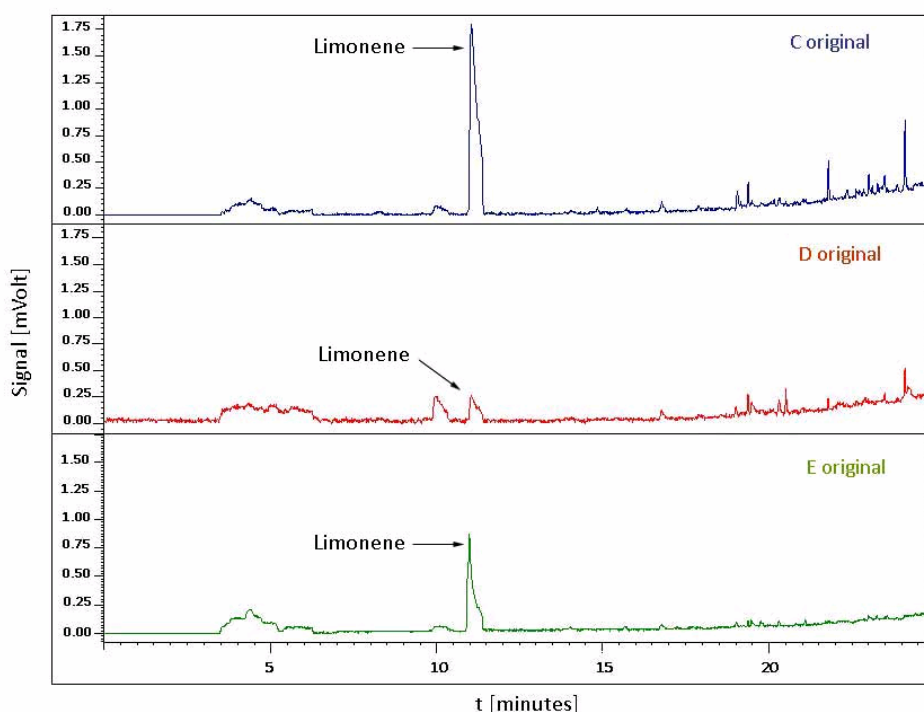


Figure 5.23. FID chromatograms of the original impregnated textiles with limonene microcapsules produced using formulations C, D and E without washing.

Comparatively to the polyurethane–urea formulation (C) the analysed impregnated textiles with formulations D (polyurethane) and E (polyurea) show a smaller limonene peak. This is particularly valid for formulation D where the limonene peak is rather small.

The amount of limonene associated with each peak, calculated based on a limonene calibration curve, is $5.4\text{E-}06$ mg for formulation C (polyurethane-urea) , $7.0\text{E-}07$ mg for formulation D (polyurethane) and $1.9\text{E-}06$ mg for formulation E (polyurea) Summarizing, comparatively to formulation C (100%), only 13% and 34% of the limonene was detected when using formulations D and E, respectively.

As it can be seen in Figure 5.24, there was a decrease of the relative limonene weight present in the impregnated textiles with limonene microcapsules produced using formulation C as a function of the number of washes. The relative weight of limonene is 0.34 after 1 wash, being the loss of flavour of 66% during the first dry cleaning cycle.

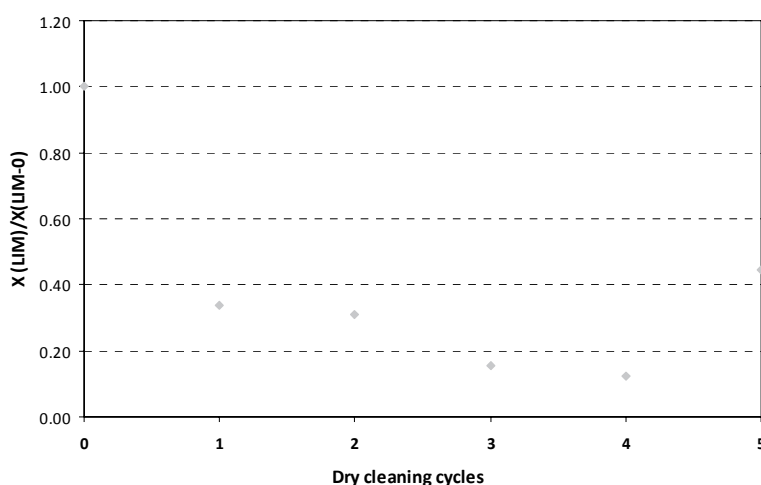


Figure 5.24. Relative weight of limonene present in impregnated textiles with limonene microcapsules produced using formulation C, depending on the number of wash cycles.

Figure 5.25 shows a significant decrease in the relative mass of limonene present in the impregnated textiles with limonene microcapsules produced using formulation C with the number of abrasion cycles; the relative weight present in the impregnated textiles with 3000 abrasion cycles is 0.19 which corresponds to a loss of aroma of 81%.

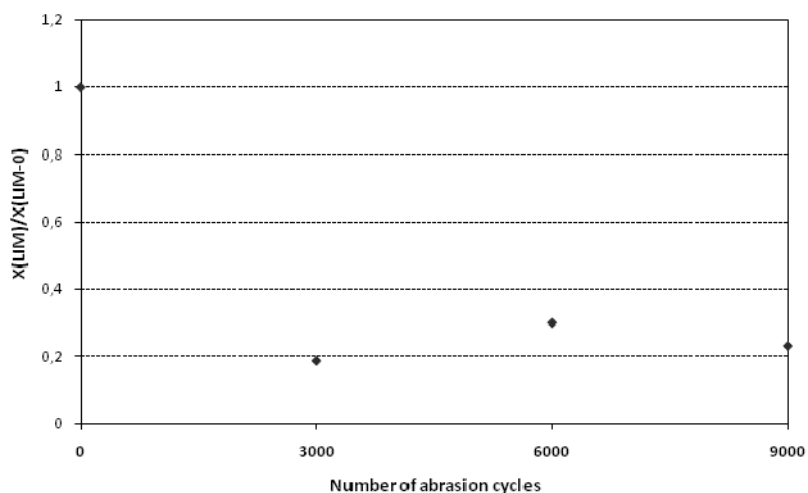


Figure 5.25. Relative weight of limonene present in impregnated textiles with limonene microcapsules using formulation C, depending on the number of abrasion cycles.

Results and discussion

The particle size distributions in volume for all the three formulations have showed a similar distribution model, i.e., a bimodal distribution.

The optical microscopy allowed to observe the spherical morphology of the produced microcapsules and to conclude that they are well defined.

Analysing the impregnated textiles with these three formulations, it was visible that limonene microcapsules produced with formulation C (polyurethane-urea) presented more limonene than the impregnated textiles with microcapsules produced with formulations D and E.

Analysing the impact of dry cleaning cycles and abrasion cycles on the impregnated textiles with microcapsules produced with formulation C it is

observed a loss of 64% after the first dry cleaning cycle and a loss of 81% after 3000 abrasion cycles.

Based on these results, it was concluded that the formulation with better performance is the Formulation C although the GC-FID-headspace analyses of impregnated textiles subjected to dry cleaning and abrasion cycles suggests that this formulations needs to be optimised in order to improve the solidness to dry cleaning cycles and to abrasion cycles.

5.4 Improvement of formulation C

Several experiments were performed to improve formulation C and get better properties of the produced microcapsules. The principal issues to be solved were the dissolution of PVA in water, removing of excess reagents used in the formulation and increasing the compatibility of lemon microcapsules with the water by post-synthesis design - adding an emulsifier.

The following changes were introduced to the originally developed formulation C:

1. The process of PVA dissolution in water is now done with heat (80°C) and stirring;
2. The new solution used two amines introduced sequentially in the process, i.e. a first reaction with EDA (one hour) followed by reaction with HYD (one hour). Hydrazine (HYD) was introduced in this formulation in order to complete the reaction with the residual NCO groups. Through the infrared spectra analysis of the previous formulations with only ethylene diamine (EDA) it was found that isocyanate conversion was not complete (presence of a peak assigned at 2270cm⁻¹). In the formulation where hydrazine was introduced, the conversion was complete (Figure 5.26). This is due to the fact that the molecule of the HYD is smaller than the molecule of the EDA, so that it can soon spread to the

interior of the microcapsule and react with remaining NCO groups. In this final step of the reaction, the microcapsule is already formed, so the reaction mechanism is controlled by diffusion of reactive groups into the heart of this, where the reaction occurs. It is not feasible to completely replace the EDA for HYD when the objective is to obtain a robust microcapsule wall. This is because the molecular chain of HYD is shorter, thus increasing the density of hard segments (urea bonds) and hence the crystallinity of the microcapsule wall, making it more brittle;

3. Removal of excess reagents and increase compatibility with water. The process of washing/separation of the produced microcapsules was identified as one of the key points to be solved during this study. The aim was to obtain a final product with characteristics similar to the commercial microcapsules (good compatibility with water and solid content between 30% and 50%).

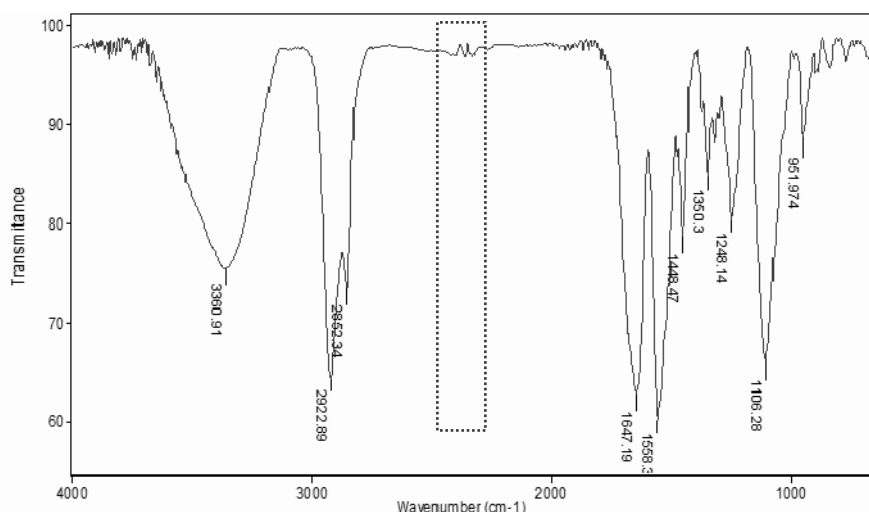


Figure 5.26. Infrared spectra (FTIR) of the microcapsules obtained using formulation C with the introduction of hydrazine in the formulation.

Regarding the stabilization of the microcapsules in water after synthesis, several emulsifiers were tested (Table 5.15). The summary of results is presented in Table 5.16.

Table 5.15. Summary of data related to the used emulsifiers.

EMULSIFIER	CHEMICAL FAMILY	HBL	SUPPLIER
Tergitol 15-S-9	Secondary Alcohol Ethoxylate (Nonionic)	13.3	Dow Company, EUA
Tergitol 15-S-20	Secondary Alcohol Ethoxylate (Nonionic)	16.3	Dow Company, EUA
Triton CA	Specialty Alkoxylate (Nonionic)	10-12	Dow Company, EUA
Renex 95	Nonylphenol ethoxylate (Nonionic)	13.0	Oxiteno, Brazil
Ultramina 200	Fatty amine ethoxylate (Nonionic)	14.3	Oxiteno, Brazil

Table 5.16. Results obtained in formulating the post-synthesis.

SURFACTANT	EXPERIMENT	OBSERVATIONS
Tergitol 15-S-9	MC010	Microcapsules disperse easily in water; Foaming occurrence.
Tergitol 15-S-20	MC012	A rigid layer is formed in the surface; Foaming occurrence (more than with Tergitol 15-S-9); The dispersion in water is worse comparatively to Tergitol 15-S-9.
Renex 95	MC013	The dispersion in water is good; Foaming occurrence.
Ultramina 200	MC014	Results similar to Tergitol 15-S-20.
Triton CA	MC023	No foaming occurrence. The dispersion in water is quite good.

LASER Dispersion

The size distribution of the produced microcapsules was determined after the reaction completion by laser dispersion. The average size of the produce microcapsules (based on the distribution in volume) of some experiments are shown in Table 5.17.

Table 5.17. Average diameter size of the microcapsules obtained using the formulations C optimized.

Formulation	Average diameter (μm)
MC000	15.82
MC003	9.24
MC009	10.90
MC010	10.03
MC012	11.08
MC013	10.79
MC014	11.27
MC015	11.47
MC023	11.07

GC-Headspace

Using the technique of GC-FID-Headspace, the amount of limonene present in the impregnated textiles with the microcapsules produced during the optimization process, was determined. The results are shown in Figure 5.27.

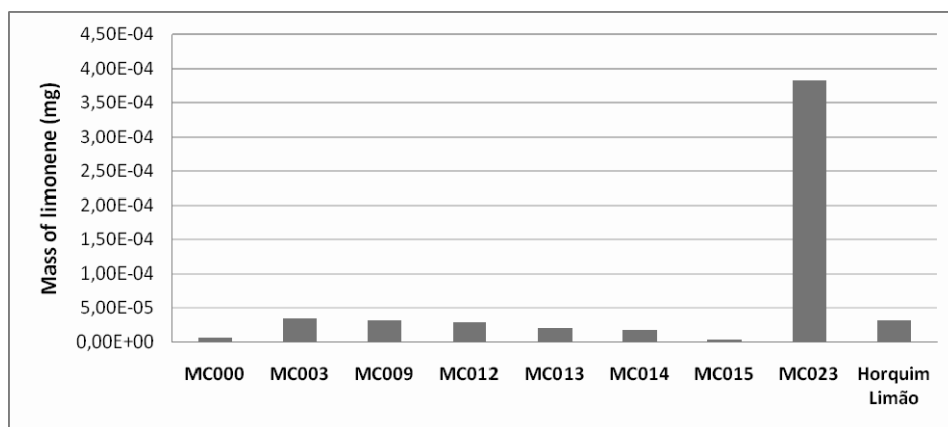
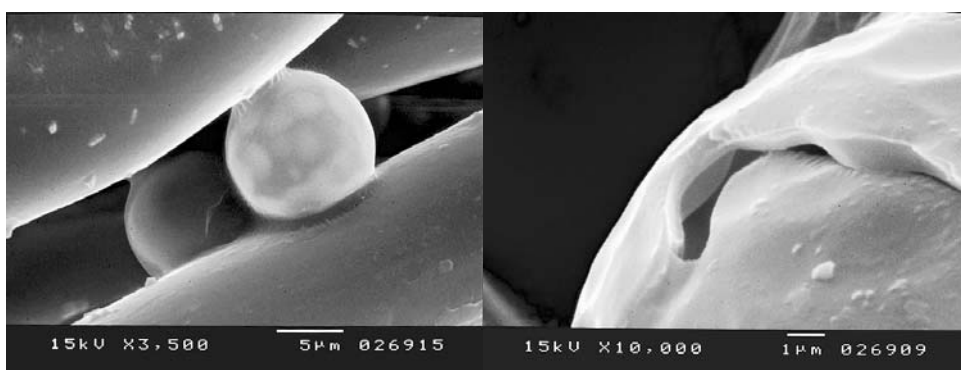


Figure 5.27. Comparison of the limonene amount detected by headspace among samples (i) Original formulation C - MC000, (ii) Formulation C optimized - MC003-MC023 and (iii) commercial lemon microcapsules - Horquim.

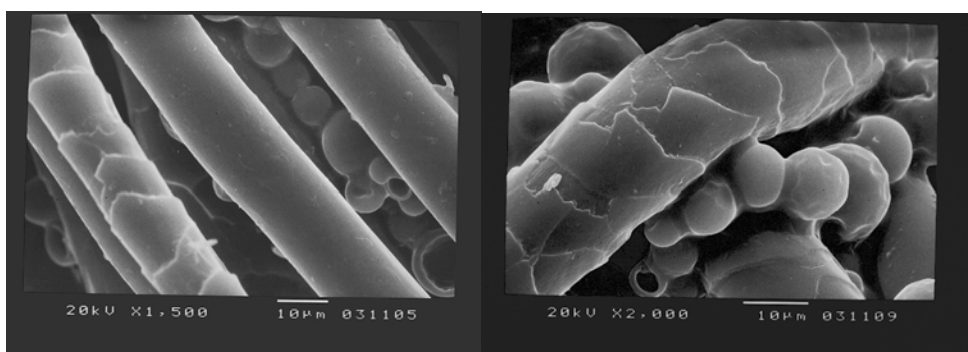
SEM

Impregnated textiles with limonene microcapsules obtained using the original Formulation C and the optimized formulation C were analyzed by SEM. In Figure 5.28 are presented some micrographs.

