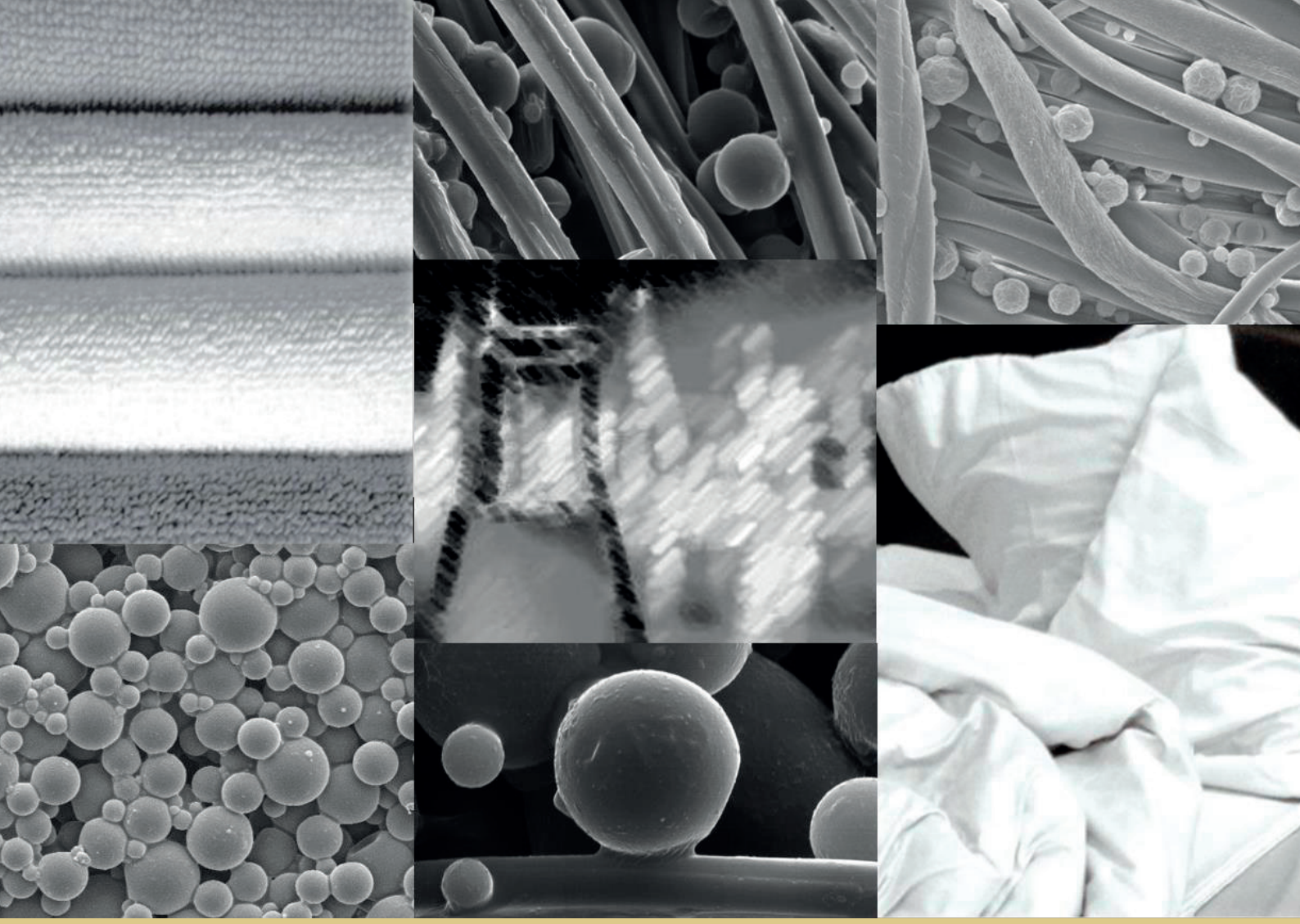

Ana de Sousa Carreira

DEVELOPMENT OF POLYMERIC PARTICLES TO ENHANCE HIGH PERFORMANCE TEXTILES

Tese de doutoramento em Engenharia Química, orientada pela Professora Doutora Maria Helena Gil e pela Professora Doutora Maria Margarida Figueiredo e apresentada ao Departamento de Engenharia Química da Faculdade de Ciências e Tecnologia da Universidade de Coimbra

Janeiro de 2016

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UNIVERSIDADE DE COIMBRA

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Development of polymeric particles to enhance high performance textiles

Thesis submitted to the Faculty of Sciences and Technology of the University of Coimbra, to obtain the degree of Doctor of Philosophy in Chemical Engineering

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Devan - Micropolis, S.A

Financing:
FCT - Portuguese Foundation for Science and Technology

Devan - Micropolis, S.A.

Doctoral degree grant: SFRH/BDE/51601/2011

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“The mind that opens to a new idea never returns to its original size”

Albert Einstein

AGRADECIMENTOS / ACKNOWLEDGMENTS

Ao finalizar este trabalho de doutoramento, não poderia deixar de expressar o mais profundo agradecimento a todos aqueles que me acompanharam e ajudaram ao longo deste percurso.

À minha orientadora, Professora Doutora Helena Gil, quero expressar o meu sincero agradecimento pela extraordinária contribuição para o meu desenvolvimento a nível profissional e pessoal. Obrigada por todo o excelente conhecimento transmitido, disponibilidade e incentivo demonstrado ao longo de todos estes anos. Tem sido um privilégio para mim trabalhar com tão excelente pessoa.

À minha orientadora, Professora Doutora Margarida Figueiredo, agradeço a disponibilidade e a sua orientação, mas acima de tudo agradeço por ter sido incansável para comigo nesta recta final do trabalho.

Ao Dr. Alexandre Beirão, supervisor na Devan - Micropolis, S.A., desejo expressar o meu agradecimento pela sua disponibilidade e orientação, bem como pelas suas sugestões para o desenvolvimento deste trabalho e pelo conhecimento transmitido.

À Fundação para a Ciência e a Tecnologia (FCT) e à Devan - Micropolis, S.A. pelo financiamento através da Bolsa de Doutoramento em Empresa.

À Dra. Raquel Vaz Vieira, o meu especial agradecimento pela oportunidade dada para trabalhar na Devan - Micropolis, S.A, trabalho que posteriormente veio originar a candidatura a este doutoramento.

Ao Doutor Roberto Teixeira, por todo o suporte e acompanhamento na realização deste trabalho, que sendo iniciado já este trabalho decorria, se tornou de vital importância.

A todos os meus colegas da Devan - Micropolis, Filipa Azevedo, Ivo Pais, Isabel Cardoso, Isabel Martins, Ricardo Vieira, Rita Prestes, Marta Costa e, claro, onde se incluem também a Raquel Vaz Vieira e o Alexandre Beirão, agradeço pela ajuda nos mais diversos campos, inclusive para discutir as minhas questões "existenciais", assim como por todos os momentos de boa-disposição e companheirismo. Um especial obrigado por tornarem a minha ida para Terras do Norte muito mais agradável.

A todos os meus colegas da Devan Chemicals, pela disponibilidade para ajudar sempre que necessário.

À Devan - Micropolis e a toda a Devan Chemicals, pelas condições proporcionadas para a realização deste projecto.

A todos os meus colegas do Departamento de Engenharia Química com os quais tive o prazer de me cruzar ao longo destes anos e com os quais, com todo a certeza, aprendi algo.

Ao Departamento de Engenharia Química da Universidade de Coimbra e a todos os seus funcionários, pelas condições e serviços proporcionados.

À Eng. Maria João Bastos desejo apresentar o meu agradecimento pela sua disponibilidade para a realização das análises termograviméricas.

À Dra. Elsa Ribeiro, obrigada pela disponibilidade e paciência para a realização das muitas análises de espectroscopia electrónica de varrimento.

A todos os meus amigos, obrigado por fazerem parte da minha vida e por estarem sempre presentes nos momentos importantes e fundamentais.

À Viviana, Anabela, Filipa, Patrícia, Eva, Adelaide e ao Rui Silva, um agradecimento especial pela amizade, companhia e bons momentos nos "nossos" anos em Coimbra, que fazem com eu sinta tanta saudade desse tempo.

Ao Joel, Catarina, Cristiana e Andreia, pela amizade e, claro, por todos os jantares e companhia nas idas à terrinha.

Ao Rui Martins, uma pessoa muito especial que eu tenho como privilégio de ter como grande amigo, obrigada por estares sempre presente e por me ouvires mesmo quando já nem eu própria conseguia.

À Raquel, a minha mana, que mesmo à distância me deu todo o incentivo e apoio para eu realizar um bom trabalho, mas especialmente pela sua amizade e companhia ao longo de toda a minha existência. O meu obrigada ao Xavier e, em especial, aos pequenos Inés e Éric por tornarem tudo mais fácil apenas com uma simples vídeo-chamada.

Aos meus pais, Joaquina e Rogério, que me ajudaram em mais uma etapa da minha vida, sempre com uma palavra de incentivo e fazendo tudo para que eu pudesse chegar até aqui. Muito obrigada por tudo!!

ABSTRACT

Microparticles containing encapsulated active compounds have been recently used in textile industry to improve their final products and to increase the market competitiveness. The incorporation of these microparticles allows the production of textile materials with new properties and functionalities without affecting their appearance, touch and original properties. These microparticles can be prepared through several microencapsulation techniques and they can have the ability to retain or release the encapsulated active compound.

The main purpose of the present study was to prepare microcapsules containing a phase change material (PCM) to be applied in the textile industry and to produce textile substrates with thermo-regulating properties. In order to microencapsulate octadecane (the selected PCM) the suspension polymerization technique by using acrylic monomers was selected.

The first well-defined microcapsules were obtained using a mixture of the monomers methyl methacrylate (MMA), butyl acrylate (BA) and methacrylic acid (MAA) and two crosslinkers (ethylene glycol dimethacrylate (EGDMA) and pentaerythritol tetraacrylate (PETRA)) and using poly(vinyl alcohol) as the stabilizer. These microcapsules were fully characterized, studying their chemical composition, morphology, size distribution and thermal properties. The obtained samples were compared with two specimens of industrial microcapsules (commercialized by Devan Chemicals) and similar characteristics with the one named as Wc-PCM28 were observed.