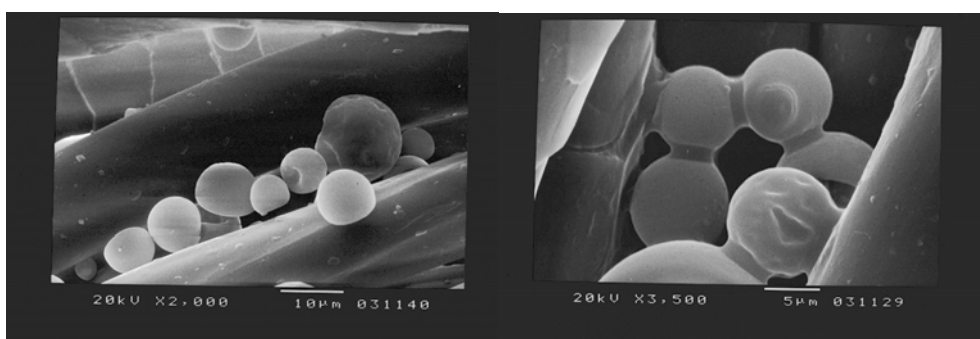
Observing these micrographs it is visible that microcapsules are bonded to the textiles and also their spherical morphology. It was also possible to measure the wall thickness of microcapsules that was around $1\ \mu\text{m}$ as it can be seen on Figure 5.28 (i) in the micrograph with 10000x magnification and was also confirmed by calculation using the equation (5-1).



(i) MC000



(ii) MC003



(iii) MC009

Figure 5.28. SEM micrographs of the impregnated textiles with limonene microcapsules produced using formulation C: (i) Original formulation C - MC000, (ii) optimized formulation C - MC003 and (iii) optimized formulation C - MC009.

According to Gosh [150] wall thickness of microcapsule can be estimated using the equation 5.1. Assuming that the density of the active agent (ρ_a) and wall (ρ_w) are identical, it is possible to demonstrate the relationship between the wall thickness ($d_w = r_e - r_a$) and the ratio between the weight of the wall material (w_w) and that of the active agent material (w_a):

$$d_w = (r_e - r_a) = \left[\left(\frac{W_w}{W_a} + 1 \right)^{\frac{1}{3}} - 1 \right] r_a \quad \text{Eq. 5-1}$$

where r_e is the exterior radius of the microcapsule, r_a is the interior radius of the microcapsule and (w_w/w_a) is the ratio between wall material weight ($w_w=93.5$ g) and active agent weight ($w_a=84.2$ g). The relationship between the wall thickness and the capsule diameter is linear when the ratio of $w_a/(w_w+w_a)$ is in the range of 0.50 to 0.95.

After several experiments the optimized formulation was set up. The details of this formulation (final formulation) are presented below, as well as, some characterization results of the produced microcapsules.

5.5 Final formulation

5.5.1 Microcapsules preparation

Polyurethane-urea microcapsules were prepared by interfacial polymerization. Figure 5.29 shows the reaction scheme for the polycondensation reactions involved in the developed process. The polymer shell is formed, in a first step by the reaction of HMDI with PEG400, followed by the reaction of HMDI with EDA and HMDI with HYD.

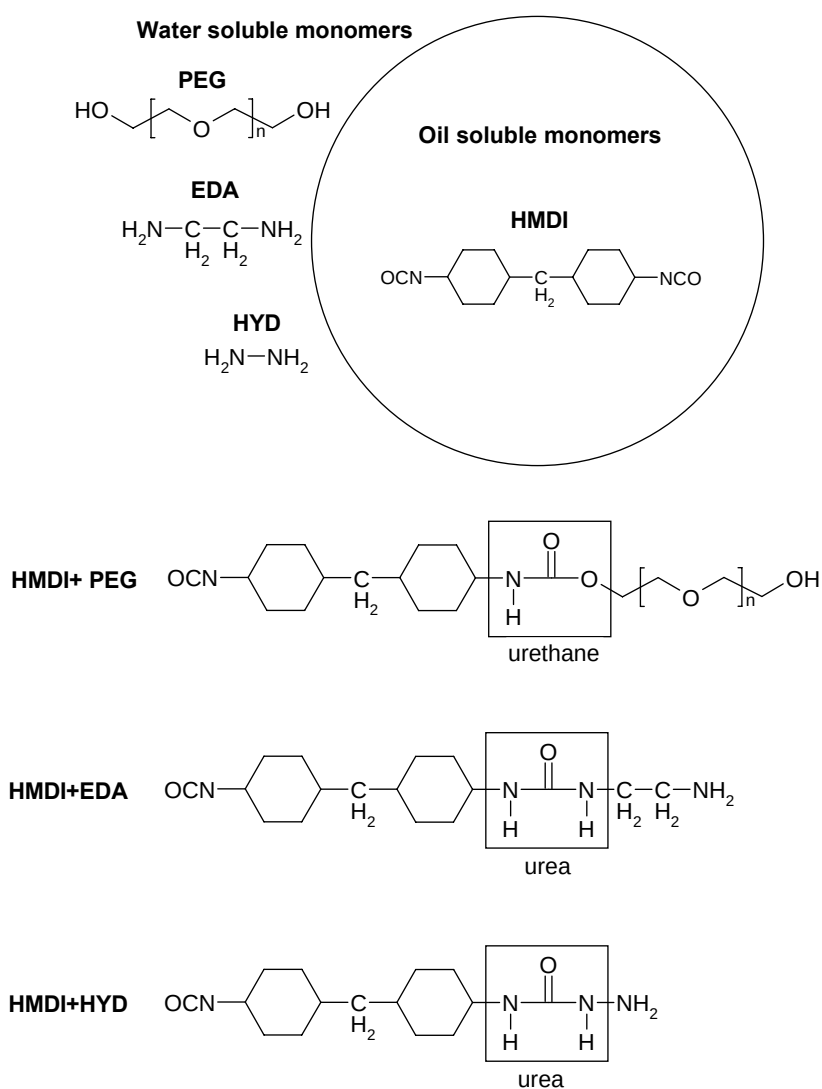


Figure 5.29. Reaction scheme for polyurethane-urea microcapsules production.

The microencapsulation process was carried out in a 1000 mL polymerization reactor with controlled temperature and equipped with a mechanical stirrer using the general procedure described in Figure 5.30. Prior to microencapsulation, the oil phase (limonene comprising the isocyanate reactant) was mixed with an aqueous phase containing the PVA (aqueous phase 1). The mixed solution was

then mechanically emulsified with an IKA mixer (model T25 Basic) at 11000 rpm during 3 minutes at room temperature. The originated oil-in-water emulsion (o/w) was thereafter transferred into the polymerization reactor and heated to 80 °C. With stirring (100 rpm), the following aqueous phases were sequentially added after one hour intervals: (1) an aqueous phase containing PEG 400 and catalyst DBTDL (aqueous phase 2), (2) an aqueous phase containing EDA (aqueous phase 3) and, (3) an aqueous phase containing HYD (aqueous phase 4). The total reaction time was 3 hours. The resulting microcapsules were collected by centrifugation, washed first with an ethanol solution (30% v/v) and thereafter twice with distilled water to remove the remaining reactants. Finally they were suspended in a solution of water containing the wetting agent (Triton CA). Table 5.18 shows the chemical system and the composition of oil and aqueous phases used to prepare the polyurethane-urea microcapsules.

Table 5.18. Chemical system and composition of oil and aqueous phases.

PHASE	COMPOSITION							
	LMN (mL)	Water (mL)	HMDI (mL)	PVA (g)	PEG400 (mL)	DBTDL (mL)	EDA (mL)	HYD (mL)
Oil	100		30					
Aq. 1		500		8.4		1.0		
Aq. 2		200			46			
Aq. 3		40					8	
Aq. 4		20						2.9

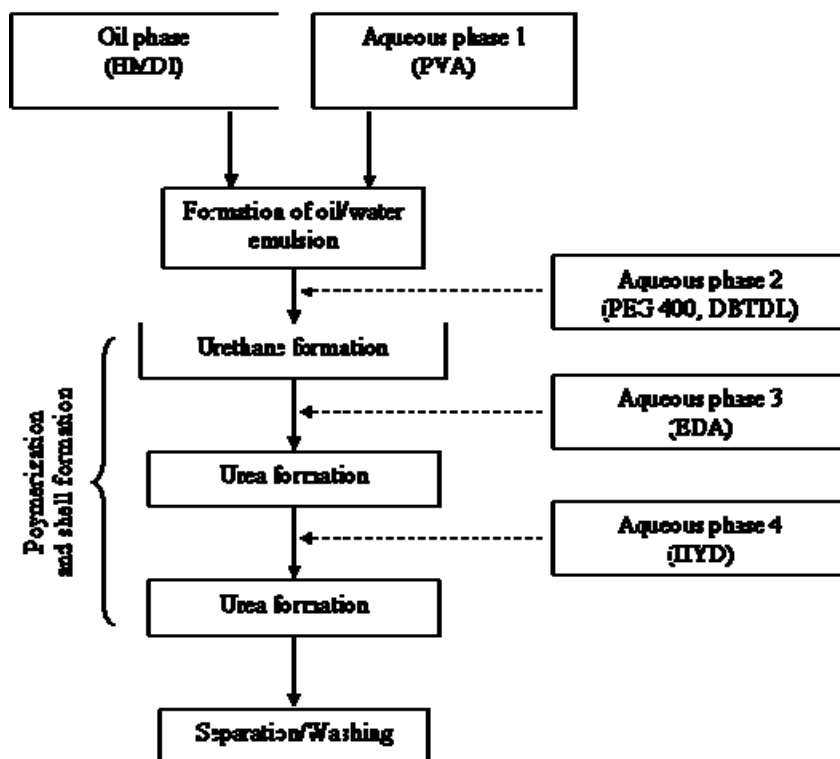


Figure 5.30. Microencapsulation process of limonene by interfacial polymerization.

Step 1. Formation of oil-water emulsion

The oil-water emulsion is formed by mixing an organic phase (FO) and an aqueous phase (FA1). The FO contains the active ingredient (limonene or fragrance) and isocyanate (HMDI). The FA1 consists of water and a protective colloid (PVA) which favours the stabilization of droplets formed and fixed distribution of particle size. This emulsion is prepared in a beaker and stirred with an ultraturrax (IKA T25 Basic model). Then it is transferred to a glass reactor equipped with heating and stirring. Typically, the emulsion is placed at 80 °C and stirring set at 100-300 rpm. To prepare the aqueous phase FA1, the PVA is dissolved in water at 80 °C with stirring.

Step 2. Formation of the capsule wall (step in two stages)

Urethane phase formation: Corresponds to the addition of FA2 aqueous phase (water, PEG 400 and DBTDL) to the emulsion prepared in the previous step. In this phase it is initiated the formation of a urethane membrane around the oil droplets. As the reaction proceeds the wall improves thickness.

Formation of the urea phase: After the initial phase of the urethane formation, the aqueous phase FA3 (water and EDA) is added. As the reaction of isocyanate with EDA leads to incomplete conversion (even for long times), another aqueous phase is added (FA4) (water and HYD). The HYD is a short diamine and has the advantage of easily spread through the capsule material, encouraging the consumption of residual isocyanates. The aqueous phases FA3 and FA4 are added dropwise.

Step 3. Separation and washing

In the process of interfacial polymerization polymer formation occurs when the monomers present in two phases spread to the oil-water interface. With the formation of polymer an additional barrier will appear - diffusion through the membrane formed. To enhance the total consumption of isocyanate groups, the polymerization process uses an excess of reactants (polyol and amine). This excess should be discarded at the end of the process otherwise it will incorporate the final product. The following procedure was used:

- Separation by centrifugation (7 minutes at 2400 rpm),
- Washing with ethanol solution (30%, v/v),
- Separation
- Washing with deionised water
- Separation

In a final step an aqueous solution containing an external emulsifier Triton CA (5% v/v) is added. The addition of this emulsifier is intended to improve the compatibility of the microcapsules with water for subsequent storage.

5.5.2 Impregnation of microcapsules on textile substrate

Microcapsules were applied to textiles at laboratory scale, reproducing the industrial application conditions. The microcapsules were applied in the finishing process of textiles fabrication using a foulard, in which the textile to be treated is impregnated using a finishing bath containing (i) microcapsules, (ii) a softener (Perisoftal Nano) and (iii) a self-crosslinking (Baypret USV).

The conditions required for this procedure are shown on Table 5.19.

Table 5.19. Conditions of textile impregnation process

Finishing conditions	Scent (Limonene microcapsules)
Substrate	Fabric Wool/Polyester
Process:	Foulard
Pressure	3 Bar
Bath Volume	1 L
Limonene microcapsules	50g/L
Perisoftal Nano (softener)	10g/L
Baypret USV (self-crosslinking)	50g/L

(Cont.)

Drying	100° - 3 min
Thermofixing	140° - 3 min
Expression rate	70-80%

5.5.3 Characterization of the microcapsules solution

FTIR analysis

Figure 5.31 shows the FTIR spectrum of the produced polyurethane-urea microcapsules. Several infrared vibrations, typical of polyurethane-urea systems, could be assigned: (1) the N-H stretching mode assigned at 3365 cm⁻¹; (2) the carbonyl zone assigned between 1780 and 1600 cm⁻¹. The strong intensity of the vibration at 1643 cm⁻¹ (urea carbonyl) comparatively to the overlapped vibration at 1732 cm⁻¹ (urethane carbonyl) indicates that, under the synthesis conditions used, urea formation is favoured over urethane formation; and (3) the amide II (1556 cm⁻¹) and amide III (1244 cm⁻¹) vibration modes. The vibration assigned at 1106 corresponds to the ether group C-O-C stretching mode. The low intensity associated to this vibration also confirms the low urethane character of the produced microcapsules, since it corresponds to the PEG 400 incorporation. C-H stretching vibrations are assigned at 2926 and 2856 cm⁻¹. The absence of the peak at 2270 cm⁻¹, due to the isocyanate stretching vibration, confirms that all the HMDI was consumed completely through the reaction with PEG 400, EDA and HYD.

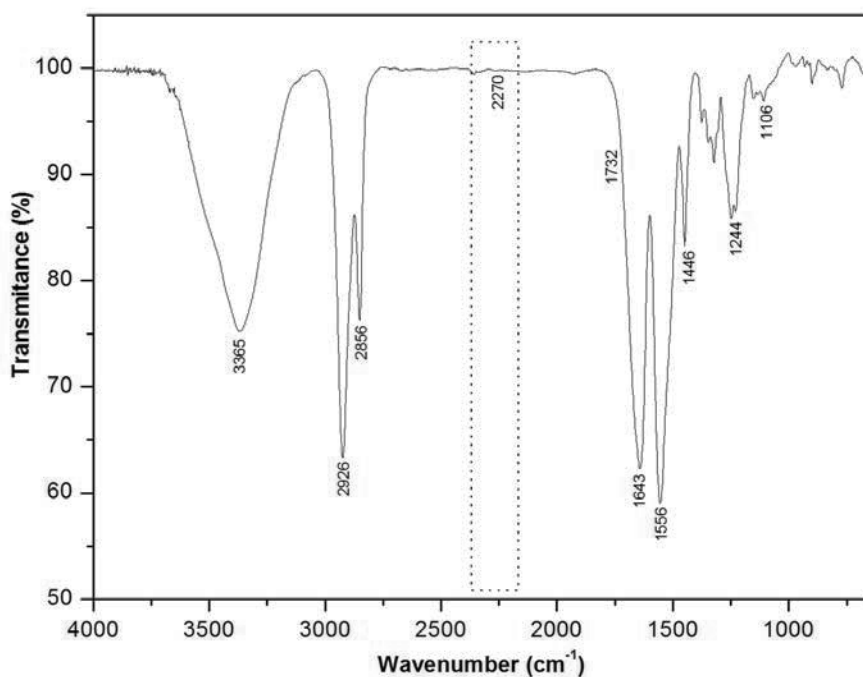


Figure 5.31. FTIR spectrum of polyurethane-urea microcapsules.

Particle size distribution

Figure 5.32 shows the particle size distribution based on volume of the prepared polyurethane-urea microcapsules containing limonene oil. The microcapsules mean size (based on volume distribution) is 10 μm . Figure 5.33 shows the particle size distribution based in number of the prepared polyurethane-urea microcapsules containing limonene oil.