Then, the influence of different reaction parameters on the polymerization process and on the microcapsules properties was investigated. The type of initiator and the polymerization temperature were the first studied parameters. It was shown that both parameters have an important role on the monomer conversion as a function of time, but not on the microcapsules properties. The effect of the monomers proportions of the mixture MMA, BA and MAA was also evaluated. Despite the different shell composition, these new acrylic microcapsules showed characteristics identical to those obtained in the previous experiments. Though the major difference was observed in their thermal stability. Finally, the influence of the core material was assessed. Here, it is demonstrated that the developed procedure could be applied to microencapsulate compounds with different chemical nature. Nevertheless, the microencapsulation success is limited by the core properties.

As a result of these studies, a wide range of microcapsules containing octadecane was prepared, apparently with suitable characteristics to produce thermo-regulating textiles. These microcapsules were incorporated in polyester and cotton woven through the technique of

padding and using a finishing formulation supplied by Devan-Micropolis. Industrial microcapsules were taken as reference.

In general, the treated fabrics with acrylic shell microcapsules exhibit a thermo-performance identical to the ones with industrial sample Wc-PCM28. The enthalpy values of treated textiles differed according to the type of substrate, changing with their capacity to absorb the finishing formulation and the rearrangement of their fibres. For treated polyester woven was obtained a higher value of melting enthalpy than for the cotton woven.

The washing tests carried out with the treated fabrics showed that the shell composition is a decisive parameter with regard to the microcapsules washing resistance. The best behaviour was achieved for polyester woven with the sample prepared with 57 wt.% of MMA, 24 wt.% of BA and 19 wt.%. MAA. This result suggested that the presence of reactive carboxyl groups in the microcapsules shell favour their fixation on the textile fibres. The washed textiles reached the value of melting enthalpy and microcapsules retention obtained for sample Wc-PCM28.

Finally, the preparation of new acrylic microcapsules was investigated, by adding to the mixture of MMA with BA new monomers with two distinct reactive groups. Here, the MAA was replaced by hydroxyethyl methacrylate (HEMA), 3-(trimethoxysilyl) propyl methacrylate (TMSMA) or glycidyl methacrylate (GMA) in order to add hydroxyl, methoxy or epoxide groups, respectively. As result, microcapsules with minor differences on their properties were obtained (except chemical composition). However, the best result of washing resistance for polyester woven was observed for microcapsules prepared with TMSMA as dual reactive monomer, while for cotton woven it was the microcapsules prepared with MAA.

Distinct studies have been found in the literature about encapsulation of octadecane based on acrylic shells. Nevertheless, to the best of our knowledge, the procedure developed to prepare microcapsules together with their incorporation into textile substrates using a coupling agent has not been reported. A procedure that includes the combination of MMA and BA with different dual reactive monomers (like MAA, HEMA, TMSMA and GMA) and the crosslinkers EGDMA and PETRA.

From all the above results, it can be concluded that the encapsulation procedure established in this research work show great potential to produce microcapsules with PCM as core material. Microcapsules that can be incorporated into textile substrates in order to produce thermo-regulating functional materials. New formaldehyde-free microcapsules that can bring added value to the current product portfolio of Devan Chemicals.

RESUMO

Recentemente, na indústria têxtil surgiu a necessidade de desenvolver materiais com novas propriedades e funcionalidades, de modo a aumentar a sua competitividade no mercado. A introdução de novas funcionalidades nos substratos têxteis, sem afectar as suas propriedades originais, pode ser alcançada através da incorporação de micropartículas contendo compostos activos. Estas micropartículas podem ser obtidas por diversas técnicas de microencapsulação e podem apresentar a capacidade de reter ou libertar o composto activo encapsulado.

No presente trabalho pretendeu-se preparar microcápsulas com um material de mudança de fase (PCM) encapsulado para aplicação na indústria têxtil e com o objectivo de funcionalizar os tecidos com propriedades termo-reguladoras. De acordo com esta aplicação final, para preparar microcápsulas com octadecano foi seleccionada a técnica de microencapsulação por polimerização em suspensão, através da reacção de adição de monómeros acrílicos.

As primeiras microcápsulas obtidas com sucesso foram preparadas com os monómeros metacrilato de metilo (MMA), acrilato de butilo (BA) e ácido metacrílico (MAA) e com dois agentes reticulantes (dimetacrilato de etilenoglicol (EGDMA) e tetraacrilato pentaeritritol (PETRA) e usando poli(álcool vinílico) como estabilizante. Durante este estudo realizou-se a caracterização completo das amostras obtidas, avaliando a sua composição química, a sua morfologia e a suas propriedades térmicas. Por fim, estas microcápsulas foram comparadas com duas amostras industriais (comercializadas pelas Devan Chemicals), onde se verificaram propriedades semelhantes à amostra denominada como Wc-PCM28.

Em seguida, estudou-se a influência de diferentes parâmetros no processo de polimerização e nas propriedades finais das microcápsulas. Os primeiros parâmetros testados foram o tipo de iniciador e a temperatura de reacção, onde se observou que ambos têm um papel fundamental na conversão dos monómeros em função do tempo de reacção, mas não nas propriedades finais das microcápsulas. Em seguida, estudou-se o efeito da proporções de monómeros na mistura MMA, BA e MAA, onde apesar das variações na composição da parede das microcápsulas, a maioria das suas características permaneceram idênticas. A maior diferença entre elas foi observada na sua estabilidade térmica. Por fim, analisou-se o efeito do material de núcleo no processo de encapsulação. Este estudo demonstrou que o procedimento desenvolvido pode ser aplicado para encapsular compostos de diferente natureza química, mas que o sucesso da microencapsulação, é limitado pelas propriedades desses compostos.

Como resultado dos ensaios anteriores foram obtidas diversas amostras de microcápsulas com octadecano, que foram posteriormente incorporadas em tecidos de poliéster e de algodão. As microcápsulas industriais foram usadas como referência.

Os tecidos tratados com microcápsulas acrílicas apresentaram valores de entalpia de fusão semelhante às amostras industriais Wc-PCM28. Em geral, os valores obtidos diferenciaram-se de acordo com o tipo de substrato, destacando-se a sua capacidade de absorção e o rearranjo das suas fibras.

Para além disso, os testes de lavagem dos tecidos mostraram que a composição da parede é um parâmetro decisivo para melhorar a resistência das microcápsulas à lavagem. Os melhores resultados foram alcançados para o tecido de poliéster impregnado com as microcápsulas preparadas com 57 % de MMA, 24 % de BA e 19 % de MAA. Estes resultados sugeriram que a presença dos grupos carboxilo nas suas paredes favorece a sua fixação sobre a fibras têxteis. Para este tecido foi obtido um resultado semelhante ao determinado para a amostra WC-PCM28.

Por fim, o presente trabalho centrou-se na preparação de microcápsulas acrílicas adicionando na mistura de MMA e BA novos monómeros constituídos por dois grupos reactivos distintos. Este estudo teve como objectivo a funcionalização das paredes das microcápsulas com diferentes grupos reactivos (grupo hidroxilo, metoxi e epóxido) e foi realizado substituindo o MAA por metacrilato de 2-hidroxietilo (HEMA), por metacrilato de 3-trimetoxissililpropilo (TMSMA) ou por metacrilato de glicidilo (GMA). Como resultado foram obtidas microcápsulas com pequenas diferenças nas suas propriedades (excepto composição química), no entanto os testes de resistência à lavagem mostraram melhores resultados no tecido de poliéster para as microcápsulas preparadas com o TMSMA e no algodão para as microcápsulas com o MAA.

Na literatura podem ser encontrados diversos estudos sobre processos de encapsulação de octadecano baseados na preparação de microcápsulas em paredes acrílicas. Contudo, tanto quanto é do nosso conhecimento, o processo de preparação de microcápsulas aqui desenvolvido, em conjunto com a sua incorporação em substratos têxteis através da adição de um agente de acoplamento, não está reportada. Um processo de encapsulação que engloba a combinação de MMA, BA com monómeros constituídos por dois grupos reactivos (como o MAA, o HEMA, o TMSMA e o GMA) e com os agentes reticulantes EGDMA e PETRA.

Face aos resultados acima apresentados, o processo de microencapsulação desenvolvido na presente investigação demonstra um elevado potencial para preparar microcápsulas com PCMs encapsulados e que podem ser incorporadas em substratos têxteis para lhes atribuir

propriedades termo-reguladoras. Estas novas microcápsulas, obtidas sem recorrer ao uso de formaldeído, poderão criar valor acrescentado ao actual portfólio de produtos da Devan Chemicals.

LIST OF ACRONYMS

AA	Acrylic acid
AIBN	Azobisisobutyronitrile
BA	Butyl acrylate
BEHA	Bis(2-ethylhexyl) adipate
BMA	Butyl methacrylate
BPO	Benzoyl peroxide
Cat01	Catalyst from Devan Chemicals
CoupA01	Coupling agent from Devan Chemicals
DBP	Dibutyl phthalate
DETA	Diethylenetriamine
DSC	Differential scanning calorimetry
DVB	Divinylbenzene
EDA	Ethylenediamine
EGDMA	Ethylene glycol dimethacrylate
EMA	Ethyl methacrylate
EPA	Ethyl phenylacetate
FT-IR	Fourier transform infrared spectroscopy
GMA	Glycidyl methacrylate
HEMA	Hydroxyethyl methacrylate
LMA	Lauryl methacrylate
MA	Methyl acrylate
MAA	Methacrylic acid
MMA	Methyl methacrylate
ODMA	n-octadecyl methacrylate
PBA	Poly(butyl acrylate)
PCM	Phase change material
PEG	Poly(ethylene glycol)
PEMA	Poly(ethyl methacrylate)
PET	Poly(ethylene terephthalate)

PETRA	Pentaerythritol tetraacrylate
PMMA	Poly(methyl methacrylate)
PPDA	Poly(oxypropylene)diamine
PSt	Polystyrene
PVA	Poly(vinyl alcohol)
PVP	Polyvinylpyrrolidone
SDC	Sebacoyl chloride
SEM	Scanning electronic microscopy
SMA	Stearyl methacrylate
SMA	Sodium salt of styrene-maleic anhydride copolymer
Soft01	Softener from Devan Chemicals
Stab01	Stabilizer from Devan Chemicals
TBAC	Tributyl 2-acetylcitrate
TDI	Toluene-2,4-diisocyanate
TG	Thermogravimetric
TGA	Thermogravimetric analysis
Thick01	Thickener from Devan Chemicals
TMC	1,3,5-benzene tricarbonyl trichloride
TMPTA	Trimethylol propanetriacrylate
TMSMA	3-(trimethoxysilyl) propyl methacrylate
TOTM	Trioctyl trimellitate
Trig23	Trigonox 23
WPU	Wet pickup

NOMENCLATURE

ΔH_c	crystallization enthalpy determined by DSC
ΔH_m	melting enthalpy determined by DSC
15W	15 cycles of normal washing
25W	25 cycles of normal washing
5W	5 cycles of normal washing
D_{10}	represents the 10^{th} percentile diameter of cumulative undersize volume distribution
$D_{4,3}$	volume mean diameter
D_{50}	represents the 50^{th} percentile diameter of cumulative undersize volume distribution
D_{90}	represents the 90^{th} percentile diameter of cumulative undersize volume distribution
log $P_{o/w}$	logarithm of n-octanol/water partition coefficient
M_w	molecular weight
$T_{10\%}$	temperature corresponding to 10% of weight loss determined by TGA
$T_{5\%}$	temperature corresponding to 5% of weight loss determined by TGA
T_g	glass transition temperature
T_{oc}	onset temperature for crystallization process determined by DSC
T_{om}	onset temperature for melting process determined by DSC
T_{on}	extrapolated onset temperature determined by TGA

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CHAPTER 1

INTRODUCTION

PROJECT BACKGROUND, OBJECTIVES AND THESIS OUTLINE

1.1 PROJECT BACKGROUND AND MOTIVATION

Textile industry represents an important part of European manufacturing sector. Currently, the European textile industry faces some challenges, such as need to follow the constant market change and to compete with the low cost of the imported products from the Far East while maintaining a viable business. Therefore, in order to increase its competitiveness in the market, this industry must be more innovative and produce unique products with higher quality [1,2]. To address this, the stakeholders are refocusing on: consumer demands for comfort and performance; advanced technologies regarding product and process innovations; and ecological concerns and compliance with eco-regulations, safety, health and aesthetics [1].

The development of solutions that allows the improvement of the textile performance, by adding new functionalities and increasing tactile and thermal comfort, introduces the new concept of *intelligent textiles.* Intelligent textile materials are textile products that possess additional intrinsic and functional properties, which are not normally associated to traditional textiles. These materials are able either to react or respond to changes in the environment conditions or to external stimuli, which can be of different nature, like mechanical, thermal, chemical, electrical or magnetic [3]. It is this capacity of response through the use of functionalities integrated in the textile structure that distinguishes them from regular materials. Intelligent textiles allow to explore new and green technologies and to widen up the market range and size. In fact, currently small and medium textile enterprises are exploiting these technologies to develop new products.

To enhance the textiles performance, several approaches can be used, such as the addition of compounds/chemicals to change the feeling when the textiles are touched (e.g.: soft, supple, dry and bouncy feel), or the introduction of new functionalities into textiles, like water or oil repellent, wrinkle free finish, moisture management, stain protection, antimicrobial properties, ultraviolet protection, flame retardant finish and thermo-regulating properties [4].

Textiles with thermo-regulating effects are currently being produced in order to increase the thermal comfort, since they have the ability to respond according to the external temperature variation [5]. These textiles are produced with phase change materials (PCMs), called this way due to their ability of phase change as the temperature varies. Such materials absorb, store and release heat when they change between solid and liquid forms: they absorb thermal energy during the heating process as phase change occurs (varying from solid to liquid) and they release that energy during the reverse cooling process. The concept of thermal comfort and

PCMs are the base of this study and, consequently, they are further detailed in section 2.1. In order to allow the incorporation of PCMs into textile substrates and to withstand the repeated phase change, these compounds must be externally protected. This external protection can be achieved through their coating by microencapsulation process, resulting in microparticles of coated PCMs [2,6]. Thus, the use of this process, by the textile industry, began from the need to provide new high added value properties into technical textiles, which was not possible using traditional technologies [7].

During the last years, a growing number of applications based on microparticles have emerged. Nonetheless, textile industry has responded slowly to the many potential applications of microencapsulation. This technique exists since the year of 1950, however, only in 1980s some applications for textile substrates were developed. Some of the main problems that have limited the use of microparticles in textiles are related to the low durability of their effect. The conventional washing and other high-input thermal processes, such as ironing and tumble-drying, are examples of treatments that might cause dramatic reductions in the desired effects [6,8]. Nevertheless, in recent years, there has been a growing interest in microparticles containing different active compounds for textile applications, especially in the textile industries of Western Europe, Japan and North America [6].

This project results from a close collaboration between the Department of Chemical Engineering of the University of Coimbra and Devan-Micropolis (from Devan Chemicals). This company has been working on microencapsulation technology and its application in textiles, in order to develop microcapsules that can be fixed on any type of textile adding new functionalities. The encapsulation research has been focused on the preparation, characterization and functional application of microparticles into different substrates (such as woven, nonwoven and foams). Currently, Devan Chemicals has a wide range of products based on microencapsulated active compounds, like insect repellent, fragrances, probiotic bacteria and PCMs. It also offers new intelligent textiles products based on other technologies, such as antimicrobials, flame retardants and special functional polymers. Concerning the thermoregulation enhancement, THERMIC® is the microencapsulated PCMs product of Devan Chemicals, brand that is established on the apparel, footwear and bedding market. In general, these microcapsules are composed of a melamine-formaldehyde shell and they are available in different sizes and containing PCMs with different melting temperatures.

The technology patented by Devan Chemicals (patent WO/2006/117702 and WO/2014/044547) [9,10] and currently used by the company to incorporate microcapsules into diverse textile substrates promotes the fixation of the microcapsules into textiles by creating

durable bonds between their shell and the textile' fibres. This technology claims the fixation of the microcapsules into the textiles through the functionalization of microcapsules with reactive groups compatible with the textile fibres and through the addition a bi-functional coupling agent that reacts with both microcapsules shell and textile substrates [9,11]. For that, the knowledge of the textile chemistry and the functional groups displayed at the microcapsules shell is required[11].

The present work began from the search of new products to enrich the company portfolio and from the quest for new environmental friendly-technologies. It was focused on searching for an alternative to the melamine-formaldehyde shell of the microcapsules that contains PCMs, being always aware that the developed product must be compatible with the methodology currently used by the company to incorporate the microcapsules into the textile substrates (the technology described above). Additionally, the knowledge acquired during this work should not be restricted only to the PCMs and its use in the encapsulation of other active compounds and different final applications can be also envisaged.

1.2 OBJECTIVES

The primary objective of this PhD was to develop microcapsules containing PCMs and incorporate them into textile substrates, in order to produce materials with thermo-regulating properties. The developed microcapsules must stand out from the current Devan Chemicals' product portfolio due to their shell composition, being formaldehyde-free, and they must present final properties similar to the microcapsules that are industrially produced and presently commercialized by the company. Thus, these microcapsules should retain permanently the encapsulated core material and present high strength in order to resist to the incorporation into textile substrates. Finally, the microcapsules when added to the textiles should exhibit a high resistance and durability to the washing cycles, allowing their application in a wide range of materials.

The first target of this project was to select a shell material suitable to encapsulate a PCM (octadecane) and to define the proper microencapsulation technique. In order to prepare microcapsules with the properties formerly described, the microencapsulation procedure need to be adjusted. Afterwards, it was intended to incorporate the produced microcapsules onto textile fibres (polyester and cotton fibres) by following the Devan Chemicals' methodology and

using a bi-functional coupling agent. With this study, it was aimed to determine the thermo-performance of treated textiles and the resistance of the microcapsules to the washing cycles. The final target was to produce microcapsules with diverse reactive groups in their shell in order to increase the fixation of the microcapsules onto the textile fibres and to enhance their washing resistance.

With the developed technology, it was intended to contribute to the creation of unique know-how and provide new added value products to the company portfolio.

1.3 THESIS OUTLINE

Besides this Chapter 1, which includes an introduction to the project's background and main motivation and it describes the objectives to be achieved, this thesis is divided in 6 more chapters. In Chapter 2, the thermo-regulating textiles and the concept of PCM and microparticles is presented. Then, also in this chapter, the main mechanisms of microencapsulation and the incorporation of microcapsules into textile substrates are briefly described. Finally, the state of the art concerning the microparticles containing PCMs, focusing on textile application, is discussed. The preliminary experiments carried out by suspension polymerization technique, which led to the formation of the first spherical and individual microcapsules, and the characterization of two industrial samples of microcapsules are presented in Chapter 3. For the microencapsulation technique previously established, Chapter 4 describes the influence of different reaction parameters: the initiator type and polymerization temperature; the monomers proportions; and the type of core material. The next chapter (Chapter 5) addresses the incorporation of industrial microcapsules (that as taken as reference) and of the microcapsules containing octadecane (formerly prepared) into polyester and cotton woven. Herein, the performance of the treated textiles is evaluated by determining their thermo-performance and the resistance of the microcapsules to the washing process. In chapter 6, the preparation of new microcapsules using monomers with other reactive groups is presented. With this final work, it was intended to add different reactive groups in the microcapsules shell and study their ability to form durable bonds with the coupling agent in order to enhance the microcapsules washing resistance. Finally, Chapter 7 includes the main conclusions from this work, along with suggestions for future work.

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CHAPTER 2

STATE OF THE ART

TEXTILE SUBSTRATES WITH THERMO-REGULATING PROPERTIES

2.1 TEXTILE SUBSTRATES WITH THERMO-REGULATING PROPERTIES

The design and development of textiles with thermo-regulating properties, i.e. functional textiles that create a dynamic heat regulation next to the skin, have attracted further attention in recent years [1]. This development aims to enhance the thermal comfort of the user, since the heat exchange from the human body with the environment plays a key role in its thermal state [2,3]. Thermal comfort is defined as the condition of mind which expresses satisfaction with the thermal environment [2]. Currently, PCMs have been incorporated in textiles to improve the thermal comfort of end-use products. The heat exchange from the PCMs produces a buffering effect in the textile material, minimizing changes in the skin temperature and prolonging the thermal comfort of the wearer [1,4].

2.1.1 Phase Change Materials (PCMs)

"Phase change" is the process of going from one physical state to another, e.g. from solid to liquid or vice versa. Any material that experiences the process of phase change is known as Phase Change Material (PCM) [2]. PCMs have the ability to change their state within a temperature range. Thus, in a heating process, when the melting temperature of a PCM is reached, the phase change from solid to liquid state occurs and the PCM absorbs and stores thermal energy. When the temperature decreases again, the stored heat energy is released and the PCM solidify [2,4].

Thermal energy storage can be accomplished by the utilization of four alternatives: latent heat, sensible heat, reversible chemical heat and heat of dilution [2]. Latent heat storage denotes the thermal energy absorbed or released by PCMs when the phase change occurs without changing temperature [2,4]. Among the various thermal storage methods, this method provides the highest storage density and it is one of the most efficient ways of storing thermal energy.