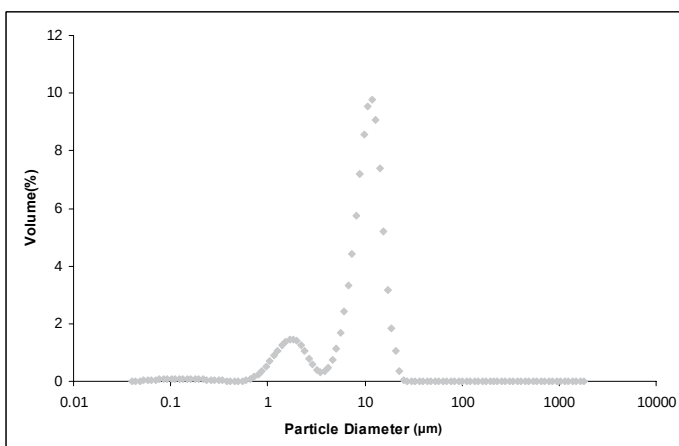


Figure 5.32. Particle size distribution in volume of polyurethane-urea microcapsules with limonene oil.

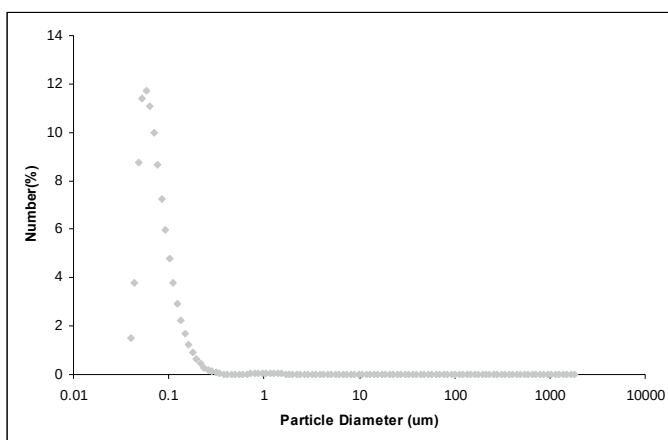
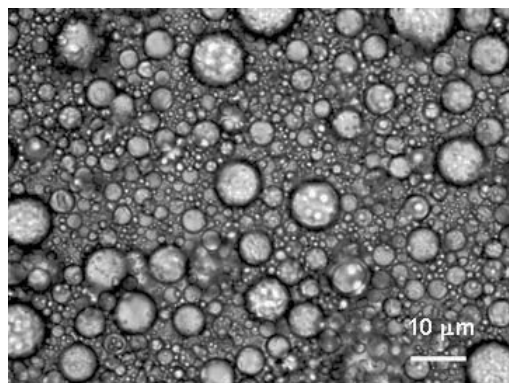


Figure 5.33. Particle size distribution in number of polyurethane-urea microcapsules with limonene oil.

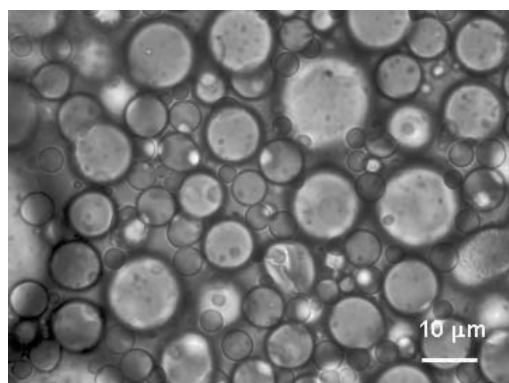
Optical microscopy

The analysis by optical microscopy had the objective to study the microcapsules morphology right after the production. Figure 5.34a) and Figure 5.34b) show the aspect of the microcapsules in the bright field option at different magnifications (200x and 1000x).

Microcapsules have spherical shape, with different sizes and one can notice also the absence of agglomerates.



a)



b)

Figure 5.34. Optical microscopy of microcapsules solution. a) 200x; b) 1000x

Solid content and pH

The solid content was measured using the procedures described on section 3.3.4.. The washing phase was monitored by measuring the pH after each washing step. As the number of washing steps increases, the free reactants diminish (including the free amines) and the pH became lower. The objective is to obtain a final microcapsule solution with a pH around 7. pH and solid content results (before and after the washing phase) are shown in Table 5.20.

Table 5.20. Values of solid content and pH determined for the produced microcapsules.

Microcapsules solution	Solid content (% m/m)	pH
With washing	41.2	7.18
Without washing	41.7	8.60

The solid content of the produced microcapsules is 41% and the pH is around 7 which are in agreement with the technical data of commercial microcapsules.

5.5.4 Textile impregnated with microcapsules characterisation

SEM analysis

Textile substrates have been analysed by SEM after being impregnated with microcapsule solutions. SEM micrographs confirmed that adhesion between textile fiber and microcapsules was effective, as can be observed in Figure 5.35. Also in this figure, surface morphologies of the microcapsules can be of two types: (i) microcapsules with a soft and smooth surface and (ii) microcapsules with rough surface. These differences on surface morphology of the microcapsules wall are favourable to the release of fragrance on the textile substrate, thus increasing the durability of fragrant textiles. It is observed that the microcapsules are individually distributed without excessive agglomeration.

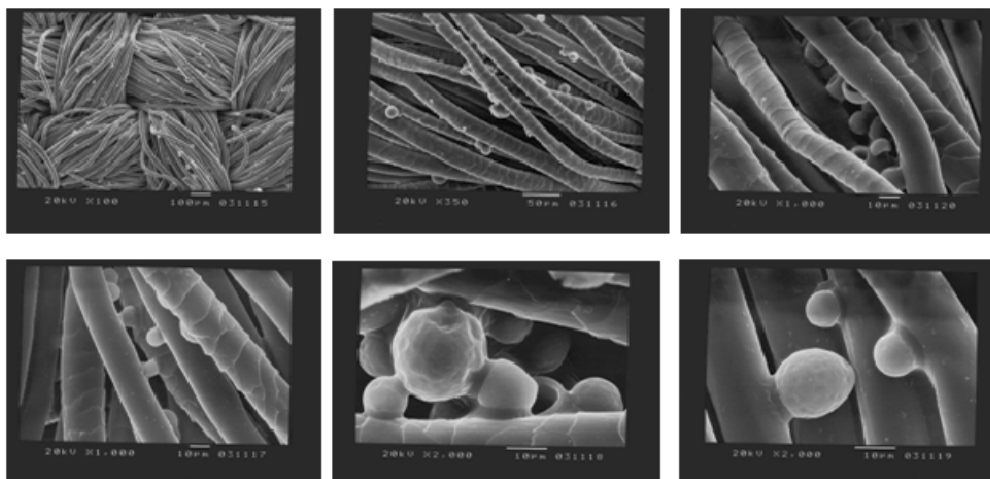


Figure 5.35. SEM micrographs of the impregnated textiles with lemonene microcapsules using different magnifications.

GC-Headspace

The effect of dry cleaning cycles on impregnated textile substrates was studied, in order to improve the lifetime of scent textiles. In Figure 5.36, it is possible to observe the chromatograms that represent textiles up to 5 cycles of dry cleaning.

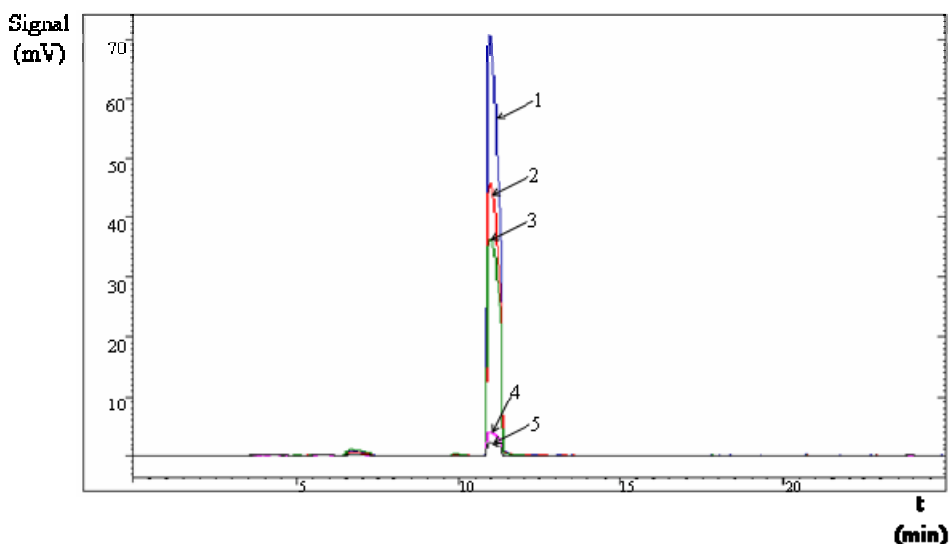


Figure 5.36. Chromatograms obtained by GC-FID-Headspace of textile substrates impregnated with microcapsules and subject to the dry cleaning. 1) with one dry cleaning; 2) with two dry cleaning; 3) with three dry cleaning; 4) with four dry cleaning and 5) with five dry cleaning.

From the GC-FID-Headspace analysis, a loss of 24% of limonene after the first dry cleaning cycle was found; a loss of 57% after the third cycle and of 97% after the fifth cycle.

The GC-headspace analysis of the textile substrates impregnated with microcapsules and subjected to different abrasion cycles, namely 3000, 6000 and 9000 abrasion cycles were performed. By GC-headspace, it was determined the quantity of limonene in function of abrasion cycles.

Figure 5.37 shows a remarkable decrease between the amount of aroma of limonene present in the textiles substrates before dry cleaning and the amount of aroma present in the textile after 5 dry cleaning cycles (0.027).

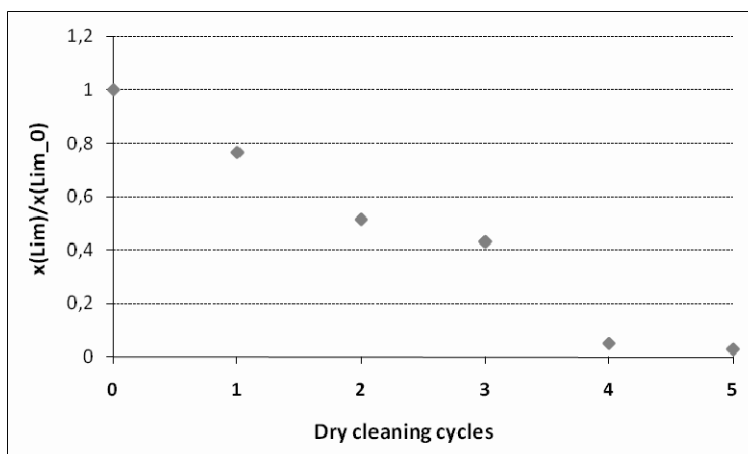


Figure 5.37. Relative weight of limonene present in impregnated textiles with lemon microcapsules, depending on the number of wash cycles.

From the GC-FID-Headspace analysis, a loss of 24% of limonene after the first dry cleaning cycle was found; a loss of 57% after the third cycle and of 97% after the fifth cycle.

The GC-headspace analysis of the textile substrates impregnated with microcapsules and subjected to different abrasion cycles, namely 3000, 6000 and 9000 abrasion cycles were performed. By GC-headspace, it was determined the quantity of limonene in function of abrasion cycles.

As can be seen in Figure 5.38, the relative amount of limonene in the impregnated textiles substrates with 3000 cycles was 0.59 and a further decline is observed for impregnated textiles substrates with 6000 cycles of abrasion and with 9000 cycles of abrasion (0.40), corresponding to a loss of aroma of 60%.

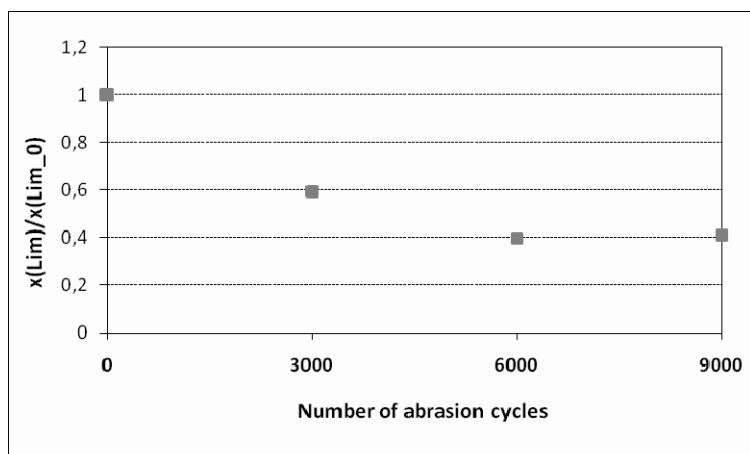


Figure 5.38. Relative weight of limonene present in impregnated textiles with lemon microcapsules, depending on the number of abrasion cycles.

Results and discussion

In the present study polyurethane-urea microcapsules were produced successfully by using the interfacial polymerisation technique and limonene as the active agent for textile applications.

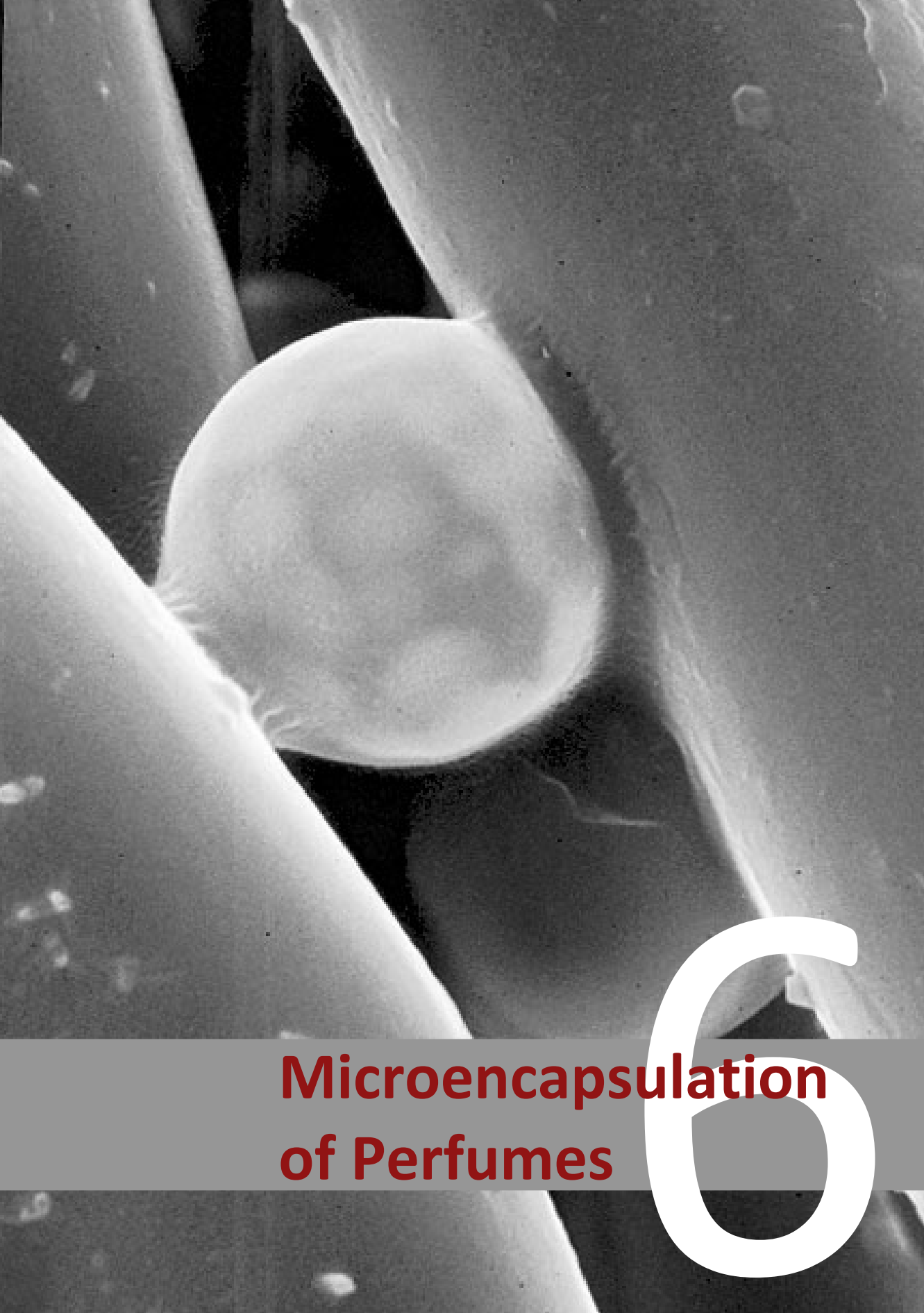
The completion of the isocyanate reaction was checked by FTIR analysis. The absence of the peak at 2270 cm^{-1} confirmed that HMDI was fully consumed through reaction with PEG 400, EDA and HYD.

The Particle Size Distribution of microcapsules measured using laser dispersion technique was bimodal in volume, with a mean particle size of $10\mu\text{m}$. The observation of microcapsules by optical microscopy confirmed the spherical shape, and the absence of agglomerates.