The amount of heat absorbed by a PCM during the actual phase change can be compared with the amount of heat absorbed in a regular heating process taking the water as example, i.e. the latent heat storage and sensible heat storage. When ice melts into water it absorbs approximately a latent heat of 335 J/g. However, when water is further heated, a sensible heat of only 4 J/g is absorbed when the water rises by one degree Celsius [2]. Then, it can be concluded that the latent heat of absorption, in the phase change from ice to water, is about 100 times greater than the sensible [2].

The PCMs can be generally divided into two distinct groups, organic compounds (e.g., paraffin waxes or poly(ethylene glycol) (PEG)) and salt-based compounds (e.g., Glauber's salt). Table 2.1 summarizes some of the advantages and disadvantages from each group [4].

Table 2.1: Advantages and disadvantages of the two PCMs groups, adapted from reference [4].

PCM	Advantages	Disadvantages
Organic	Simple to use Noncorrosive No supercooling No nucleating agent	Generally more expensive Lower latent heat Lower heat transfer due to low thermal conductivity Can be flammable
Salt-based	Inexpensive Good latent heat Lower heat transfer due to high thermal conductivity Non flammable	Need careful preparation Need additives to stabilize for long-term use Can be corrosive for some metals Prone to supercooling

Several natural and synthetic PCMs are known, which differ in their phase change temperatures range and their heat storage capacity. However, only a few of these PCMs change phases within a temperature range just above and below human skin temperature. The required properties for application of these materials in textile products are [2].

- Melting point between 18 and 35 ºC;
- High latent heat capacity;
- Small temperature difference between the melting point and crystallization point;
- Harmless to the environment and low toxicity;
- Stability for repetition of melting and crystallization;
- Easy to obtain and relatively inexpensive.

The most common PCMs applied to textiles are the n-paraffin waxes, such as heptadecane, hexadecane, octadecane, nonadecane and eicosane. The difference between melting temperature of these several PCMs depend on the number of carbons and on their structures [5]. Nevertheless, these compounds can be mixed in order to obtain the desired melting temperature range. In this work, the chosen PCM was the octadecane, as it fits perfectly in the properties mentioned above, and mainly because it has a melting point at around 28 ºC [6].

In order to allow the incorporation of PCMs, namely the octadecane, into textile substrates and to ensure that they are not lost during the process of phase change, the PCMs can be coated through the process of microencapsulation.

2.1.2 Microparticles and microencapsulation process

The process of microencapsulation allows the immobilization of solid or liquid active compounds in a second material. In general, this process can have several purposes, namely: to increase the stability of the active compound (e.g., against oxidation or deactivation due to reaction with surrounding material); to promote the separation of the active compound from an incompatible material; to mask the odour, taste and activity of the active compound; to protect the sensitive compounds from external environment; to enable controlled release of the active compound (with a sustained or delayed release profile) [7,8].

Microparticles

After the immobilization of the active compound, the resulting particles are, normally, composed by a core (the active compound) and a shell. According to the final size, these particles can be divided in **micro**particles and **nano**particles, when their diameter is in the micrometer or nanometer range, respectively. Additionally, according to their morphology/structure, these microparticles can be further divided into microcapsules and microspheres (see Figure 2.1). In microcapsules the core is surrounded by a polymer shell (constituting a reservoir system), while in the microspheres the core can be either molecularly dissolved or heterogeneously dispersed into the matrix polymer (forming a matrix system) [9]. However, there are various intermediate cases between these two extreme situations, like microcapsules composed of several discrete domains of active compound within. The morphology of the internal structure of the microparticles highly depends on the shell materials and on the microencapsulation methods used.

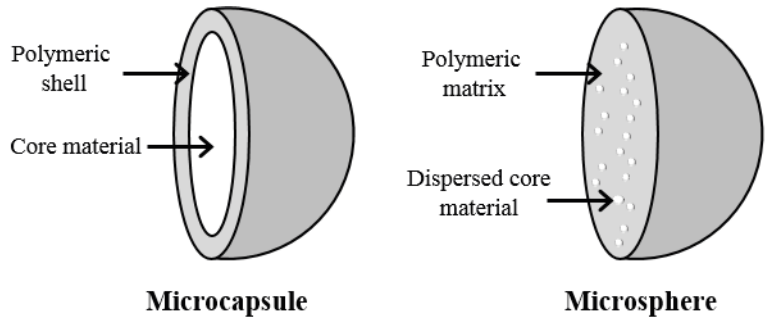

Figure 2.1: Schematic representation of a microcapsule and a microsphere.

Depending on the final application of the microparticles the entrapment of the active compound can be of two kinds: permanently entrapped or temporarily entrapped. In this first group are included the microparticles in which the active compounds are encapsulated to allow their mixing with incompatible products/materials, as it is the case of PCMs. The second group, corresponding to the microparticles with the active compound temporarily entrapped, includes microparticles that can promote the controlled release or can protect the core material for a certain period of time. Regarding the microcapsules for controlled release, these are normally used as a tool to obtain a sustained release profile of the active compound or to delay the release until the particle be submitted to a stimulus (e.g. mechanical, chemical or thermal stimulus) [4].

The development of microparticles has stimulated research in a wide range of products, such as agrochemical products (herbicides, repellents and pesticides), food ingredients, pharmaceuticals products for oral or injectable use, cosmetics, curing agents, encapsulation of living cells (including enzymes and microorganisms) and textile materials [10,4]. Concerning the textiles, besides the PCMs, diverse core materials can be encapsulated, like fragrances, skin moisturizers, cosmetics, insect repellents, dyes, antimicrobial agents and drugs [11,12].

The immobilization of these active compounds can be achieved through an extensive variety of microencapsulation techniques. The selection of the most adequate methodology is based on the type of active compound to encapsulate and on the final application required. As encapsulating agents, several polymeric materials can be used, either natural polymers (polysaccharides, such as alginate, dextran and chitosan), semi-synthetic polymers (cellulose derivatives, such as ethyl cellulose) or synthetic polymers (acrylics polymers, polyesters and polyurethanes) [10]. The combination of the initial materials and the preparation methods result in a wide variety of particles with different compositions and structures.

Microencapsulation techniques

The techniques that allow the microencapsulation of active compounds can be broadly divided into two groups: physical methods and chemical methods, being the first further subdivided into physico-chemical and physico-mechanical techniques [4]. The first category includes the techniques that involve mainly physical processes, whereas the second one involve chemical reactions, being the starting materials monomers/prepolymers. The use of these methods has been limited to the high cost of processing, the regulatory affairs and the use of some organic solvents, which are of concern for health and environment. Table 2.2 lists some

of the techniques used for microencapsulation of active compounds. Then, some of them are further detailed.

Table 2.2: Examples of techniques used for microencapsulation of active compounds [4].

Physical methods		**Chemical methods**
Physico-chemical	**Physico-mechanical**	
Coacervation	Spray drying	Interfacial polycondensation
Sol-gel encapsulation	Spray cooling	Emulsion polymerization
Layer-by-layer assembly	Solvent evaporation	Miniemulsion polymerization
	Fluid bed coating	Suspension polymerization

Physical methods

a) Coacervation technique

One of the most used physico-chemical techniques is the coacervation method [7]. For example, this method has been widely used to prepare microcapsules of gelatin and of cellulose derivatives. It was the first reported process to be adapted for the industrial production of microcapsules. Basically, it consists of promoting partial desolvation of a homogeneous polymer solution into a polymer-rich phase (coacervate) and a poor polymer phase (coacervation medium) [4].

This technique can be distinguished in simple and complex coacervation. The simple method involves the use of a single polymer whereas the complex method involves the use of two oppositely charged polymers to promote the complexation. The main difference between these methods is the way in which the phase separation is carried out, since the mechanism of microparticles formation is similar [4]. Microencapsulation by simple coacervation is carried out by preparing an aqueous polymer solution into which the core material (hydrophobic) is dispersed. A suitable desolvating agent is gradually added to the dispersion (e.g. introduction of a salt solution), leading to the formation of partially desolvated polymer molecules and hence their precipitation onto the surface of the core material. At the end, a crosslinking agent is added to the coacervation mixture in order to harden the microcapsule shell [7,8] (see Figure 2.2).

In order to encapsulate a hydrophobic material by complex coacervation, the core material is dispersed into a polymer solution (e.g. cationic polymer), containing a stabilizer. Then, a second polymer solution is prepared (anionic polymer) and added to the former dispersion. The interaction between these polymers forms a complex that leads to the formation of a shell onto

the core. The reaction is activated by changing the pH, temperature or by adding a salt. At the end, the shell is solidified by addition of a crosslinking agent or by thermal treatment [4,13]. This technique has been used to encapsulate fragrant oils, liquid crystals, flavours, dyes or inks [4].

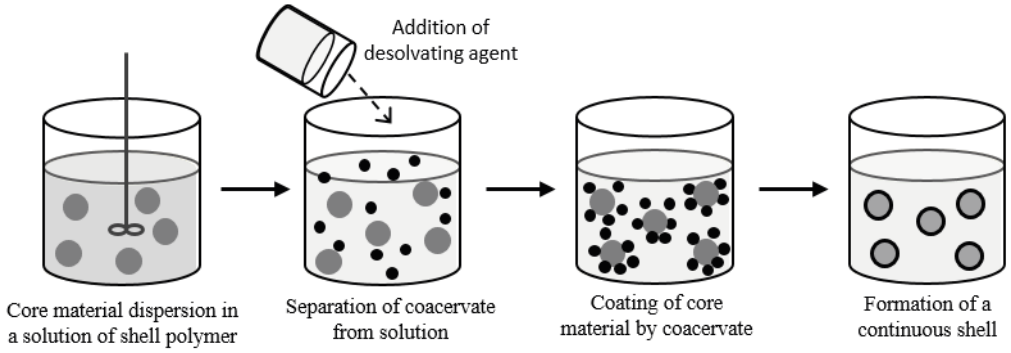

Figure 2.2: Schematic representation of microencapsulation by coacervation technique.

b) Spray drying technique

Among the most used physico-mechanical methods is the spray drying technique. This technique is economical and can be used with a large range of microencapsulation matrices, being commonly used for the encapsulation of fragrances, oils and flavours [14]. In this method, the core material (active compound) is dispersed in a polymer solution (creating a feed suspension), which is sprayed into a hot chamber. In the drying chamber, the solvent evaporates and the shell material solidifies at the surface of the droplets. The microparticles fall to the bottom of the drier and they are collected [4,14]. A disadvantage of using this technique is the probable formation of aggregated and uncoated particles as final product, mainly when a large amount of core material is used [4].

c) Solvent evaporation technique

Microencapsulation by solvent evaporation technique can be performed using different methods, according to the hydrophobicity degree of the active compound to be encapsulated. When the purpose is to encapsulate an insoluble or poorly water soluble active compound, the oil-in-water method is used [15] (see Figure 2.3). In this technique, the polymer and the hydrophobic active compound are dissolved in a volatile organic solvent (e.g. dichloromethane or chloroform), constituting the dispersed phase **(1)**. This solution is added drop-wise and under stirring to the continuous phase (composed by water and a stabilizer), in order to produce small

droplets of dispersed phase (composed by solvent, polymer and active compound) **(2)**. The transformation of the droplets of dispersed phase into solid microparticles is accomplished by removal of the volatile solvent from the droplets by solvent evaporation **(3)**. Finally, the microparticles can be recovered and dried to eliminate residual solvents **(4)** [7,15].