SEM micrographs have confirmed the good adhesion between microcapsules and textile fibers, and also confirmed the spherical morphology and size of microcapsules.

The solid content achieved through this formulation is about 41% and pH of 7.18 after the washing procedure.

Through GC-headspace analysis, the presence of limonene on textile substrate was quantified. During dry cleaning, the loss of limonene is of 24% in the first cycle and up to 97% after five dry cleaning cycles. When impregnated textile substrates are subjected to abrasion cycles, the loss of limonene is of 40% for 3000 cycles and up to 60% for 9000 cycles.

A scanning electron micrograph (SEM) showing a spherical microcapsule in the center. The capsule has a smooth surface with some fine texture. It is surrounded by several elongated, fibrous structures that appear to be part of a larger material or a network. The background is dark and textured.

Microencapsulation of Perfumes

6

In this chapter a perfume formulation was developed taking into account the target market, textile substrate for man suits. In the perfume conception special attention was given to the performance of different components of perfume.

After create the perfume the previously developed microencapsulation process was applied to produce microcapsules with this fragrance. The work presented in this chapter involves the production and characterization of microcapsules, impregnation of textile substrate at laboratory and industrial scale and product characterization in terms of resistance to abrasion and dry cleaning cycles.

6.1 Preparation of PUU microcapsules

PUU microcapsules were prepared by interfacial polymerization using the procedure described in chapter 5 for limonene encapsulation.

6.2 Preparation of perfume

Four men's fragrances were developed, classified as follows:

- Fougère
- Floral-Woody-Musk
- Spicy-Woody-Musk
- Citric-Woody-Musk

In Figure 6.1 are the pyramid structures on these men's fragrance.

This chapter is based on the following publication:

S. N. Rodrigues, et al. "Scentfashion (R): Microencapsulated perfumes for textile application". *Chemical Engineering Journal* **2009**, 149, 463.

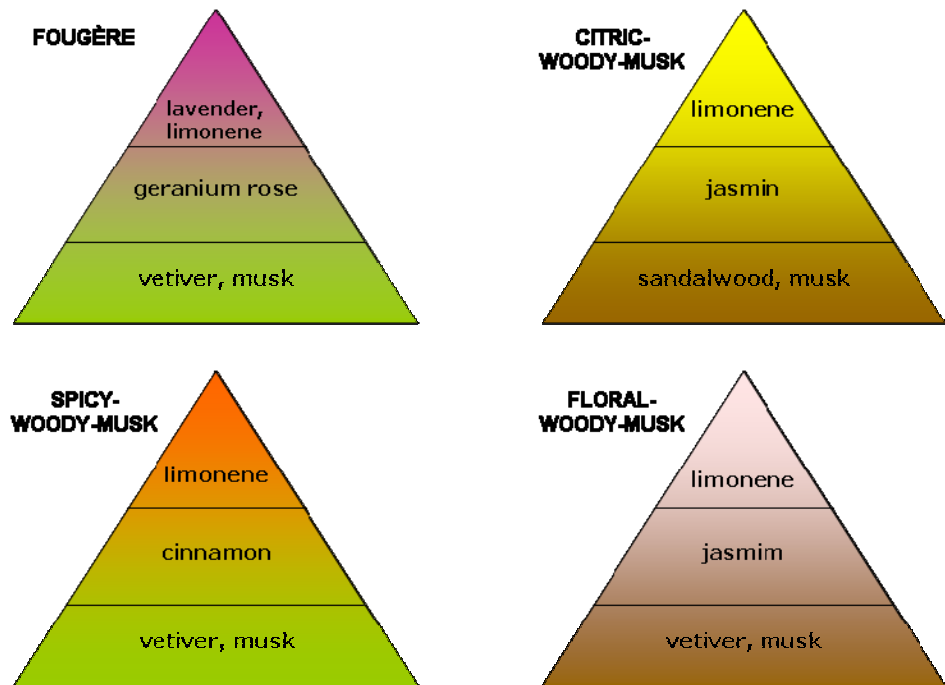


Figure 6.1. Pyramid structures on these men's fragrance.

Several perfume formulations were developed and a panellist created by the Scentfashion project staff was used to choose the fragrance more appropriated to the target-market: high quality men clothes. The chosen fragrance belongs to the Floral-Woody-Musk family and it was prepared with Limonene, Methyl dihydrojasmonate, Methyl cedryl ketone and Galaxolide (see Table 6.1).

Table 6.1. Floral-Woody-Musk fragrance compounds

FRAGRANCE NOTE	COMPONENT	ODOUR	LIQUID PHASE COMPOSITION (wt%)
TOP	Limonene (LMN)	Lemon	19.51

(cont.)

(cont.)

MIDDLE	Methyl dihydrojasmonate (MJD)	Jasmine	35.67
BASE	Methyl cedryl ketone (MCK)	Vetiver	35.67
	Galaxolide (MUSK)	Musk	9.15

The proportion of the fragrant compounds in this composition was chosen using perfumery rules, and in particular, the scientific methodology PTD – Perfumery Ternary Diagram[®] developed in our laboratory by Mata et al (2005) [155]. As a result, this formulation represents a typical perfume, having a highly volatile top note – LMN - which is noticeable when smelling directly from the solution or until some minutes after application. It means that the odour value (defined as the ratio of gas phase concentration and odour threshold) of the top note is higher than that of the middle and base notes. The middle note – MJD - is noticeable only after application and after the top note has disappeared; that is, because of the decrease in the concentration of the top note, the odour value of the middle note becomes higher than that of the top note. Finally, the base notes – MCK and MUSK - will be smelled after the middle note has disappeared.

The odour threshold of MCK was not available in the literature and therefore it was measured and determined in our laboratory using the equipment Olfatometer Ecoma model T07 (Germany). The detailed protocol is described in previous work by Gomes et al (2008) [156].

Table 6.2 shows the molecular weight, vapour pressure and odour threshold for the components present in the perfume. This information is necessary to map the Perfumery Ternary Diagram.

Table 6.2. Floral-Woody-Musk fragrance: vapour pressure and threshold values of components.

Component	Molecular Formula	Molecular weight M_w (g/mol)	Vapour pressure P_i (Pa) ^a	Odour Threshold (g/m ³)
LMN	C ₁₀ H ₁₆	136.2	20.5×10^1	2.5×10^{-3} ^b
MJD	C ₁₃ H ₂₂ O ₃	226.31	9.5×10^{-2}	2.8×10^{-4} ^c
MCK	C ₁₇ H ₂₆ O	246.39	1.1×10^{-2}	3.8×10^{-5} ^d
Musk	C ₁₈ H ₂₆ O	258.4	5.5×10^{-2}	6.3×10^{-7} ^e
^a From database ChemSpider TM [157] ^b From Calkin and Jellinek [158] ^c From Leffingwell [159] ^d Obtained by measurement using an olfactometer in our laboratory ^e From Frater et al.[160]				

6.3 Impregnation of microcapsules on textile substrate

Fabrics of wool/polyester with different grammages were impregnated with perfume microcapsules. Microcapsules were applied by an industrial foulard at the finishing process of textile fabrication. The finishing bath was prepared according to the conditions of industrial textile impregnation process described previously in chapter 4. Briefly, perfume microcapsules (50 g/L) were suspended in a 70L bath containing softener at 10 g/L (Perisoft Nano, Bayer) and a self-crosslinking agent at

50 g/L (Baypret USV, Bayer). The Foulard (3 rollers) was used at a working speed of 10 m/min with fabrics of different grammages and with 1.55 m width. The impregnated textile was dried for 3 minutes at 100 °C and thermofixed at 140 °C during 3 minutes.

6.4 Results and discussion

FTIR analysis

The objectives of these assays were mainly two: (1) Before encapsulation, analyze the composition of the created perfume in order to guarantee the absence of hydroxyl and/or amine groups. These chemical groups are reactive towards isocyanates thus can compete with the used monomers and modify the aromatic properties of the fragrance; and (2) After microcapsules production, analyze the composition of the formed shell material and confirm total isocyanate consumption. For that purpose, samples of microcapsules solution were let to dry overnight in an oven at 60 °C and thereafter crushed and dried again until constant weight was achieved. Finally, they were transferred to a desiccator until analysis. This procedure allows perfume evaporation thus enabling shell material analysis. Moderate temperatures were used in order to avoid shell material degradation.

Figure 6.2 shows the obtained perfume spectrum. Among other particularities the absence of hydroxyl groups (absence of a broad band in the region $3400\text{--}3300\text{cm}^{-1}$) and amine groups (absence of a band of medium intensity around 3400 cm^{-1}) were confirmed. The weak vibration centred approximately at 3460 cm^{-1} corresponds to a carbonyl overtone.

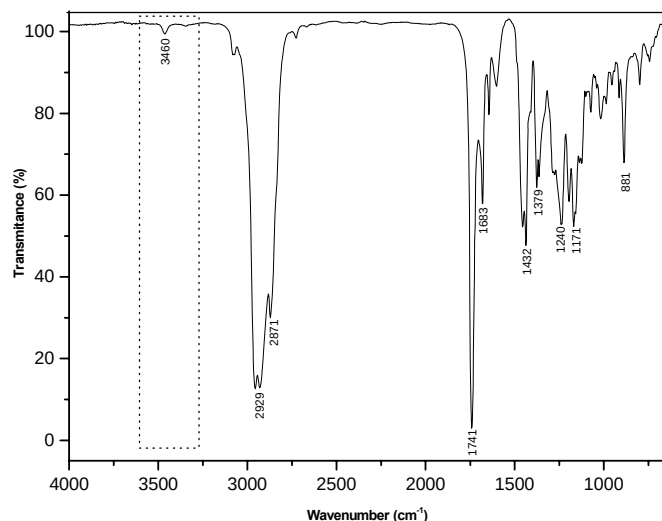


Figure 6.2. FTIR spectrum of the encapsulated perfume with the following composition: limonene (19.51%), musk (9.15%), jasmine (35.67%) and vetiver (35.67%).

Figure 6.3 shows the FTIR spectrum of the produced polyurethane-urea microcapsules. Several infrared vibrations, typical of polyurethane-urea systems, could be assigned. No residual isocyanates have been detected.

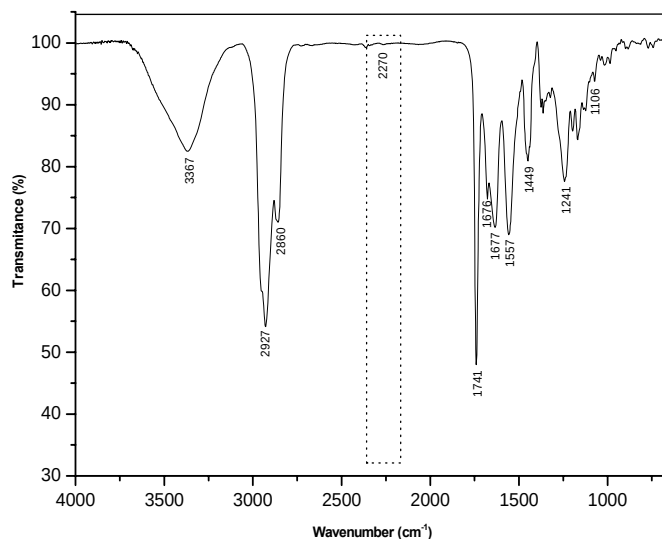
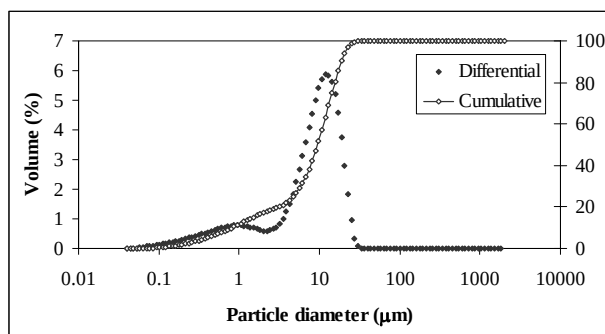


Figure 6.3. FTIR spectrum of polyurethane-urea microcapsules with perfume.

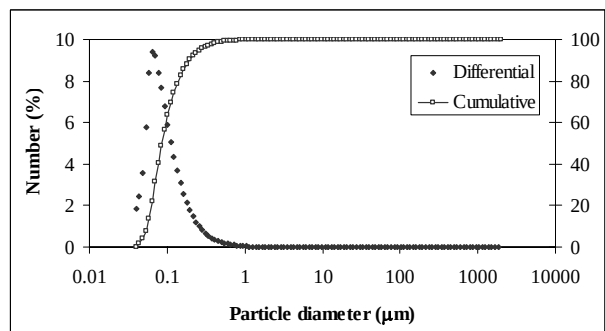
According to our previous study presented on chapter 4, and for the chemical system used, urea formation is favoured over urethane formation. The N-H stretching mode is assigned at 3367 cm^{-1} , the urea carbonyl at 1677 cm^{-1} , and the amide II and amide III vibration modes at 1557 cm^{-1} and 1241 cm^{-1} , respectively. The vibration assigned at 1106 cm^{-1} corresponds to the ether group C-O-C stretching mode. The low intensity associated to this vibration indicates the low urethane character of the produced microcapsules, since it corresponds to the PEG 400 incorporation. C-H stretching vibrations are assigned at 2927 and 2860 cm^{-1} . The carbonyl assigned at 1741 cm^{-1} in Figure 6.2, which could be confused with urethane formation, could be easily detected in the original perfume spectrum (more precisely it was due jasmine contamination). Nevertheless, it was possible to verify the absence of the peak at 2270 cm^{-1} , due to the isocyanate stretching vibration and thereafter confirm that all the HMDI was consumed completely through the reaction with PEG 400, EDA and HYD.

Particle size distribution

After production and storage of perfume microcapsules, the particle size distribution was measured by laser dispersion and quantified both relative to the total volume of particles (a) and to the total number of particles (b), as shown in Figure 6.4. The microcapsules mean size (based on volume distribution) is $10\text{ }\mu\text{m}$. It was observed that 88% by volume of particles have diameters higher than $1\text{ }\mu\text{m}$ ($12\% < 1\text{ }\mu\text{m}$), but this represents 1% of the particles by number ($99\% < 1\text{ }\mu\text{m}$). This means that, even if a large number of microcapsules have small size, most of the perfume was encapsulated in larger particles.



(a)



(b)

Figure 6.4. Differential and cumulative Particle size distribution in volume (a) and number (b) of polyurethane-urea microcapsules with perfume.

Optical microscopy

The shape and morphology of the microcapsules is shown in Figure 6.5. The optical microphotograph was taken after the polymerisation, washing and storage steps using bright field option at different magnifications, and it shows many small particles of $1\mu\text{m}$ and large particles of about $10\mu\text{m}$. Moreover, they show the spherical morphology of perfume microcapsules and confirm the bimodal size distribution.

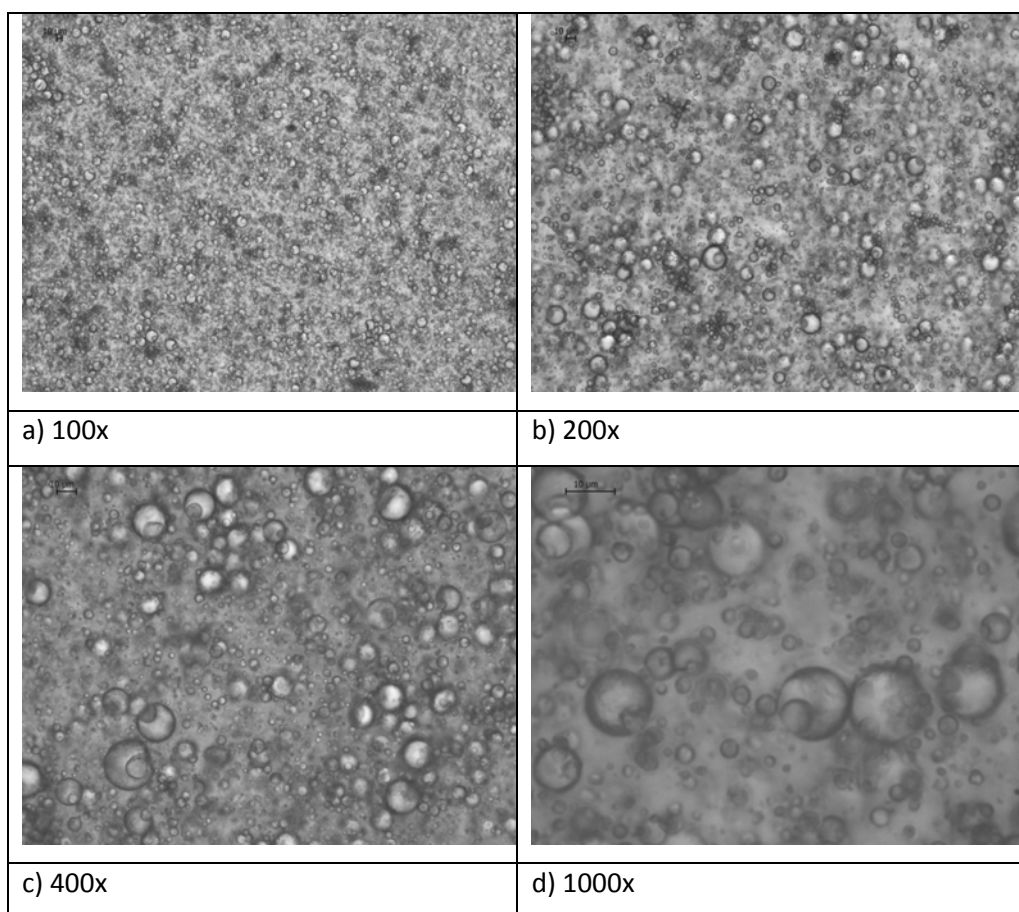


Figure 6.5. Optical micrographs of microcapsules containing perfumes. A)100x; b)200x; c)400x; d)1000x.

Scanning electron microscopy (SEM)

Figure 6.6 shows SEM photographs of fabric after being impregnated with microcapsules solutions in the laboratory application. This figure confirmed that adhesion between textile fibre and microcapsules was effective and that the microcapsules are individually distributed without excessive agglomeration. The surface morphology of microcapsules was soft and smooth. It can be also observed

that some microcapsules are broken and empty but still remain on the fabric protected by neighbouring fibres.

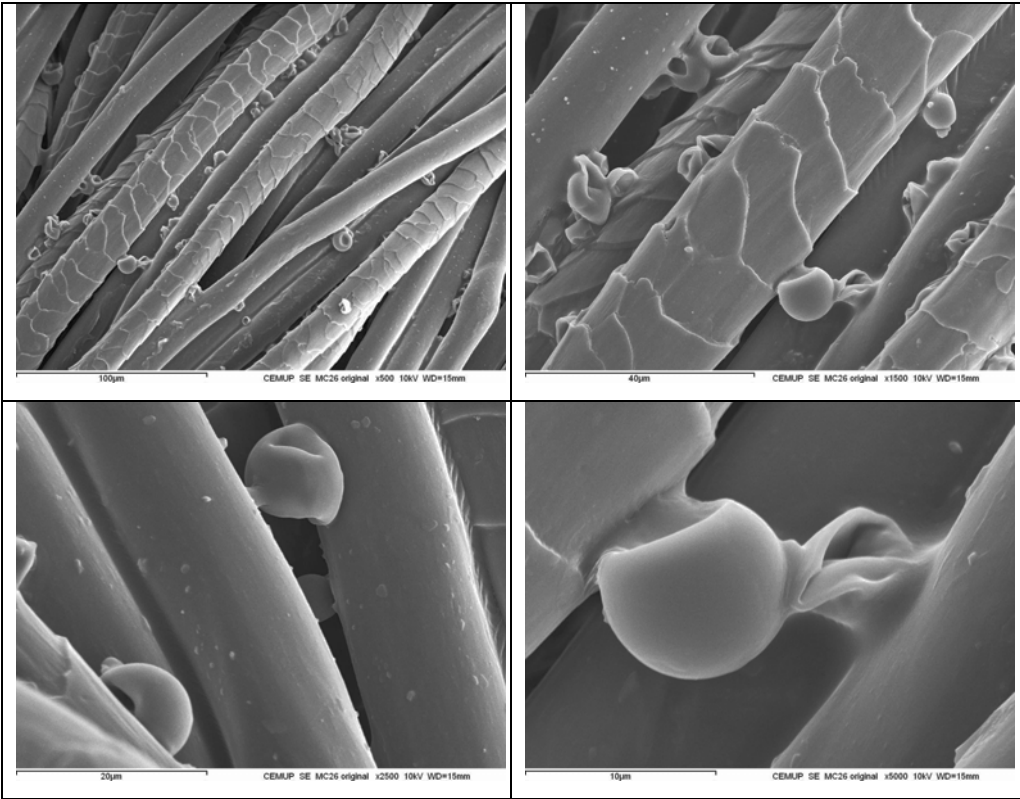


Figure 6.6. SEM photographs of fabrics in laboratory application

Figure 6.7 shows SEM photographs of fabrics impregnated with perfume microcapsules in the industrial application. It can be observed the adhesion of microcapsules to the fabrics, although their stability was apparently affected by the foulard process. During the industrial process microcapsules tend to agglomerate and to lose perfume, as it can be seen by the shape change of the microcapsules.

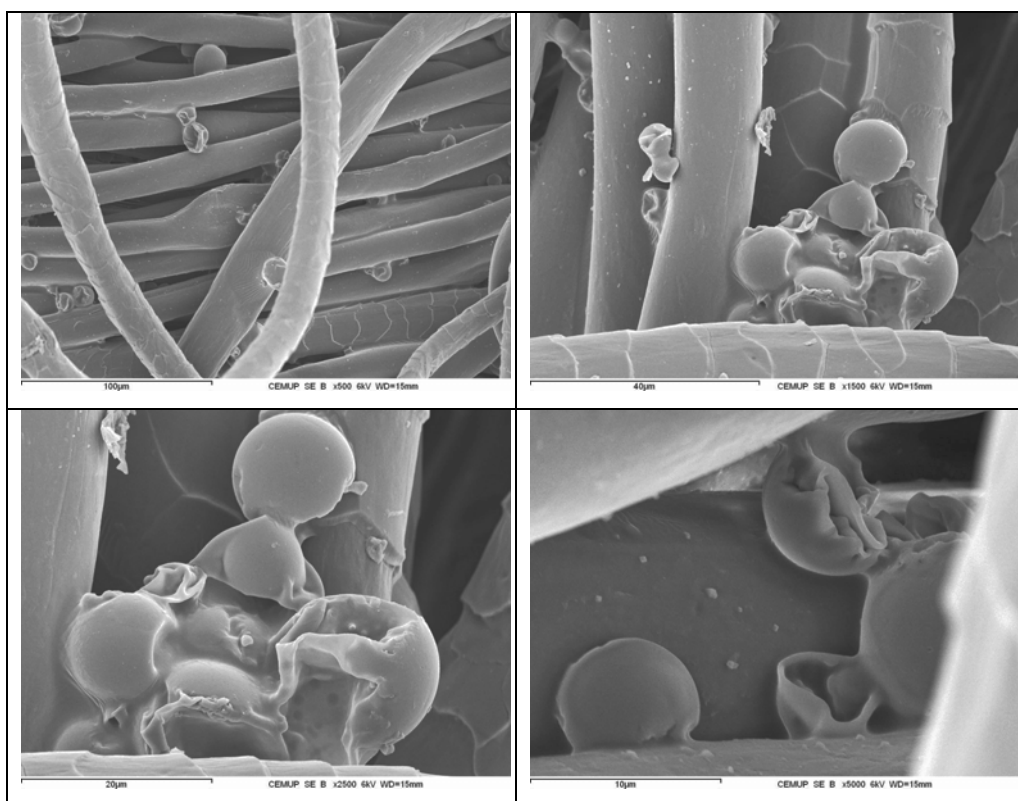


Figure 6.7. SEM photographs of fabrics in industrial application.

GC-FID-HEADSPACE

Table 6.3 shows the comparison between the percentage of each component in the liquid phase and the percentage of each component in the gas phase of the fragrance released from the microcapsules.

Table 6.3. Fragrance components in liquid and gas phases.

Fragrance Component	Liquid Phase Composition (wt %)	Gas Phase Composition (wt %)
Limonene (LMN)	19.51	97.68
Methyl dihydrojasmonate (MJD)	35.67	1.33
Methyl cedryl ketone (MCK)	35.67	0.43
Galaxolide (MUSK)	9.15	0.56

Once limonene is the most volatile compound (top note), it appeared in the gas phase (headspace) at higher concentration, as it was expected. This way, although the perfume is composed by four components, the evaluation of the concentration of fragrance inside the microcapsules was based on the determination of limonene in the headspace.

The amount of perfume weight present on microcapsules was determined using the GC-FID-Headspace technique. There were four peaks detected: the limonene peak appears at 12 min, the vetiver peak at 65 min, the jasmine peak at 69 min, and finally the musk peak at 72 min. The GC-Headspace analysis allowed the quantification of the perfume present inside the microcapsules. The mass of encapsulated perfume has been calculated using a mass balance. The yield of encapsulation (percentage of perfume present inside microcapsules) was calculated based equation (6-1):

$$\text{Encapsulation Efficiency (\%)} = \frac{m_{total} - m_{out}}{m_{total}} \times 100 \quad \text{Eq. 6-1}$$

where m_{total} = amount of loaded perfume (g) and m_{out} = amount of nonencapsulated perfume (g).

The two phases obtained after separation by centrifugation (aqueous phase and microcapsules phase) were analysed in order to quantify the nonencapsulated perfume. 1 ml of the aqueous phase and 1 ml of the microcapsules phase were collected using a syringe equipped with a 0.45 μm pore size filter and thereafter analysed by GC-FID. The mass of encapsulated perfume was obtained by difference between the loaded original quantity and the nonencapsulated determined quantity. Table 6.4 shows total, encapsulated and nonencapsulated masses for each component of the perfume, the liquid phase composition and the encapsulation efficiency. The encapsulation efficiency accounts for 55% of the loaded perfume used in the encapsulation process.

Table 6.4 also shows that after encapsulation the proportion of the fragrant components in the liquid phase composition present some differences relative to the initial composition.

Table 6.4. Total, encapsulated and nonencapsulated masses discriminated by perfume components and encapsulation efficiency.

Component	m_{total} (g)	$m_{\text{nonencapsulated}}$ [*] (g)	$m_{\text{encapsulated}}$ ^{**} (g)	LPC ^{***} (wt%)	EE ^{****} (%)
LMN	35.73	23.88	11.86	11.74	33.18
MCK	65.33	29.05	36.28	35.93	55.53
MJD	65.33	20.80	44.53	44.1	68.16
MUSK	16.76	8.44	8.32	8.24	49.64
Total	183.15	82.16	100.99	100	55.14

* - calculated based on GC-FID peak area

** - obtained by difference between total mass and nonencapsulated mass

*** - Liquid phase composition

**** - Encapsulation efficiency

For the impregnated textiles in the industrial foulard, 35 g of microcapsules per m² of fabric were used.

The amount of perfume applied in the impregnation is roughly 0.1 g perfume/g fabric. The fabric sample of 16 cm² weights approximately 0.3g after impregnation. A perfume system consists of a complex fragrant liquid mixture and a corresponding air phase above it, the headspace, which we smell. The intensity of a fragrant compound *i* can be expressed in terms of its odour value OV_i , which is defined as equation 6-2:

$$OV_i = \frac{C_i^g}{Thr_i} \quad \text{Eq. 6-2}$$

where C_i^g is the concentration of component *i* in the headspace and Thr_i is the threshold concentration of *i* in air.

The concentration of each perfume component in the fabric was compared with their threshold and the odour value was calculated. Comparing each component of the perfume with their odour threshold the results showed that musk and limonene scent odour values are the highest so these are the components that we smell more.

The effect of the number of dry washing cycles on the concentration of fragrance inside the microcapsules in the textile substrate impregnated at the laboratory scale was assessed by the determination of limonene in the headspace. Figure 6.8 shows the relative amount of limonene in the headspace as a function of the number of dry washes.

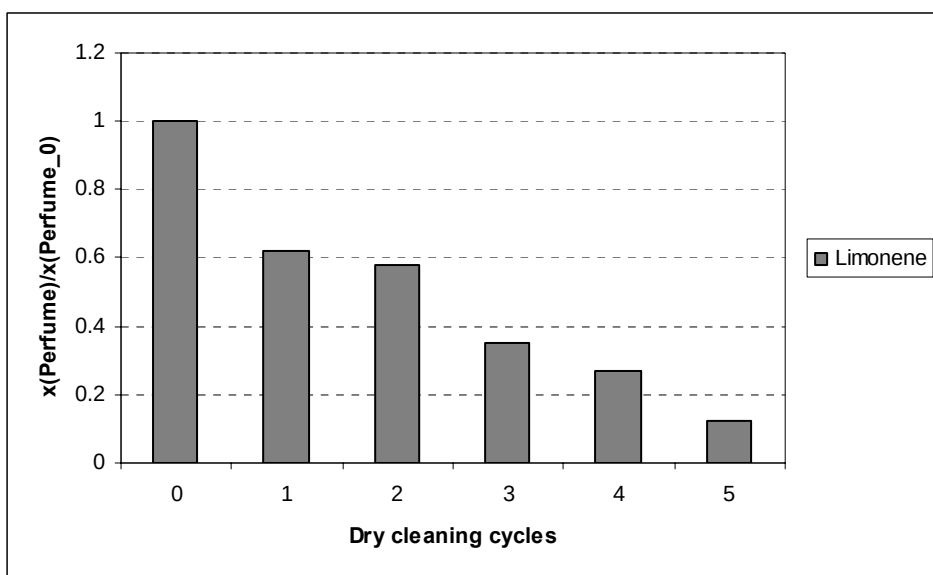


Figure 6.8. Quantity of limonene present in the headspace according to the number of dry cleaning cycles.

As it can be seen, there is a decrease of limonene with the number of dry washing cycles. However, after five washes the lemon scent can still be detected due to the use of a microencapsulated perfume.

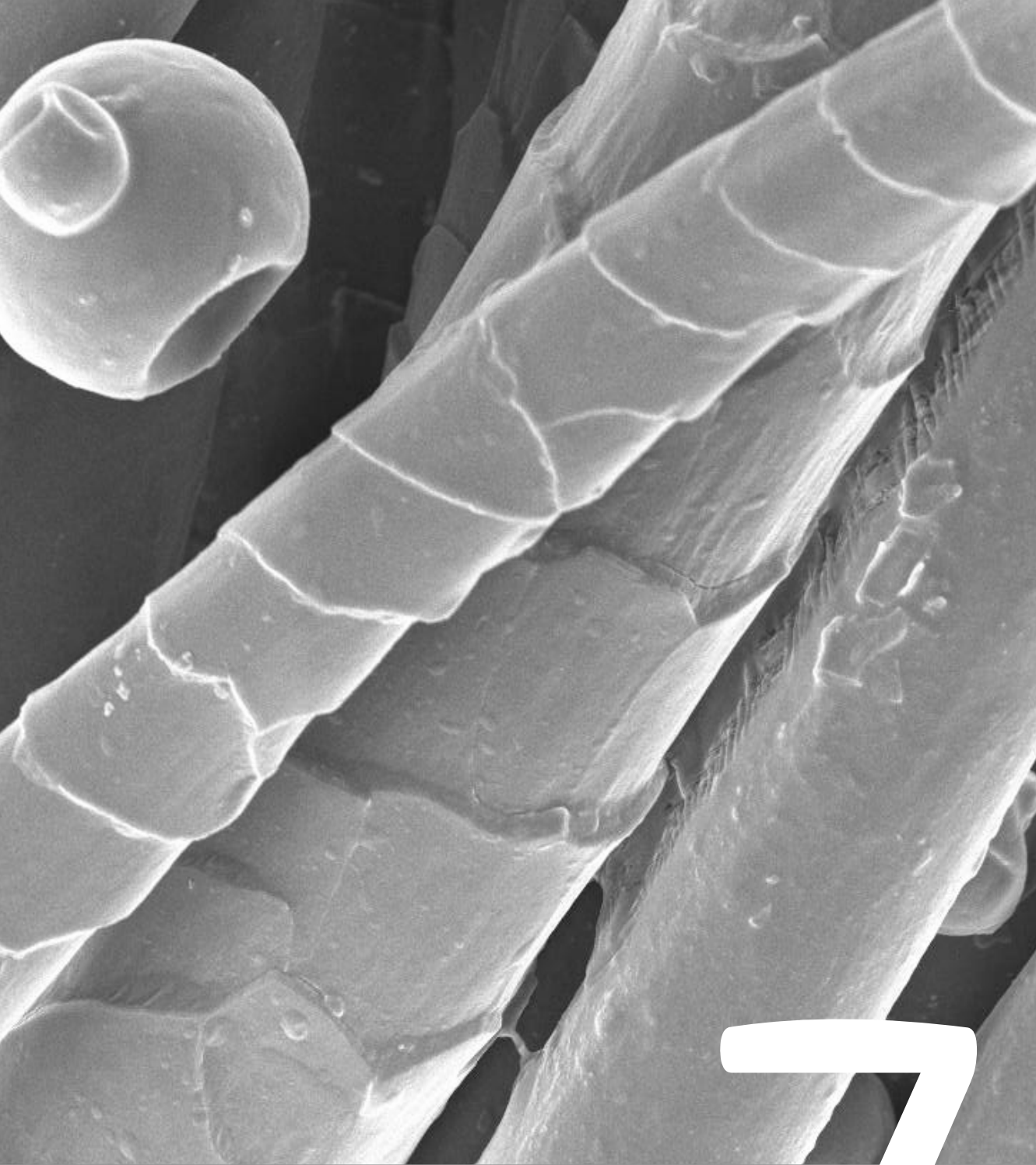
The amount of limonene component in the fabric was compared with its threshold and the odour value was calculated. The results have shown that there is a decrease on odour value of 87% with 5 dry cleaning cycles.