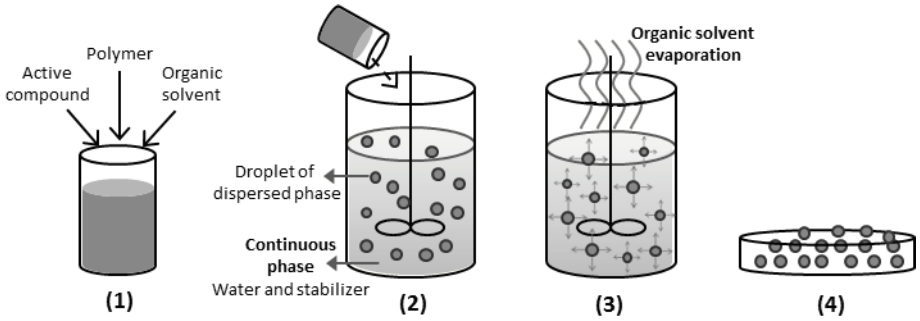

Figure 2.3: Schematic representation of microencapsulation by solvent evaporation technique (O/W emulsion), adapted from reference [10].

Chemical methods

a) Interfacial polymerization

One of the most popular techniques used for the microparticles preparation is the interfacial polycondensation or interfacial polymerization. This methodology is characterized by a step reaction polymerization (designation according to polymerization mechanism) that occur at the boundary between two immiscible solutions (one of them containing the active material) [7]. In this polymerization two monomers with different types of reactive (or functional) groups are used, which will react and produce the final polymer by losing a small molecule (such as water or methanol). Polyamide, polyurea, polyurethane and polyimide are examples of polymers obtained by this method and its step reaction polymerization [16].

The technique of interfacial polymerization by using oil-in-water (O/W) emulsion is used to microencapsulate hydrophobic core materials, as depicted in Figure 2.4. This technique is started by the droplets formation through the emulsification of an organic phase in a continuous aqueous phase. The organic phase is composed by an oil soluble reactive monomer (monomer A) and the core material. After the emulsification, a water soluble reactive monomer (monomer B) is added to the emulsion and the monomers react at the interface of the droplet generating the polymeric shell of the microparticles [17]. The advantages of this method are the high reaction velocity and the high active compound loading that can be obtained [4,18].

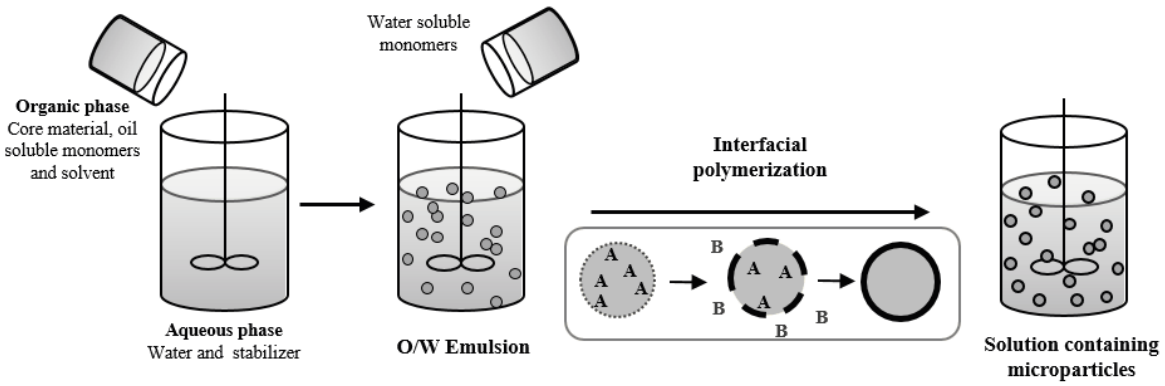

Figure 2.4: Schematic representation of microencapsulation by interfacial polymerization technique, where the oil and the water soluble monomers are represented as A and B, respectively.

Contrary to the interfacial polymerization technique, which involves a step reaction polymerization, the microencapsulation techniques by emulsion, miniemulsion and suspension polymerization implicate a chain reaction polymerization. This type polymerization consist on a different reaction mechanism, as it will be further detailed in section 3.1.

b) Emulsion polymerization

The most common type of emulsion polymerization is the oil-in-water type. In which, the monomer and the core material (a hydrophobic active compound) are dispersed in the aqueous phase using an emulsifier. This emulsifier will form small micelles when its critical level is reached (critical micelle concentration). Here the polymerization is started by using a water soluble initiator. Thus, the initiator radicals are formed in the aqueous phase and, subsequently, combined with the monomers molecules, diffusing into the micelles (hydrophobic part). During the reaction, in order to continue the reaction other monomers migrate into the micelles. This polymerization can be stopped, for example, by the reaction of a new radical with a polymer chain [16]. This polymerization method offers desirable characteristics, such as, ready heat dissipation, less reliance on volatile organic solvents and low viscosities even at high molecular weights [19].

c) Miniemulsion polymerization

The mechanisms of conventional emulsion and miniemulsion polymerization are significantly different. The emulsion polymerization, as previously presented, involves the use

of an emulsifier and the formation of micelles in the continuous phase, whereas the particles prepared via miniemulsion are mainly formed by droplet nucleation, stabilized by an emulsifier (without micelles formation). After the addition of the dispersed phase (organic solvent, monomers, initiator and core material) to the continuous phase (water and emulsifier) the miniemulsions are formed by high-energy homogenization using, for example, ultrasounds or a homogenizer. The reaction of the monomers is carried out in these small droplets, producing nanoparticles, in most cases. Generally, these miniemulsions are composed by narrowly distributed droplets with a size ranging from 50 to 500 nm [20].

d) Suspension polymerization

A typical suspension polymerization is performed by suspending a dispersed phase as droplets in a continuous phase (see Figure 2.5). The dispersed phase is constituted by monomer, core material and initiator, whereas the continuous phase is composed by solvent (which is usually water) and a stabilizer. In this technique, the initiator (oil-soluble initiator) is dissolved in the monomer droplets and the reaction is carried out only in these droplets. Here, each monomer droplet is considered as a small reactor, where the polymerization occurs and the microparticles with a polymeric shell are produced. During the reaction, the suspension of the droplets is maintained by permanent agitation and by addition of stabilizer (e.g. poly(vinyl alcohol)). If the process is carefully controlled, the polymer is obtained in the form of granules. This method present reduced cost and it is technically easy, thus a feasible process for the encapsulation of active compounds [16,21].

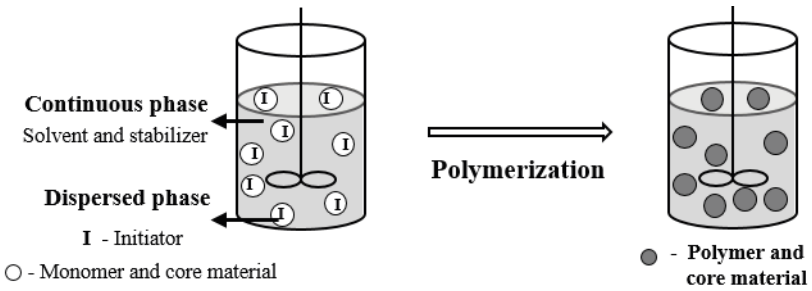

Figure 2.5: Schematic representation of microencapsulation by suspension polymerization technique.

With the preparation of microparticles containing PCM and to finalize the production of textile substrates with thermo-regulating properties, the microparticles must be incorporated in the substrates, as it is described below.

2.1.3 Incorporation of microparticles into textile substrates

One of first technologies developed to apply microencapsulated PCMs into textile structure was carry out by the National Aeronautical and Space Administration (NASA), during the 1970s for the US space light sector [4]. These materials were applied in the space suits of astronauts to improve the thermal protection against the extreme temperature fluctuations in outer space [2].

Currently, the microparticles containing PCMs have been used in a variety of applications, including home textiles (in pillows, mattress ticking and bed linen), footwear, technical textiles and apparel, including shirts, shorts, underwear, socks, jackets, rainwear, gloves and pants, being the main merits in sport and in protective clothing [4]. According to the type and final application of the substrate, different characteristics are required, namely the resistance of the microparticles to the washing process. It is clear that the requirements for the clothing are not the same as for the mattress ticking or for the foam of mattresses and pillows.

The microparticles can be incorporated in textile substrates by using two different approaches: they can be integrated either inside the fibres or they can be incorporated directly onto the surface of the fibres. In the first case, the microparticles are added to the polymeric solution that is subsequently spun using conventional methods, such as dry or wet spinning and extrusion of molten polymer [2]. Alternatively, the incorporation of microparticles onto the fibres can be made by finishing processes, usually using several methods such as coating, spraying, exhaustion or impregnation by padding. Additionally, the microparticles can also be incorporated using foam as substrate, either through their addition into the polyurethane foam matrix or through their coating onto the surface of the foam.

The final goal of these processes is to incorporate the microparticles into the substrates in order to add new functionalities to them without changing their original features, namely without changing their appearance and texture [4]. Moreover, the selection of the process to incorporate the microparticles is mostly associated to the type of substrate and its final application.

In this work, the microcapsules were impregnated onto the fibres by the technique of padding using a foulard and performing drying and curing steps. This process involves several stages, as represented in Figure 2.6. Firstly, the fabric is immersed in a solution containing the microcapsules. Then, it is passed between two rolls to increase their penetration inside the fabric and to squeeze out the excess of solution (the rollers are pressed closely together along their

length and rotating in opposite directions to carry the fabric through the system at a constant speed). Finally, the fabric containing the microcapsules passes to a dry heater for the fixation of the microparticles, obtaining treated fabric (see Figure 2.6) [22].