The GC-headspace analysis of impregnated fabrics with perfume microcapsules and subjected to different abrasion cycles, namely 3000, 6000 and 9000 abrasion cycles were performed. By GC-headspace, it was determined the quantity of each component of the perfume in function of abrasion cycles number. Abrasion tests were performed to evaluate the resistance of fabrics.

The effect of the number of abrasion cycles on the concentration of the microencapsulated perfume in fabrics was also studied at the laboratory scale. There is still a significant amount of fragrance inside the microcapsules after 9000

cycles of abrasion, although the musk scent was not detected. The relative amounts of limonene, vetiver and jasmin scents were reduced, respectively to 78%, 59% and 50%, of the initial content.

The impregnated textile fabrics with perfume microcapsules obtained with an industrial foulard showed resistance to five dry washing cycles although the musk scent was absent as already noticed in the laboratory scale experiments; after 5 cycles vetiver was around 30 % of the initial amount, jasmin scent around 60 % of the initial amount and limonene was still present. The industrial impregnated fabric supported 3000 abrasion cycles but failed the test of 9000 abrasion cycles, for which no fragrance was detected. This agrees with the observed aspect of microcapsules in SEM shown in Figure 6.7.



7 Conclusions & Future work

The objective of this thesis was the microencapsulation of fragrances and perfumes to be applied in textile industry, in particular in the production of men's suits. The main requirements for the impregnated textiles were resistance to dry cleaning (5 cycles) and resistance to abrasion (9000 cycles).

Based on some preliminary work it was decided to produce polyurethane-urea microcapsules by interfacial polymerization. The majority of the microencapsulated fragrance systems commercially available for textile applications are based on formaldehyde systems (phenol-formaldehyde or melamine-formaldehyde resins), which are facing several restrictions under the present environmental policies. In such context, polyurethane-urea systems are a more attractive and environmental friendly solution. Moreover, they are known as versatile polymer systems which can be tailor-made from a wide range of raw materials in order to achieve the desired physical, chemical and mechanical properties. The only drawback is that polyurethane-urea systems must be designed and optimized to take into consideration the physico-chemical properties of the active principle to be encapsulated.

Characterization of commercial microcapsules showed that they are spherical in shape, with mean particle size below 6 μm and that their wall material is mainly based on melamine copolymers. As lemon is one of the most widely used fragrances in perfumery, impregnated textiles with commercial lemon microcapsules from Horquim were analyzed after 0, 1 and 20 domestic washes by GC-FID-Headspace. The results pointed out for a limonene loss of 46% in the first wash cycle and 97% after 20 wash cycles.

Five formulations for the production of polyurethane/polyurethane-urea microcapsules containing limonene as the active ingredient were carried out. The results obtained using these five formulations are presented below:

FORMULATION A: polyurethane microcapsules with mean size (in volume) of 2 μm were prepared. SEM analysis of the impregnated textiles put in evidence the

absence of microcapsules. The amount of limonene released estimated by GC-Headspace analysis of impregnated textiles was very small.

FORMULATION B: polyurethane-urea microcapsules with mean size (in volume) of 14 μ m were produced. The GC-FID-Headspace analysis of impregnated textiles showed a clear loss of odor (72%) after the first dry cleaning wash.

FORMULATION C: polyurethane-urea microcapsules with mean size (in volume) of 16 μ m were obtained. The amount of limonene of impregnated textiles without washing, calculated based on a limonene calibration curve using GC-FID headspace, was 5.4E-06 mg

FORMULATION D: polyurethane microcapsules with mean size (in volume) of 16 μ m were prepared. The amount of limonene of impregnated textiles of impregnated textiles without washing, calculated based on a limonene calibration curve using GC-FID headspace, was 7.0E-07 mg

FORMULATION E: polyurea microcapsules with mean size (in volume) of 13 μ m were produced. The amount of limonene of impregnated textiles of impregnated textiles without washing, calculated based on a limonene calibration curve using GC-FID headspace, was 1.9E-06 mg

From these five formulations, the most promising one was ascribed to formulation C, i.e., it produces well defined spherical microcapsules and it was the one that presented better results in what concerns textiles impregnation (good adhesion and durability of the odor).

The impregnated textiles with those microcapsules had a loss of limonene of 64% after the first dry cleaning cycle and a loss of 81% after 3000 abrasion cycles. The binder used was polyurethane since it gave better results than acrylate binder in a test using microcapsules with mint aroma.

Formulation C was further improved for better performance on the industrial application. It was concluded that the introduction of hydrazine in the formulation

lead to the total conversion of the reacting isocyanates. The excess of reactants was removed after washing the microcapsules. Furthermore, to avoid phase separation and cluster formation during storage, the stabilization of the microcapsules solution was achieved by studying the addition of different surfactants at the final step. This procedure increased the compatibility of microcapsules with water and avoided the formation of foam.

Summarizing, a final formulation to produce polyurethane-urea microcapsules using the interfacial polymerisation technique, with (i) limonene and (ii) perfume as the active agent was successfully achieved and can be described in three steps:

Step 1: Formation of an oil-in-water (o/w) emulsion by mixing an organic phase which contains the active substance and HMDI and an aqueous phase that consists of water and PVA. PVA favours the stabilization of droplets formed thus fixing the particle size distribution.

Step 2. Polyurethane-urea wall formation, in a first step by the reaction of HMDI with PEG400 (Urethane formation), followed by the reaction of HMDI with EDA and with HYD (Urea formation).

Step 3. Washing (firstly with a 30% ethanol solution, followed by washing with deionised water), separation and storage using an emulsifier for microcapsules stabilization.

The determination of isocyanate groups conversion of the produced microcapsules was obtained by FTIR analysis. The absence of the peak at 2270 cm^{-1} confirmed that all the HMDI was consumed through reaction with PEG 400, EDA and HYD.

Characterization of produced polyurethane-urea microcapsules showed that their mean particle size is $10\text{ }\mu\text{m}$, the wall thickness is around $1\text{ }\mu\text{m}$ and they are spherical in shape without agglomerates. The solid content achieved for this formulation (final microcapsules after the washing steps) was 41% and pH 7.18.. SEM micrographs have shown a good adhesion between microcapsules and textile fibbers.

Through GC-FID-headspace analysis, the presence of limonene on textile substrate was quantified. During dry cleaning the loss of limonene was 24% in the first cycle and up to 97% after five dry cleaning cycles. During abrasion cycles, the loss of limonene was of 40% for 3000 cycles and up to 60% for 9000 cycles.

Polyurethane-urea microcapsules of a masculine perfume were produced. The produced perfume microcapsules have shown the same characteristics as the limonene microcapsules, i.e., in what refers size, wall thickness and morphology. The impregnation of textile fabrics with the microencapsulated perfumes was studied both at laboratory and industrial scale. In the industrial foulard, 35 g of microcapsules per m² of fabric were used. The amount of perfume applied in the impregnation is roughly 0.1 g perfume/g fabric. A fabric sample of 16 cm² weights approximately 0.3 g after impregnation.

The encapsulation efficiency and the presence of perfume on textile substrates were quantified through GC-FID-Headspace analysis. The encapsulation efficiency accounts for 55% of the loaded perfume used in the encapsulation process.

During dry cleaning of lab-scale impregnated fabrics, the loss of limonene was 38% in the first cycle and up to 87% after five dry cleaning cycles. The industrial scale impregnated textiles also showed resistance to five dry cleaning cycles.

Suggestions for future work

Research lines for future work include the following topics:

1) Scale-up of polyurethane-urea microcapsules production using a miniplant reactor from IKA with higher capacity (10L).

There is a need to produce larger quantities of microcapsules to be applied by the industry, since a single test requires generally 3-5 kg of microcapsules. The

capacity of the reactor available for this work only has 2L, which means that it produces 200g of microcapsules per batch.

2) Continuous production of emulsion of nanocapsules using the NetMix technology developed at the LSRE.

This technology allows a continuous large-scale production of microcapsules containing perfumes and other active ingredients.

3) Production of polyamide microcapsules for textile application.

Polyamide based microcapsules present stability to hypochloride bleaches, which is a very desirable property in the point of view of textile applications.

4) Production of nanocapsules (~200nm) for textile application without binder using "green" materials as chitosan and tannins.

Chitosan, a water-soluble polymer, is a natural polymer widely used for controlled release purposes because of its properties of biocompatibility, biodegradability, antibacterial, antimicrobial and antifungal, and because it exists in abundance in natural marine resources. The use of tannic acid is of interest as it is a natural crosslinking agent, non toxic, and may functionalise the microcapsules providing them antioxidant and anti microbial properties.

5) Understand washing and storage of microcapsules.

A better understanding of washing and storage will help in removing barriers when going to large scale production.

Acknowledgements

This work was carried out in the project SCENTFASHION, contract ADI/2004/M2.3/0015POCI funded by Agência de Inovação (AdI) in the framework of POCI 2010-Medida 2.3-IDEIA. We also acknowledge the support of our partners CITEVE and A Penteadora, SA.

References

- [1] C. Thies, in "Kirk-Othmer Encyclopedia of Chemical Technology", Microencapsulation edited by I. John Wiley & Sons (2000) p. 438.
- [2] D. Fredj and F. Dietlin. New method of encapsulation of volatile substances and phyto-aromatic compositions thereby obtained FR 2570604, 1984.
- [3] M. R. Juliá Ferres, et al. Procedimiento para la preparación de cápsulas y encapsulación de sustancias. ES 2112150 B1, 1999.
- [4] O. Lapidus, et al. Textile or clothing article, toiletries or body care product, bearing microcapsules, and methods for making the same WO/2000/005446, 2000.
- [5] Y. Yamato, et al. MICROCAPSULE, TREATMENT LIQUID CONTAINING MICROCAPSULES, AND TEXTILE STRUCTURE HAVING MICROCAPSULES STUCK THERETO. WO/1991/001801, 1991.
- [6] Y. Yamato, et al. Microcapsule, treating liquids containing the same, and textile structure having microcapsules adhering thereto. 5232769, 1993.
- [7] M. Kukovic and E. Knez. PROCESS FOR PREPARING CARRIERS SATURATED OR COATED WITH MICROENCAPSULATED SCENTS. WO/1996/009114, 1996.
- [8] D. Rase and A. Salhi. Antimicrobial composition for the skin, applied as body deodorant and antibacterial bodyagent. EP0423002, 1991.
- [9] D. Rase and A. Salhi. Antimicrobial composition for the skin, applied as body deodorant and antibacterial bodyagent. EP0423002, 1994.
- [10] T. Tanimoto, et al. Antibacterial zeolite causing little discoloration and method of the production thereof. US 6071542, 2000.
- [11] M. Colombet. TEXTILE ARTICLES HAVING EXCELLENT MECHANICAL PROPERTIES. WO/1993/024690, 1993.
- [12] J. I. N. R. Gomes and C. J. E. Lima, in Technical textiles, edited by Autex (Portugal, 2001).
- [13] J. D. Mcgalliard. Nylon hose treated with microencapsulated hair dissolving solution. 4152784, 1979.
- [14] M. Akasaka, et al. Insectproofing fibers and method for preparing the same. EP0488294, 1992.
- [15] R. Mathis and H.-J. Sladek. Fibres and textile sheet prepared for repelling insects. EP1845186, 2007.
- [16] D. R. Collins. Method for treating garments with insect repellent. 6054182, 2000.
- [17] M. Kamata, et al. Aroma-imparting method and aroma-emitting textile product. EP0581274, 1994.
- [18] A. Ono, et al. Fibrous structure having a durable fragrance and a process for preparing the same. EP0328937, 1989.
- [19] T. Trinh, et al. Treatment of fabric with perfume/cyclodextrin complexes. EP0392607, 1990.
- [20] K. Tanaka and K. Ezaki. FRAGRANT CLOTH. JP05163676, 1993.

- [21] J. A. Scarpelli and J. C. Soper. Small, oily, free-flowing, silky-smooth, talc-like, dry microcapsules and aqueous formulations containing them. 5043161, 1991.
- [22] G. F. Brunner, et al. Absorbent articles for odor control with positive scent signal. 5733272, 1998.
- [23] G. D. Moggridge and E. L. Cussler. "An introduction to chemical product design". *Chemical Engineering Research & Design* **2000**, 78, 5.
- [24] J. A. Wesselingh, et al., *Design&Development of biological, chemical, food and pharmaceutical products* edited by wiley (Chichester, u.k., 2007).
- [25] J. Wei, in "Product Engineering", Molecular structure and properties edited by (Barnes & Noble, 2006).
- [26] R. Costa, et al. "Chemical product engineering: An emerging paradigm within chemical engineering". *Aiche J* **2006**, 52, 1976.
- [27] F. C. Bernardo, R.; Saraiva, P. M.; Moggridge, G. D. , in International Conference in Engineering Education ICEE 2007 (Coimbra, Portugal, 2007).
- [28] K. Ulrich and S. Eppinger, *Product design and development* (McGraw Hill New York 2003).
- [29] G. Nelson. "Application of microencapsulation in textiles". *International Journal of Pharmaceutics* **2002**, 242, 55.
- [30] K. Hirech, et al. "Microencapsulation of an insecticide by interfacial polymerisation". *Powder Technology* **2003**, 130, 324.
- [31] P. Monllor, et al. "Characterization of the behaviour of flavour microcapsules in cotton fabrics". *European Polymer Journal* **2007**, 43, 2481.
- [32] G. Nelson. "Microencapsulation in textile finishing". *Review of Progress in Coloration and Related Topics* **2001**, 31, 57.
- [33] G. Nelson. "Microencapsulation in textile coloration and finishing". *Rev. Prog. Color* **21** **1991**, 72.
- [34] M. I. Re and B. Biscans. "Preparation of microspheres of ketoprofen with acrylic polymers by a quasi-emulsion solvent diffusion method". *Powder Technology* **1999**, 101, 120.
- [35] S. Vasiliu, et al. "Polyelectrolyte capsules made of two biocompatible natural polymers". *European Polymer Journal* **2005**, 41, 923.
- [36] C. Muzzarelli, et al. "Spray-drying of solutions containing chitosan together with polyuronans and characterisation of the microspheres". *Carbohydrate Polymers* **2004**, 57, 73.
- [37] K. Gnietek. "Odour measurements in textile industry". *Fibres & Textiles in Eastern Europe* **2003**, 11, 53.
- [38] T. Oktem. "Surface treatment of cotton fabrics with chitosan". *Coloration Technology* **2003**, 119, 241.
- [39] S. Mondal. "Phase change materials for smart textiles - An overview". *Applied Thermal Engineering* **2008**, 28, 1536.

- [40] R. Arshady. "Microspheres and microcapsules: a survey of manufacturing techniques. I: Suspension cross-linking". *Polymer engineering and science* **1989**, 29, 1746.
- [41] C. Thies, in "Microencapsulation: Methods and industrial applications;" A survey of microencapsulation processes edited by S. Benita (Marcel Dekker, New York, 1996) p. 20.
- [42] A. Madene, et al. "Flavour encapsulation and controlled release - a review". *International Journal of Food Science and Technology* **2006**, 41, 1.
- [43] E. N. Brown, et al. "In situ poly(urea-formaldehyde) microencapsulation of dicyclopentadiene". *J Microencapsul* **2003**, 20, 719.
- [44] B. Boh, et al. "Microencapsulation of higher hydrocarbon phase change materials by in situ polymerization". *J Microencapsul* **2005**, 22, 715.
- [45] H. Y. Lee, et al. "Microencapsulation of fragrant oil via in situ polymerization: effects of pH and melamine-formaldehyde molar ratio". *J Microencapsul* **2002**, 19, 559.
- [46] J. J. Xu and H. Ye. "Polymer gel electrolytes based on oligomeric polyether/cross-linked PMMA blends prepared via in situ polymerization". *Electrochemistry Communications* **2005**, 7, 829.
- [47] W. J. Luo, et al. "Microencapsulation of decabromodiphenyl ether by in situ polymerization: Preparation and characterization". *Polymer Degradation and Stability* **2007**, 92, 1359.
- [48] H. Kage, et al. "Effects of core material, operating temperature and time on microencapsulation by in situ polymerization method". *Advanced Powder Technology* **2002**, 13, 377.
- [49] P. S. Pal, et al. "Microencapsulation of bovine serum albumin by solvent evaporation and in situ polymerization techniques". *Journal of the Indian Chemical Society* **2002**, 79, 455.
- [50] R. G. Gupta and B. C. Rao. "Microencapsulation of Vitamin-B12 by Emulsion Technique". *Drug Development and Industrial Pharmacy* **1985**, 11, 41.
- [51] T. Ouchi, et al. "Preparation of poly[DL-lactide-co-glycolide]-based microspheres containing protein by use of amphiphilic diblock copolymers of depsipeptide and lactide having ionic pendant groups as biodegradable surfactants by W/O/W emulsion method". *Polymer* **2004**, 45, 1583.
- [52] S. Nakhare and S. P. Vyas. "Preparation and characterization of multiple emulsion based systems for controlled diclofenac sodium release". *J Microencapsul* **1996**, 13, 281.
- [53] http://www.gate2tech.com/article.php3?id_article=9
- [54] S. I. Ali, et al. "Polymer Encapsulated Gibbsite Nanoparticles: Efficient Preparation of Anisotropic Composite Latex Particles by RAFT-Based Starved Feed Emulsion Polymerization". *Langmuir* **2009**, 25, 10523.
- [55] L. Sanchez-Silva, et al. "Microencapsulation of PCMs with a polystyrene shell". *Colloid & Polymer Science* **2007**, 285, 1377.

- [56] L. Sanchez-Silva, et al. "Microencapsulation of PCMs with a styrene-methyl methacrylate copolymer shell by suspension-like polymerisation". *Chemical Engineering Journal* **2010**, 157, 216.
- [57] Y. Ai, et al. "Microencapsulation of n-hexadecane as phase change material by suspension polymerization". *E-Polymers* **2007**.
- [58] Q. Gao, et al. "Dual nanocomposite multihollow polymer microspheres prepared by suspension polymerization based on a multiple pickering emulsion". *Polym. Chem.*, **2009**, 1, 75.
- [59] G. H. Ma, et al. "Synthesis and characterization of polyurethaneurea-vinyl polymer (PUU-VP) uniform hybrid microspheres by SPG emulsification technique and subsequent suspension polymerization". *Journal of Applied Polymer Science* **2003**, 89, 163.
- [60] D. Duchêne. "Cyclodextrins in targeting application to nanoparticles". *Advanced Drug Delivery Reviews* **1999**, 36, 29.
- [61] R. L. Graves, et al. "The effect of coencapsulation of bovine insulin with cyclodextrins in ethylcellulose microcapsules". *J Microencapsul* **2005**, 22, 661.
- [62] S. J. Kim, et al. "Improvement of oxidative stability of conjugated linoleic acid (CLA) by microencapsulation in cyclodextrins". *Journal of Agricultural and Food Chemistry* **2000**, 48, 3922.
- [63] J. Szejtli, et al. "Molecular Encapsulation of Volatile, Easily Oxidizable Labile Flavor Substances by Cyclodextrins". *Acta Chimica Academiae Scientiarum Hungaricae* **1979**, 101, 27.
- [64] A. R. Hedges, et al. "Use of Cyclodextrins for Encapsulation in the Use and Treatment of Food-Products". *Encapsulation and Controlled Release of Food Ingredients* **1995**, 590, 60.
- [65] T. A. Reineccius, et al. "Encapsulation of flavors using cyclodextrins: Comparison of flavor retention in alpha, beta, and gamma types". *Journal of Food Science* **2002**, 67, 3271.
- [66] A. N. Assimopoulou and V. P. Papageorgiou. "Encapsulation of isohexenylnaphthazarins in cyclodextrins". *Biomedical Chromatography* **2004**, 18, 240.
- [67] H. J. Buschmann, et al. "New textile applications of cyclodextrins". *Journal of Inclusion Phenomena and Macrocyclic Chemistry* **2001**, 40, 169.
- [68] A. G. Grechin, et al. "Quantification of cyclodextrins fixed onto cellulose fibers". *Textile Research Journal* **2007**, 77, 161.
- [69] H. J. Buschmann, et al. "Textile materials with fixed cyclodextrins as a fragrance depot". *Perfumer & flavorist* **2002**, 27, 36.
- [70] www.techexchange.com/thelibrary/innovateor.html
- [71] I. Ribeiro Dos Santos, et al. "Microencapsulation of protein particles within lipids using a novel supercritical fluid process". *International Journal of Pharmaceutics* **2002**, 242, 69.

- [72] H. Kröber and U. Teipel. "Microencapsulation of particles using supercritical carbon dioxide". *Chemical Engineering and Processing* **2005**, 44, 215.
- [73] J. Jung and M. Perrut. "Particle design using supercritical fluids: Literature and patent survey". *The Journal of Supercritical Fluids* **2001**, 20, 179.
- [74] J.-H. Kim, et al. "Microencapsulation of Naproxen Using Rapid Expansion of Supercritical Solutions". *Biotechnology Progress* **1996**, 12, 650.
- [75] M. Perrut and J.-Y. Clavier. "Supercritical Fluid Formulation: Process Choice and Scale-up". *Industrial & Engineering Chemistry Research* **2003**, 42, 6375.
- [76] http://www.gate2tech.com/article.php3?id_article=11
- [77] B. K. Green and S. Lowell. Oil-containing microscopic capsules and method of making them. US2800457, 1957.
- [78] C. Jegat and J. L. Taverdet. "Stirring speed influence study on the microencapsulation process and on the drug release from microcapsules". *Polymer Bulletin* **2000**, 44, 345.
- [79] J. C. Soper, et al. METHOD OF ENCAPSULATING FLAVORS AND FRAGRANCES BY CONTROLLED WATER TRANSPORT INTO MICROCAPSULES. WO/2001/003825, 2001.
- [80] J. C. Soper, et al. METHOD OF ENCAPSULATING FLAVORS AND FRAGRANCES BY CONTROLLED WATER TRANSPORT INTO MICROCAPSULES. EP1194225, 2002.
- [81] P. L. Madan. "Microencapsulation .1. Phase Separation or Coacervation". *Drug Development and Industrial Pharmacy* **1978**, 4, 95.
- [82] K. Matsuyama and K. Mishima. "Coacervation microencapsulation of talc particles with a fluoropolymer by pressure-induced phase separation of supercritical carbon dioxide solutions". *Industrial & Engineering Chemistry Research* **2006**, 45, 6162.
- [83] K. Matsuyama and K. Mishima. "Coacervation microencapsulation of talc particles with poly(methyl methacrylate) by pressure-induced phase separation of CO₂-expanded ethanol solutions". *Industrial & Engineering Chemistry Research* **2007**, 46, 6244.
- [84] L. Genc, et al. "Microencapsulation of ketorolac tromethamine by means of a coacervation phase separation technique induced by the addition of non-solvent". *J Microencapsul* **1998**, 15, 45.
- [85] S. Stassen, et al. "Microencapsulation by Coacervation of Poly(Lactide-Co-Glycolide) .1. Physicochemical Characteristics of the Phase-Separation Process". *Polymer* **1994**, 35, 777.
- [86] F. Ishii, et al. "Procedure for Preparation of Lipid Vesicles (Liposomes) Using the Coacervation (Phase-Separation) Technique". *Langmuir* **1995**, 11, 483.
- [87] L. Baruch and M. Machluf. "Alginate-chitosan complex coacervation for cell encapsulation: Effect on mechanical properties and on long-term viability". *Biopolymers* **2006**, 82, 570.
- [88] M. Samejima, et al. "Studies on Microcapsules .1. Role and Effect of Coacervation-Inducing Agents in the Microencapsulation of Ascorbic-Acid by a Phase-Separation Method". *Chemical & Pharmaceutical Bulletin* **1982**, 30, 2894.

- [89] A. Gupta and H. B. Bohidar. "Kinetics of phase separation in systems exhibiting simple coacervation". *Physical Review E* **2005**, 72.
- [90] I. M. Martins, et al. "Microencapsulation of thyme oil by coacervation". *J Microencapsul* **2009**, 26, 667.
- [91] J. C. Soper, et al. Method of encapsulating flavors and fragrances by controlled water transport into microcapsules. 6045835, 2000.
- [92] S. Magdassi, et al. METHOD OF PREPARING NATURAL-OIL-CONTAINING EMULSIONS AND MICROCAPSULES AND ITS USES. WO/1996/000056, 1996.
- [93] A. M. Schobel. Encapsulated active agents, for instance encapsulated fragrances and flavours, and process therefor. EP0170752, 1986.
- [94] D. M. Whitaker Sr. Stabilized perfume-containing microcapsules and method of preparing the same. US5051305, 1991.
- [95] J. SOPER, C. METHOD OF ENCAPSULATING FOOD OR FLAVOR PARTICLES USING WARM WATER FISH GELATIN, AND CAPSULES PRODUCED THEREFROM. WO/1996/020612, 1996.
- [96] K. G. H. Desai and H. J. Park. "Recent developments in microencapsulation of food ingredients". *Drying Technology* **2005**, 23, 1361.
- [97] K. G. H. Desai and H. J. Park. "Preparation of cross-linked chitosan microspheres by spray drying: Effect of cross-linking agent on the properties of spray dried microspheres". *J Microencapsul* **2005**, 22, 377.
- [98] A. Soottitantawat, et al. "Microencapsulation by spray drying: Influence of emulsion size on the retention of volatile compounds". *Journal of Food Science* **2003**, 68, 2256.
- [99] http://www.niroinc.com/drying_dairy_food/spray_drying_dryers.asp
- [100] M. P. Aronson and L. Tsaur. "Spray coating and spray drying encapsulation with latex polymers". *Glassy State in Foods* **1993**, 417.
- [101] J. Elversson and A. Millqvist-Fureby. "In situ coating - An approach for particle modification and encapsulation of proteins during spray-drying". *International Journal of Pharmaceutics* **2006**, 323, 52.
- [102] L. Tsaur and M. P. Aronson. "Spray Coating and Spray Drying Encapsulation - Role of Glass-Transition Temperature and Latex Polymer Composition". *Polymeric Delivery Systems* **1993**, 520, 84.
- [103] http://www.gate2tech.com/article.php3?id_article=6
- [104] R. C. Mciver and J. R. Mutka. "Encapsulation of Flavors by Extrusion". *Abstr Pap Am Chem S* **1987**, 194, 75.
- [105] R. C. Mciver, et al. ENCAPSULATED FLAVOR AND/OR FRAGRANCE COMPOSITION. WO/2002/065858, 2002.
- [106] D. Zasytkin and M. Porzio. "Extrusion encapsulation of flavors using modified starch-sugar/polyol glassy matrices.". *Abstr Pap Am Chem S* **2002**, 223, U34.
- [107] L. L. Westing, et al. "Shelf-Life of Orange Oil - Effects of Encapsulation by Spray-Drying, Extrusion, and Molecular Inclusion". *ACS Symposium Series* **1988**, 370, 110.

- [108] V. Manojlovic, et al. "Application of electrostatic extrusion - Flavour encapsulation and controlled release". *Sensors* **2008**, 8, 1488.
- [109] G. Yilmaz, et al. "Encapsulation of sunflower oil in starch matrices via extrusion: effect of the interfacial properties and processing conditions on the formation of dispersed phase morphologies". *Carbohydrate Polymers* **2001**, 45, 403.
- [110] <http://www.maheshindia.com/Microspheres/Expancel.Processes.htm>
- [111] K. Bouchemal, et al. "Synthesis and characterization of polyurethane and poly(ether urethane) nanocapsules using a new technique of interfacial polycondensation combined to spontaneous emulsification". *International Journal of Pharmaceutics* **2004**, 269, 89.
- [112] K. Bouchemal, et al. "Nano-emulsion formulation using spontaneous emulsification: solvent, oil and surfactant optimisation". *International Journal of Pharmaceutics* **2004**, 280, 241.
- [113] H. B. Scher, et al. "Microencapsulation of pesticides by interfacial polymerization utilizing isocyanate or aminoplast chemistry". *Pesticide Science* **1998**, 54, 394.
- [114] J. S. Cho, et al. "Microencapsulation of octadecane as a phase-change material by interfacial polymerization in an emulsion system". *Colloid and Polymer Science* **2002**, 280, 260.
- [115] B. L. Duell and D. B. Pendergrass. "Microencapsulation by Interfacial Polymerization of Polyfunctional Aziridines". *Abstr Pap Am Chem S* **1994**, 208, 336.
- [116] X. Z. Lan, et al. "Microencapsulation of n-eicosane as energy storage material synthesized by interfacial polymerization". *Acta Physico-Chimica Sinica* **2007**, 23, 581.
- [117] K. Mizuno, et al. "A fundamental study on encapsulation of an oil phase ingredient by polycondensation polymerization: The effect of water-soluble polymer on stability of limonene droplets". *Journal of Chemical Engineering of Japan* **2004**, 37, 882.
- [118] K. Mizuno, et al. "The effect of the surfactant adsorption layer on the growth rate of the polyurethane capsule shell". *Journal of Chemical Engineering of Japan* **2005**, 38, 45.
- [119] L. Ouali and D. Benczedi. PROCESS FOR PRODUCING NANO-CAPSULES CONTAINING A FRAGRANCE. WO/2006/027664, 2006.
- [120] D. Lensen, et al. "Polymeric Microcapsules for Synthetic Applications". *Macromolecular Bioscience* **2008**, 8, 991.
- [121] K. Hong and S. Park. "Preparation of poly(L-lactide) microcapsules for fragrant fiber and their characteristics". *Polymer* **2000**, 41, 4567.
- [122] M. Kubo, et al. "Modeling of the formation kinetics of polyurea microcapsules with size distribution by interfacial polycondensation". *Journal of Chemical Engineering of Japan* **2001**, 34, 1506.
- [123] M. Takasu and H. Kawaguchi. "Preparation of colored latex with polyurea shell by miniemulsion polymerization". *Colloid and Polymer Science* **2005**, 283, 805.

- [124] H. B. Scher. "Microencapsulation of pesticides by interfacial polymerization.". *Abstr Pap Am Chem S* **1999**, 217, U63.
- [125] F. Gaudin and N. Sintès-Zydowicz. "Core-shell biocompatible polyurethane nanocapsules obtained by interfacial step polymerisation in miniemulsion". *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **2008**, 331, 133.
- [126] G. Oertel, Polyurethane Handbook (Munich, 1985).
- [127] J.-D. Chen, et al. Microcapsules, their preparation and their use in photosensitive material. EP0433094, 1991.
- [128] H. B. Scher, et al. NOVEL MICROCAPSULES. EP1292386, 2003.
- [129] D. P. Haas, et al. Process for the preparation of foamed polyurethanes that are fitted with or covered by another material. EP0176013, 1986.
- [130] H. Reiff, et al. Aqueous polyurethane dispersions from solvent-free prepolymers using sulfonate diols. 4108814, 1978.
- [131] O. Lorenz and G. Rose. Process for the preparation of aqueous dispersions of polyurethanes containing chemically fixed carboxylate and/or sulphonate groups. 4528323, 1985.
- [132] K. M. Zia, et al. "Methods for polyurethane and polyurethane composites, recycling and recovery: A review". *Reactive & Functional Polymers* **2007**, 67, 675.
- [133] P. Krol. "Synthesis methods, chemical structures and phase structures of linear polyurethanes. Properties and applications of linear polyurethanes in polyurethane elastomers, copolymers and ionomers". *Progress in Materials Science* **2007**, 52, 915.
- [134] S. Budriene, et al. "Synthesis and characterization of polyurethane microspheres and their application for immobilization of maltogenase". *Polymers for Advanced Technologies* **2007**, 18, 67.
- [135] H. J. Oh, et al. "Membranes of polyurethanes containing crystalline soft segments: Oxygen permeability and morphology". *Bulletin of the Korean Chemical Society* **2001**, 22, 194.
- [136] R. B. Wieland and J. C. Soper. ENCAPSULATION METHOD FOR COMPOUNDS. WO/2006/079236, 2006.
- [137] M. Kleban, et al. Leather finished with scent-containing microcapsules. 20060216509, 2006.
- [138] A. Markus and C. Linder. ENCAPSULATED ESSENTIAL OILS. WO/2004/098767, 2004.
- [139] J. Carles, A method of creation in perfumery. Soap Perfumes Cosmet. 1962).
- [140] W. A. Poucher. "A classification of odors and its uses". *J Soc Cosmet Chem* **1955**, 81.
- [141] W. A. Poucher. "A classification of odors and its uses". *Am perfumer Essent Oil rev* **1955**, 17.
- [142] L. Harris and L. F. Blevins. PROCESS FOR APPLYING MICROCAPSULES TO TEXTILE MATERIALS AND PRODUCTS FORMED BY THE PROCESS. WO/2002/090643, 2002.