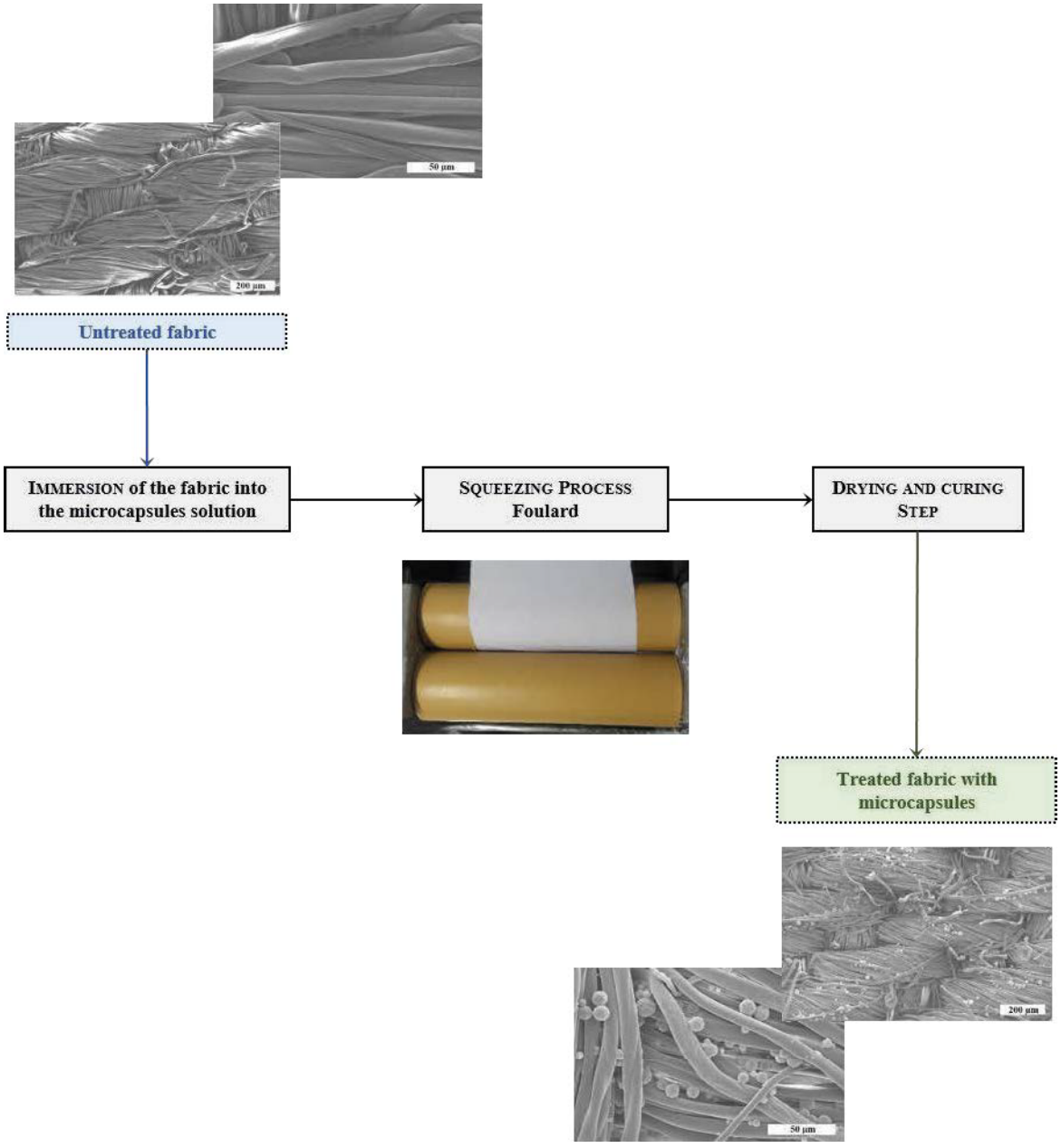

Figure 2.6: Schematic representation of the procedure to impregnate the microcapsules using the process of padding. Picture of the two rolls of a foulard (used to squeeze the fabrics) and SEM micrographs of untreated and treated fabrics (cotton woven), magnification x100 and x600.

The incorporation of microparticles by padding can be applied on any fabric (woven, knitted, nonwoven) that, in turn, can be composed of wool, silk, cotton, polyester or polyamide

fibres. The big challenge, not only for this process but in general for all the other finishing processes, is to improve the durability and resistance of the microparticles to the washing procedure, trying to overcome the chemical action of the detergent and the mechanical action and temperature of the washing cycles [4].

The solution that contains the microcapsules and in which the textile substrates are immersed can be called as "finishing formulation". In the procedures commonly applied, besides the microcapsules dispersed in water, this solution contains stabilizer, thickener, antifoam agent, softener and a polymeric binder [23,2]. The polymeric binder is the responsible to enhance the fixation of the microcapsules onto the fibres and to keep them in place, including during the washing process. The binder can be an acrylic, polyurethane or silicone compound and it can require the using of a catalyst to promote the fixation of the microcapsules during the curing stage [24,4]. It is during this curing stage, that a continuous film is formed by the binder, covering the microcapsules and the fibres and, consequently, immobilizing these microcapsules in the fabrics [25,4].

The enhancement of microcapsules lifetime into the textiles by using binders has negative effects, namely the loss of flexibility of the textile, harsh handle when in direct contact with skin and low permeability to transpiration, issues that cause discomfort for the user. Additionally, the polymeric film formed by the binder can also act as a thermal barrier, decreasing the thermo-regulator effect of the microcapsules [25, 26].

The methodology developed by Devan Chemicals to incorporate the microcapsules into textile substrates overcomes these drawbacks, since it does not involve the addition of binders in the finishing formulation [25]. As described before (section 1.1), its technology promotes the fixation of the microcapsules into the textile substrates by using microcapsules with reactive groups and adding a bi-functional coupling agent [25,27].

In the present work, the incorporation of microcapsules into the fabrics was based on this methodology, using a finishing formulation supplied by company. In this formulation, among other components, is included a coupling agent in order to promote its reaction with both microcapsules shell and textile fibres. The process implemented to incorporate the obtained microcapsules into textile substrates and the role and main characteristics of used coupling agent are detailed in Chapter 5.

2.2 PREPARATION OF MICROPARTICLES CONTAINING PCMS

In this section, an overview of studies based on the preparation of microparticles containing PCM will be presented, focusing on the textile application. The majority of the works developed so far for microencapsulation of PCMs for textile applications, or even microparticles for thermal energy storage, are related to particles whose shells are synthesized by reactions that include formaldehyde, e.g. melamine-formaldehyde microparticles [5,28–32] or urea-formaldehyde microparticles [1,33,34].

As it is known, formaldehyde is a product considered toxic and carcinogenic, which causes environmental and health problems [35]. After the polymerization and the shell formation, and despite all efforts in its elimination, some remnant formaldehyde can exist in the microparticles. This compound can be continuously released from the textiles, creating adverse consequences for the human beings. Hence, currently, the use of formaldehyde starts to be avoided.

Thus, from the several studies published in the literature based on the microencapsulation of PCMs, only those technologies that do not involve the use of formaldehyde were selected for discussion. Additionally, and due to the large amount of published works, these will be grouped according to the method used for the PCM encapsulation (described in section 2.1.2).

Firstly, the physical methods will be introduced followed by chemical methods, which are the vast majority of studies. Regarding the chemical methods those involving interfacial polymerization will be discussed in the first place. Subsequently, the techniques of emulsion, miniemulsion and suspension polymerization will be presented. To facilitate this review, some of the most important works corresponding to each technique have been condensed in tables, showing, whenever possible, the best results of PCM content of the microparticles, value of melting enthalpy (ΔH_m) and other relevant details.

2.2.1 Physical methods

a) Coacervation technique

Regarding the physico-chemical techniques, which are include in the physical methods, the coacervation technique was the main technique used for this purpose. The complex coacervation method was used by Onder and co-workers to prepare microcapsules containing

PCMs and to apply onto woven fabrics [13]. The authors used natural and biodegradable polymers (a mixture of gum and gelatin) to encapsulate n-hexadecane, n-octadecane and n-nonadecane. The three different coacervates tested resulted in different values of melting enthalpy (144.7 J/g for n-hexadecane, 165.8 J/g for n-octadecane and 57.5 J/g for n-nonadecane). Several percentages (from 9.5 % to 22.5 %) of coacervate were applied in fabrics. The results showed that, for particular temperature intervals, the energy absorption capacities improved 2.5 - 4.5 times relative to the reference [13]. With also complex coacervation technique, Hawlader *et al.* [36–38] carried out a series of studies to microencapsulate paraffin wax using gelatin and Bayés-García *et al.* [39] prepared microcapsules with Rubitherms RT27 using sterilized gelatin/arabic gum and agar-agar/arabic gum [39].

The main disadvantage of this technique is the low mechanical resistance of the used polymers. Thus, the addition of a hardening agent in final of the microcapsules production is required. In the majority of the cases, formaldehyde or glutaraldehyde are used as hardening agent compounds.

b) Spray drying technique

There are a limited number of studies reporting the success of the production of PCMs-containing microcapsules via spray drying technique [38,40]. One of these works was reported by Borreguero *et al.* [40]. In this study, the authors encapsulated the RubithermsT27 paraffin (with and without carbon nanofibers) using low density polyethylene-ethylvinylacetate as a polymer shell. They obtained a thermal energy storage capacity of only 98 J/g [40]. In present work, this method was not considered to prepare the microcapsules due to the absence of this equipment in the laboratory.

2.2.2 Chemical methods

a) Interfacial polymerization

As described before, to produce microparticles by interfacial polymerization two types of reactive monomers are required: an oil soluble reactive monomer and a water soluble reactive monomer. The chemical structure of these monomers plays an important role in the polymeric shells properties [41]. Table 2.3 summarizes several studies where the microencapsulation of the PCMs was performed via interfacial polymerization, highlighting the used monomers.

As Table 2.3 shows, different types of monomers were used to produce different types of polymeric shells through interfacial polymerization, namely polyurea, polyurethane and polyamide [18]. As it is known, polyurea derives from the polycondensation of diisocyanate (hard segments with –N=C=O groups) and diamine (soft segments with $–NH_2$ groups), the polyurethane also comes from a diisocyanate that reacts with a diol, and the polyamide is originated from the condensation reaction of, for instance, an amine group and acyl chloride group.

Table 2.3: Studies on the preparation of particles containing PCMs by interfacial polymerization.