- [143] M. Kleban, et al. Leather finished with scent-containing microcapsules. 20020198392, 2002.
- [144] D. Benczedi, et al. PROCESS FOR THE PREPARATION OF EXTRUDED DELIVERY SYSTEMS. WO/2003/056938, 2003.
- [145] A. Bochot, et al. MICROENCAPSULATION SYSTEMS AND APPLICATIONS OF SAME. WO/2004/066906, 2004.
- [146] P. Schöcker, et al. LOW-VISCOSITY MICROCAPSULE DISPERSIONS. WO/2006/048169, 2006.
- [147] L. Ouali and D. Benczedi. POLYURETHANE AND POLYUREA MICROCAPSULES. WO/2007/004166, 2007.
- [148] J. F. Rodriguez Romero, et al. PROCESS FOR MICROENCAPSULATION OF PHASE CHANGE MATERIALS, MICROCAPSULES OBTAINED AND USES THEREOF. WO/2007/107171, 2007.
- [149] J. Gravalos Moreno, et al. Procedure for microencapsulation of phase change materials by spray-drying. EP2119498, 2009.
- [150] S. K. Ghosh, in "Functional Coatings", Functional Coatings and Microencapsulation: A General Perspective edited by S. K. Ghosh (Wiley-VCH Verlag GmbH & Co. KGaA, 2006) p. 1.
- [151] Relatório final de execução material do projecto Scentfashion, 2008
- [152] G. D. Moggridge and E. L. Cussler. "Wider usage is coming - Chemical product design". *Chemical Engineering* **2002**, 109, 133.
- [153] www.mathisag.com
- [154] <http://www.worldoftest.com/martindale.htm>
- [155] V. G. Mata, et al. "Engineering perfumes". *Aiche J* **2005**, 51, 2834.
- [156] P. B. Gomes, et al. "Experimental validation of perfumery ternary diagram (R) methodology". *Aiche J* **2008**, 54, 310.
- [157] www.Chemspider.com
- [158] R. R. Calkin and J. S. Jellinek, *Perfumery: Practice and Principles* edited by Willey (New York, 1994).
- [159] J. C. Leffingwell. "Chirality and Bioactivity I.: Pharmacology. ". *Leffingwell Reports* **2003**, 3.
- [160] G. Frater, et al. "Purification and olfactory characterization of the enantiomerically pure isomers of the perfumery synthetic Galaxolide® ". *Helv. Chim. Acta* **1999**, 82, 1656.

Press release



ACS News Service Weekly PressPac: June 25, 2008

Toward perfumed-clothing: Fabric-friendly “microcapsules” hide unpleasant body odors

Researchers in Portugal are reporting development of a new type of “microcapsule” filled with perfume and embedded in fabric for production of scented suits, socks, undergarments and other clothing. The same technology can be used in many other applications, such as to mask unpleasant body odors when using textile products. They describe the material, which is also environmentally-friendly, in a report scheduled for the July 2 issue of ACS’ *Industrial & Engineering Chemistry Research*, a bi-weekly journal.

In the new study, Alirio E. Rodrigues and colleagues point out that microcapsules, or submicroscopic shells, have been used for years to deliver fragrances in commercial products ranging from scratch-and-sniff stickers to the peel-apart fragrance samples found in magazine inserts. But current microcapsules are made using formaldehyde, a known cancer-causing agent that is also an environmental hazard. Safer, more effective materials are needed to extend this scented technology to textiles, the researchers say.

The researchers identified polyurethane-urea, a type of environmentally-friendly plastic that is compatible with fabrics, as a solution. They used the material to prepare microcapsules containing limonene, the familiar scent abundant in lemons and widely-used in perfumes, and applied the capsules onto wool and polyester samples. In laboratory tests, the microcapsules showed good performance in terms of prolonged fragrance production and durability, the researchers say. — MTS

Journal Information

Journal: *Industrial & Engineering Chemistry Research*

Journal Article: “Microencapsulation of Limonene for Textile Application”

- [Read the full text article](#)



Science Briefing: Plants evade global warming

By Clive Cookson

Published: June 27 2008 02:36 | Last updated: June 27 2008 02:36

Lemon scent for smelly socks

Chemical engineers in Portugal have come up with a solution to the smelly socks problem. A new type of "microcapsule" filled with perfume can be embedded in fabric for producing scented suits, socks, underwear and other clothing.

Alirio Rodrigues and colleagues at Porto University point out in the journal [Industrial & Engineering Chemistry Research](#) that microcapsules, or microscopic shells, have been used to deliver fragrances in products such as scratch-and-sniff stickers. But these microcapsules are made with formaldehyde, which is toxic.

Instead the Portuguese researchers used polyurethane-urea, a less harmful plastic that is compatible with textiles. Their microcapsules contain limonene, the main component of lemon scent.

[Copyright](#) The Financial Times Limited 2010. You may share using our article tools. Please don't cut articles from FT.com and redistribute by email or post to the web.



Science News

Share Blog Cite

Toward Perfumed-Clothing: Fabric-Friendly 'Microcapsules' Hide Unpleasant Body Odors

ScienceDaily (July 1, 2008) — Researchers in Portugal are reporting development of a new type of "microcapsule" filled with perfume and embedded in fabric for production of scented suits, socks, undergarments and other clothing. The same technology can be used in many other applications, such as to mask unpleasant body odors when using textile products.

See Also:

Matter & Energy

- Materials Science
- Engineering
- Chemistry
- Energy Technology
- Nanotechnology

Reference

- Plastic
- Formaldehyde
- Polymer
- Metallurgy

They describe the material, which is also environmentally-friendly, in a report scheduled for the July 2 issue of ACS' Industrial & Engineering Chemistry Research, a bi-weekly journal.

In the new study, Alirio E. Rodrigues and colleagues point out that microcapsules, or submicroscopic shells, have been used for years to deliver fragrances in commercial products ranging from scratch-and-sniff stickers to the peel-apart fragrance samples found in magazine inserts. But current microcapsules are made using formaldehyde, a known cancer-causing agent that is also an environmental hazard. Safer, more effective materials are needed to extend this scented technology to textiles, the researchers say.

The researchers identified polyurethane-urea, a type of environmentally-friendly plastic that is compatible with fabrics, as a solution. They used the material to prepare microcapsules containing limonene, the familiar scent abundant in lemons and widely-used in perfumes, and applied the capsules onto wool and polyester samples.

In laboratory tests, the microcapsules showed good performance in terms of prolonged fragrance production and durability, the researchers say.

Email or share this story:

| [More](#)

Story Source:

The above story is reprinted (with editorial adaptations by ScienceDaily staff) from materials provided by American Chemical Society, via EurekAlert!, a service of AAAS.

Journal Reference:

1. Rodrigues, Sofia N., Fernandes, Isabel, Martins, Isabel M., Mata, Vera G., Barreiro, Filomena, and Rodrigues, Alirio E. Microencapsulation of Limonene for Textile Application. *Ind. Eng. Chem. Res.*, 47, 12, 4142-4147, 2008 DOI: 10.1021/ie800090c

Ads by Google

TRINA modules 230Wp Poly
TRINA modules 230Wp Poly
Immediate delivery. Reserve now.
www.proinso.net

LIFE antimicrobial
Built-in antimicrobial protection
for plastics, coatings, textiles.
www.life-materials.com

Textile Textile
Search Thousands of Catalogs
for Textile Textile
www.globalspec.com

P.I.N.D. Test Systems
Manufacturers of P.I.N.D., vibration
shock and acoustics test equipment
www.spectraldynamics.com

Related Stories

 **A Boost For Bamboo-Based Blouses And Blankets** (Apr. 7, 2008) — Chemists in Colorado now are reporting solutions to two major problems with bamboo fabrics that may speed adoption of this amazing plant -- which grows like Jack's beanstalk without special care -- ... [> read more](#)

Mother Nature's Antibacterial Dyes: Bright Colors And A Knockout Punch For Germs (June 4, 2008) — A strain of marine bacteria produces large amounts of bright red pigments that can be used as a natural dye for wool, nylon, silk and other fabrics, scientists in California are reporting. The dyes ... [> read more](#)

 **Some Color Shades Offer Better Protection Against Sun's Ultraviolet Rays** (Oct. 15, 2009) — Economy-minded consumers who want protection from the sun's harmful ultraviolet rays -- but rather not pay premium prices for sun-protective clothing -- should think blue and red, rather than yellow. ... [> read more](#)

 **Killer Kevlar: Clothing That Shields From Germs** (July 21, 2008) — Protective clothing worn by firemen and other emergency workers may soon get a germ-fighting upgrade. Researchers in South Dakota report progress toward the first Kevlar fabrics that can kill a wide ... [> read more](#)

Ads by Google



Breaking News on Cosmetics Formulation & Packaging - North America

Greener microcapsules for fragrant fabrics

By Katie Bird, 01-Jul-2008

Related topics: Fragrance

A new type of microcapsule may allow manufacturers to embed fragrances in textiles without resorting to formaldehyde, according to scientists in Portugal.

Using a polyurethane-urea capsule, the researchers, led by Sofia N Rodrigues from the University of Porto, Portugal, were able to impregnate textiles with limonene, a common lemon fragrance.

Environmentally friendly option

The polyurethane-urea capsule can provide a more environmentally friendly alternative to the current commercially available systems that contain formaldehyde, according to the study published in the ACS' Industrial and Engineering Chemistry Research.

Rodrigues and the team prepared the limonene containing microcapsules by interfacial polymerisation, which they then applied to the textiles during the final processes of manufacture.

The microcapsules came in two forms, rough and smooth surfaced, which according to the scientists improves fragrance release.

In addition, the team noted that the capsules adhered strongly to the textile's fibres.

However, the fragrance was not particularly robust when faced with five dry cleaning cycles.

According to the results, a 24 per cent loss of limonene occurred after the first dry cleaning attempt, 57 per cent after the third wash, and 97 per cent after the fifth cycle.

In contrast, the fragrance was fairly hardwearing when subjected to numerous abrasion cycles - a test to evaluate the resistance of a textile to shock, stretching, rubbing and other mechanical forces.

Cosmeto-textiles - a trend to watch

Fragrant fabrics are just one of the many possibilities being explored by manufacturers who wish to capitalise on potential partnerships between the two industries.

Earlier this week Macy's saw the US release of shaping underwear impregnated with anti-cellulite actives that promise to slim the wearer whilst ridding them of orange peel skin at the same time.

Skineez Skincarewear similarly suffers problems relating to durability when the product is washed repeatedly. However, the company retails refill bottles of the active ingredient that can be used to top up the product's anti-cellulite action.

Cognis came up with the technology behind Skineez Skincarewear back in 2004 and at the time it was tipped as the next big thing.

Although the market is not yet inundated with such products it certainly seems like the opportunities for product innovation are endless.

Source: *Industrial and Engineering Chemistry Research*

2008, Volume 47, Issue 12, pages 4142-4147, DOI: 10.1021/ie800090c

Microencapsulation of Limonene for Textile Application

Rodrigues, Sofia N., Fernandes, Isabel, Martins, Isabel M., Mata, Vera G., Barreiro, Filomena, and Rodrigues, Alirio E.

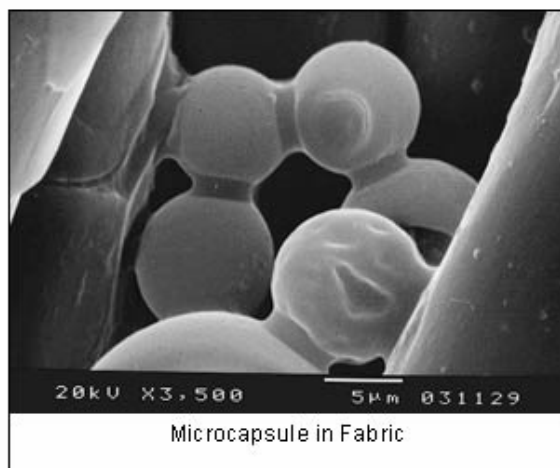
Copyright - Unless otherwise stated all contents of this web site are © 2000/2010 - Decision News Media SAS - All Rights Reserved - For permission to reproduce any contents of this web site, please email our Syndication department: [Administration & Finance](#) - Full details for the use of materials on this site can be found in the Terms & Conditions

www.fibre2fashion.com

World of Garment - Textile - Fashion

Scented microcapsule technology for value added fabrics

July 11, 2008 (Portugal)



Researchers in Portugal have been working for the development of a new type of 'microcapsule' which can be used to increase high added value of textiles.

Alirio E Rodrigues, Chief Researcher of [University of Porto](http://www.up.pt), engaged in the development, told [Fibre2fashion](http://www.fibre2fashion.com), "The microcapsule is filled with perfume and embedded in fabric for production of scented suits, socks, undergarments and other clothing. The same technology can be used in many other applications, such as to mask unpleasant body odors when using these textile products."

The material is also said to be environmentally friendly and the submicroscopic shells, have been used for years to deliver fragrances in commercial products that ranges from scratch-and-sniff stickers to the peel-apart fragrance samples found in magazine inserts. However, researchers still believe that more effective materials are required to extend this scented technology to textiles.

As a solution, polyurethane-urea, an environmentally-friendly plastic that is compatible with fabrics, was identified as a more suitable option to the ones already in use. Researchers, used the material to prepare microcapsules containing limonene, the familiar scent, abundant in lemons and widely-used in perfumes, and applied the capsules onto wool and polyester samples. Laboratory tests proved that these microcapsules indeed gave good performance in terms of prolonged fragrance production and durability.

Fibre2fashion News Desk - India

[More Textiles News - Portugal](#)



Edição nº 123 :: 11 / 2008

- Nas páginas do Observatório das Ciências e Tecnologias do Cluster Têxtil – O2CT, saiba por que cheira tão bem o vestuário desenvolvido no âmbito do projecto "Scentfashion" e conheça os prós e contras dos têxteis geneticamente modificados.

EM PROL DA COMPETITIVIDADE

Quando a roupa lança perfume

A competitividade do sector têxtil é determinada essencialmente pela capacidade de compreender e reagir às necessidades dos clientes e de se ajustar à evolução e mobilidade das tecnologias e dos recursos humanos. A intervenção de uma tecnologia de ponta, como a microencapsulação, numa indústria tradicional como a têxtil, permite apresentar uma maior versatilidade de produtos e processos respondendo aos requisitos da moda, contribuindo assim para que a indústria têxtil fique mais imune à concorrência dos países com factores competitivos baseados no preço da mão-de-obra e onde não existe uma preocupação social muito acentuada.

Foi partindo destes princípios, activos, que uma equipa do LSRE – entidade do sistema científico com elevado know-how na área de Engenharia Química –, dirigida por Sofia Rodrigues, empreendeu o projecto "Scentfashion", que tem como objectivo «a produção de uma linha de vestuário perfumado», como revela a responsável.

Financiado pelo Programa Ideia, o projecto juntou um leque de competências singular: a vertente industrial, com a empresa A Penteadora do grupo Paulo Oliveira, o Citeve e o próprio LSRE. «Este consórcio permitiu transformar um projecto ambicioso numa realidade «exequível», sublinha Sofia Rodrigues.

A grande novidade do Scentfashion reside na aplicação de microcápsulas de poliuretano-ureia que, segundo a responsável do projecto, permite um melhor controlo da rigidez da parede da cápsula e não apresenta quaisquer problemas ambientais como acontece com as que incluem formaldeído na sua composição.

«Após a fase de pesquisa da tecnologia de microencapsulação com melhor desempenho em aplicação têxtil, desenvolvemos uma nova metodologia de produção de microcápsulas, e respectiva optimização, tendo em consideração os ensaios de fixação das mesmas aos substratos têxteis seleccionados», explica Sofia Rodrigues.

«Foram produzidas microcápsulas com o princípio activo de limoneno; a tecnologia/processo de microencapsulamento utilizada foi a polimerização interfacial, e o material da cápsula é de poliuretano-ureia. Produzidas as microcápsulas, foram depois aplicadas à escala laboratorial, de forma a optimizar as condições para aplicação industrial e a liga-



A Penteadora aposta na microencapsulação.

ção, mais ou menos permanente, que foi conseguida entre a microcápsula e o substrato têxtil». O processo foi já aplicado com sucesso em misturas de lã e poliéster.

«Pretendemos, com este projecto, actuar de forma inovadora no mercado têxtil. Os potenciais mercados para o produto alvo de inovação, são nu-

merosos e ultrapassam o sector têxtil tradicional. As tecnologias desenvolvidas permitirão, além de perfumes, a microencapsulação de outras substâncias como anti-odores, hidratantes, anti-bacterianos e ainda a possibilidade de incorporar microcápsulas vitamínicas», conclui a responsável pelo Scentfashion.