Shell material (References)	**Monomers**	**Core material**	**Observations**	**Application**
Polyurea [17]	TDI and DETA	Octadecane	PCM content = 46 % and ΔH_m = 63 J/g	Thermal adaptable fibres
Polyurea [41]	TDI and EDA, DETA, JeffamineT403	Octadecane	PCM content = 87 % and ΔH_m = 189 J/g	Heat energy storage and thermal regulation
Polyurea [42, 43]	TDI and DETA	Octadecane	ΔH_m = 117 J/g [42]	---
Polyurea [18]	TDI and EDA	Butyl stearate	ΔH_m = 86 J/g	---
Polyurea [44]	TDI and DETA	Octadecane	ΔH_m = 55 J/g Treated fabrics ΔH_m = 5.6 J/g (finishing formulation with 40% of microcapsules)	Incorporation on polyester fabric
Polyurea [45]	TDI and DETA	Octadecane	PCM content = 70% (before cyclohexane wash)	---
Polyurethane-urea [46]	TDI and EDA, PEG	Hexadecane Octadecane Eicosane	Preparation and application of microcapsules using a polyurethane-urea shell For the octadecane: ΔH_m = 79 J/g	Textiles (coating on nylon fabrics)
Polyamide [47, 48]	SDC, TMC and PPDA, DETA	Paraffin LINPAR18	Development of an optimal formulation to prepare oily core polyamide microcapsules	---
Polyamide [49]	TMC and EDA	Paraffin wax (C30)	PCM content = 88 % and ΔH_m = 122 J/g	---

TDI: toluene-2,4-diisocyanate; **DETA:** diethylenetriamine; **EDA:** ethylenediamine; **Jeffamine T403**: amine-terminated polyoxypropylene; **PEG:** poly(ethylene glycol); **SDC:** sebacoyl chloride; **TMC:** 1,3,5-benzene tricarbonyl trichloride; **PPDA:** poly(oxypropylene)diamine

Zhang and co-workers [41] prepared polyurea microcapsules with octadecane by interfacial polymerization in an emulsion system. The authors investigated the effect of different kinds of amines (ethylenediamine (EDA), diethylenetriamine (DETA) and Jeffamine T403 (an amine-terminated polyoxypropylene) in the production of microcapsules by reacting with toluene-2,4-

diisocyanate (TDI). Their highest value of encapsulation efficiency obtained by these investigators was found for the microcapsules produced using Jeffamine T403 with a core/shell ratio of 70/30 wt./wt., corresponding to a PCM content of around 87 % and a enthalpy of melting of 188.9 J/g [41]. This melting enthalpy was considered a high value. In fact, as illustrated in Table 2.3, the combination of TDI (the oil soluble monomer), with DETA [17,42-45] and EDA [18] was also implemented in other studies, but the achieved latent heats were always lower than the value obtained with Jeffamine T403.

Polyurethane-urea microcapsules containing different PCMs were incorporated into nylon fabrics, by Know and co-workers [46]. The interfacial polycondensation was performed by using TDI, EDA, PEG as monomers. In this study, the authors intended to study the influence of the stirring rate, of the emulsifier content and of the content and type of PCM on the mean particle size and encapsulation efficiency. The microcapsules with higher of octadecane content showed a ΔH_m of around 80 J/g. After fabric coating with the microcapsules, the buffering levels of this fabrics were measured, i.e. the difference between the temperature of the coated fabrics and the untreated fabrics was determined, when both were submitted to a process of heating and cooling. It was verified that the maximum buffering levels measured at the phase transition points was obtained for the eicosane, reaching the value of -4.0 ºC, for the cooling conditions, and 4.7 ºC, for the heating conditions. Thus, the authors concluded that the microcapsules prepared by this method have potential for coatings with high heating and cooling functions [46].

Organic solvents, like cyclohexane and acetone, were used in most of the works described in Table 2.3. However, in industrial practice the use of these solvents must be avoided due to them being hazardous and also due to being expensive. Soto-Portas and co-workers [47,48] prepared polyamide microparticles without using organic solvents which is a great advantage from the environmental point of view [47]. The encapsulated agent (paraffin) was used as the internal phase and replacing the solvent. The authors produced microcapsules by interfacial polycondensation of sebacoyl chloride (SDC) with poly(oxypropylene)diamine. These monomers were also combined with DETA and 1,3,5-benzene tricarbonyl trichloride (TMC) (trifunctional monomers). The optimal formulation was achieved by the combination of SDC and poly(oxypropylene)diamine with both trifunctional monomers, which were used to minimize the paraffin released. A similar study was later performed by Wei *et al.* [49], using TMC as the oil soluble monomer and EDA as the water soluble monomer [49].

b) Emulsion polymerization

Using the same methodology as before, Table 2.4 summarizes the most relevant works that employed the emulsion polymerization in the production of microparticles with PCMs.

Table 2.4: Studies on the preparation of particles containing PCMs by emulsion polymerization.

Shell material (References)	**Core material**	**Main results**	**Application**
PMMA [50,19]	Docosane [50]	PCM content = 28% and ΔH_m = 55 J/g	Solar space heating
	n-eicosane [19]	PCM content = 35% and ΔH_m = 84 J/g	Fibres, fabrics or foams *
PMMA [51, 52]	n-octacosane [51]	PCM content = 43% and ΔH_m = 86 J/g	----
	n-heptadecane [52]	PCM content = 38 % and ΔH_m = 81 J/g	
PMMA [53]	n-hexadecane	Preparation, characterization and application of microcapsules into textiles PCM content = 61 % and ΔH_m = 145 J/g ΔH_m of treated fabrics varied between 3 J/g - 10 J/g	Incorporation onto distinct fabrics
PBA [54]		Preparation, characterization, and determination of thermal properties PCM content = 51 % and ΔH_m = 120 J/g Cotton and 50/50% cotton/polyester blend fabrics showed a ΔH_m = 6.6 and 28.6 J/g	Incorporation on cotton and 50/50% cotton/polyester
P(MMA/GMA) [55]		Incorporation of PCM microparticles within fibres PCM content = 63 % and ΔH_m = 148 J/g	Incorporate within fibres by means of electrospinning
PMMA[56]	Paraffin	Emulsion polymerization method in the presence of a photoinitiator PCM content = 61% and ΔH_m = 101 J/g	Solar space heating applications, textiles * and building materials

***** without results of microparticles incorporated in textiles.

PMMA: Poly(methyl methacrylate); **PBA:** Poly(butyl acrylate); **P(MMA/GMA):** Poly(methylmethacrylate-glycidyl methacrylate) copolymer.

In 2009, Alkan and co-workers [50] prepared poly(methyl methacrylate) (PMMA) microcapsules with docosane for thermal energy storage, namely solar space heating applications [50]. Later, the same authors prepared PMMA to encapsulate n-eicosane, a PCM with a melting temperature of 35 ºC. These microcapsules were able to be applied onto fibres, fabrics or foams [19]. The microcapsules prepared had a smooth and compact surface with an average diameter of 0.7 μm (for a stirring rate of 2000 rpm). By thermal analysis it was possible to check that the melting and crystallization temperatures were 35.2 ºC and 34.9 ºC, respectively, and the melting enthalpy was 84.2 J/g. During the thermal cycling tests (repetition of the melting/crystallization processes), the microcapsules remained with the same chemical

composition. The authors considered that these PCM-containing microcapsules had potential for thermal energy storage applications [19]. PMMA microcapsules were also prepared by Sari and co-workers, being encapsulated n-octacosane [51] and heptadecane [52].

Alay and co-workers encapsulated a PCM (n-hexadecane) into distinct polymeric microcapsules to be applied in textiles, by emulsion polymerization [53–55]. In all these works the preparation of microparticles was based on the procedure presented by Alkan and co-workers [50]. Particularly, these authors prepared poly(n-butyl acrylate) microcapsules with n-hexadecane crosslinked with several compounds, namely allyl methacrylate and ethylene glycol dimethacrylate [54]. This process leaded to particles that ranged in size between 0.47 and 4.5 μm and that exhibited a PCM content between 27.7 % and 50.7 %, and latent heat that ranged from 65.7 J/g and 120.2 J/g. To develop thermo-regulating fabrics, the microcapsules prepared with the allyl methacrylate were added to cotton and cotton/polyester blend fabrics, by padding - cure processes. The results of DSC revealed that cotton/polyester fabrics were more suitable for the application of microcapsules, showing 28.6 J/g of heat capacity, while the cotton had only 6.6 J/g (for a concentration of microcapsules of 50 g/L and using 2 bar of pressure in the foulard) [54].

The technique of emulsion polymerization can also be performed by using a photoinitiator, as Ma e*t al.* described [56]. In their work, the authors successfully prepared microcapsules containing a paraffin with a peak melting temperature of 33.6 ºC by using MMA (methyl methacrylate) as monomer [56].

In the studies formerly described, the highest values of PCM content of the presented microcapsules were around 60% and they were obtained by Alay and co-workers in their study concerning hexadecane encapsulation [53,55]. It seems that, in general, the value of PCM content of the microparticles obtained by suspension polymerization technique is lower than the ones obtained by interfacial polymerization.

c) Miniemulsion polymerization

As referred before, the miniemulsion polymerization allows the synthesis of nanoparticles, mainly due to the high degree of agitation applied to form the dispersed phase droplets. Table 2.5 summarizes some of the reported studies involving this technique for the encapsulation of PCMs. In general, the authors of the listed studies did not indicate the final application of the obtained nanoparticles.

Table 2.5: Studies on the preparation of particles containing PCMs by miniemulsion polymerization.

Shell material (References)	**Core material**	**Main results**	**Application**
PSt [57, 58]	Octadecane	Preparation of nanocapsules containing PCM Particle diameter = 100 -123 nm [57]	---
		Study the influence of polymerization factors Particle diameter =124 nm and ΔH_m = 124 J/g [58]	
PSt [59]	Paraffin wax	Spherical particles with nanosize range ΔH_m=145 J/g	---
PEMA and PMMA [60]	Octadecane	PEMA: ΔH_m =198 J/g and average diameter = 140nm PMMA: ΔH_m =209 J/g and average diameter = 119 nm	---

PSt: Polystyrene; **PEMA:** Poly(ethyl methacrylate); **PMMA:** Poly(methyl methacrylate)

Fang and co-workers [57] prepared nanocapsules containing PCM by using polystyrene (PSt) as shell and n-octadecane as core (using ultrasonic technique) [57]. Later, the authors completed this work by studding the influence of polymerization factors, such as the initiator, the chain transfer agent, the surfactant, the n-octadecane/styrene ratio and the hydrophilic co-monomer [58]. The nanoparticles obtained by employing the optimized conditions had 124 nm of z-average size diameter and a latent heat of 124.4 J/g [58]. Nanoparticles containing PCM were also prepared by Park *et al.* [59] using styrene as the monomer and by Zhang *et al.* [60] using acrylic monomers, such as ethyl methacrylate (EMA) and MMA.

d) Suspension polymerization

Table 2.6 summarizes the studies carried out via suspension polymerization technique. Most of the works presented in this table were performed only by two research groups. The first one performed by Sanchez and co-workers and focused on producing microcapsules for textile application [61–68] and a second one performed by Qui and co-workers and focused in thermal energy storage for building applications [69–73].

Table 2.6: Studies on the preparation of particles containing PCMs by suspension polymerization.

Shell material (References)	**Core material**	**Main results**	**Application**
PSt [61]	Several types of PCMs	From tetradecane, nonadecane, PEG 800, PRS® paraffin wax, Rubitherm® RT27, Rubitherm®RT20, only the PEG800 cannot be encapsulated	thermo-regulating textiles *****
PSt [62–66]	PRS® paraffin wax	PCM content = 50 % ΔH_m = 102 J/g [63]	thermo-regulating textiles
		Thermo-regulating textiles were successfully produced by coating [65]	
P(St/MMA) [67]	PRS® paraffin wax	PCM content = 48 % and ΔH_m = 96 J/g	thermo-regulating textiles *****
PMMA; P(MMA/MA); P(MMA/MA/MAA) [68]	PRS® paraffin wax	PCM content = 47% and ΔH_m = 95 J/g for microcapsules of P(MMA/MA/MAA)	---
P(St/DVB) [74]	Octadecane	PCM content = 56% and ΔH_m = 126 J/g	---
P(MMA/MAA) [75]	Octadecane	PCM content = 70% and ΔH_m = 155 J/g	---
PSt [76]	Octadecane	PCM content = 67% and ΔH_m = 156 J/g	Building materials
P(MMA-co-AA) [77]	Paraffin	PCM content = 60% and ΔH_m = 113 J/g	---
PMMA [70]	Octadecane	PCM content = 69 % and ΔH_m = 154 J/g for microcapsules of PMMA crosslinked with TMPTA	building materials
PMMA, P(MMA/ BA) P(MMA/ BMA) P(MMA/ LMA) P(MMA/ SMA) [69]		PCM content = 79 % and ΔH_m = 180 J/g for microcapsules of P(MMA/ BMA) crosslinked with PETRA	---
P(BMA) and P(BA) [71]		PCM content = 56 % and ΔH_m = 126 /g for microcapsules of P(BMA) crosslinked with DVB	building materials
P(BMA/MAA) [72]		PCM content = 60 % and ΔH_m = 130 J/g	building materials (gypsum board)
P(BMA/BA) P(BMA/BA/MAA) P(BMA/MAA) P(BMA/AA) [73]		PCM content = 66 % and ΔH_m = 144 J/g for microcapsules of P(BMA/MAA)	building materials
P(ODMA/ MAA) [78]	Octadecane	Fabrication of microcapsules containing PCM with low supercooling effect	---
PMMA [79]	Rubitherm®RT21	PCM content = 86 % and ΔH_m = 132 J/g	---

***** without results of microparticles incorporated in textiles.

St: styrene; **MMA**: methyl methacrylate; **MA**: methyl acrylate; **MAA**: methacrylic acid; **DVB**: divinylbenzene; **AA**: acrylic acid; **BA**: Butyl acrylate; **BMA**: Butyl methacrylate; **LMA**: lauryl methacrylate; **SMA**: stearyl methacrylate, **TMPTA**: trimethylol propanetriacrylate: **PETRA**: pentaerythritol tetraacrylate; **ODMA**: n-octadecyl methacrylate; **PEG**: Poly(ethylene glycol)

As the Table 2.6 shows, Sanchez and co-workers carried out an extensive investigation focusing the preparation and characterization of PCMs microcapsules by suspension polymerization [61–68]. The authors started by preparing and characterizing polystyrene (PSt) microcapsules with different types of PCMs (such as tetradecane, nonadecane, PEG800 and PCMs of commercial grade as the Rubitherm® RT27, Rubitherm® RT20 and PRS® paraffin wax) [61]. By studying the thermal properties, the morphology and the particle size distribution of the obtained microcapsules, they found out that only the PEG could not be encapsulated applying this technique, due to its hydrophilic properties [61]. This team continued the study of PSt microcapsules with PRS® paraffin wax in other works, as listed in Table 2.6. The influence of the different parameters (reaction temperature, stirring rate and mass ratio of paraffin to styrene) in the properties of these microcapsules was studied [62]. Subsequently, an experimental design approach was developed to study the variables of the synthesis procedure [63]. However, despite this study, the best result corresponded only to 50 % of encapsulated paraffin and to a melting enthalpy of 102 J/g [63]. Although all these PSt microcapsules were developed in order to be incorporated into textile materials, only in the later studies this research team applied them into the fabrics [65]. In this study, several types of commercial binders were tested in the coating process, reaching good results in terms of durability after washing, rubbing and ironing treatments [65]. Finally, Sanchez-Silva and co-workers also carried out a study of scale-up for this microencapsulation process [66].

Based on these works of PRS® paraffin microencapsulation using PSt [62–66], different shell materials were further used, namely: copolymer of styrene and methyl methacrylate (St/MMA)[67], homopolymer of MMA; copolymer of methyl methacrylate and methyl acrylate (MMA/MA); and a copolymer of methyl methacrylate, methyl acrylate and methacrylic acid (MMA/MA/MAA) [68]. The combination of these monomers aimed to increase the amount of encapsulated paraffin. Though, the highest value of latent heat was only 95 J/g obtained for the copolymer MMA/MA/MAA and the produced microparticles did not present a well-defined core/shell structure [68].

More recently, Qui and co-workers based their research on the preparation of acrylic microcapsules containing octadecane via suspension polymerization, carrying out an extensive work [69–73]. As listed in Table 2.6, the authors implemented this technique using different acrylic monomers, such as MMA, BA, butyl methacrylate (BMA), lauryl methacrylate (LMA) and stearyl methacrylate (SMA) and MAA, and using different combinations of these monomers. One of the best results, concerning the amount of encapsulated octadecane, was achieved by using a polymeric shell of MMA and BMA crosslinked with pentaerythritol tetraacrylate

(PETRA) [69]. In this study, a core content of around 79 % and a ΔH_m of 180 J/g were reached. In contrast to the acrylic microcapsules prepared by Sánchez-Silva *et al.* [68] (earlier described), these microcapsules present a core/shell structure, which should be the main responsible for this high value of encapsulated octadecane.

Additionally, PCM-containing microcapsules based on styrene and divinylbenzene (DVB) [74], on styrene crosslinked with different types diacrylates [76], on MMA and MAA [75] and on MMA crosslinked with PETRA [79] were also prepared, by suspension polymerization technique.

2.2.3 Relevant methodologies for the present work

The research on microparticles with encapsulated PCMs has been progressively growing and, currently, these microparticles play an important role on the production of thermal energy storage systems, including in textile sector.

The literature review revealed that to encapsulate PCMs the most common techniques are based on chemical methods, with great emphasis on interfacial polymerization and suspension polymerization. In recent years, the production of acrylic microcapsules, via suspension polymerization, to encapsulate active compounds (such as the PCMs) has increased, revealing to be a very promising technique. Out of the studies previously presented, the work developed by Qiu and co-workers [69–73] must be highlighted, given the high values of PCM content and melting enthalpy that were reached. Their results, together with the remaining studies presented in Table 2.6, suggest that the success of the microcapsules production and their final properties are extremely related to the type of monomers and crosslinkers used. In general, by changing only this two components, microcapsules with different properties can be obtained. This feature can be used in order to adjust the microcapsules properties according their final requirements and to obtain microcapsules with good performance when incorporated onto the fibres of different textile substrates.

In general, the suspension polymerization technique is easy to implement, as it not requires a specific equipment, like in the case of spray dying technique. In general, a stirred reactor vessel is used, allowing an easy heat removal and temperature control and also a low dispersion viscosity [80]. Additionally, this technique does not involve the use of organic solvents and it allows to use water as the continuous phase. Nevertheless, when implemented to encapsulate active compounds, one of the main challenges of this technique is the formation of microcapsules with core/shell structure and, consequently, the encapsulation of a high amount

of core material. Despite the number of published articles concerning the production of acrylic microcapsules with PCMs (Table 2.6), including with octadecane (the selected PCM), in most of the cases the authors do not report their incorporation in textile substrates. Therefore, limited information about their behaviour during and after the incorporation process is available.

Concerning the patented technologies there are a wide number of patents based on the microencapsulation of PCMs for textile applications. However, only a small number of them claim the use of only acrylic monomers to produce microcapsules via suspension polymerization. Table 2.7 summarizes the most important patents related to this latter topic.

Table 2.7: Selection of patented processes relates to the microencapsulation of PCM, which claim the use of acrylic monomers to produce microcapsules via suspension polymerization.

Patent Assignee (Reference)	**Summary**
Universidad de Castilla-la Mancha WO2007/107171A1 [81]	***Title:*** Process for microencapsulation of phase change materials, microcapsules obtained and uses thereof Process for microencapsulation of phase change materials based on free radical polymerization Use of microcapsules in the thermal protection and storage of heat.
BASF SE US2010/0068525 [82]	***Title:*** Microcapsules Preparation of microcapsules comprising a capsule core and a capsule wall constructed of C1-C24-alkyl esters of acrylic and/or methacrylic acid, acrylic acid, methacrylic acid and/or maleic acid, crosslinkers and also, if appropriate, miscellaneous monomers. Moreover, their use in binding construction materials, textiles and heat transfer liquids
BASF SE US 2012/112122 A1 [83]	***Title:*** Microcapsules with polyvinyl monomers as crosslinker Preparation of microcapsules comprising a capsule core and a capsule wall constructed from C1-C24-alkyl esters of acrylic acid and/or methacrylic acid, polyvinyl monomers, and, if appropriate, other monomers without ionisable radicals. Identical to Patent US2010/0068525 [82]
BASF SE US 2012/205576 A1 [84]	***Title:*** Microcapsules with a paraffin composition as capsule core Identical to Patent US2012112122A1 [83]
Microtek Laboratories, Inc. WO 2015/085141 A1 [85]	***Title:*** Microcapsules having acrylic polymeric shells Preparation of microcapsules having a hydrophobic core material within an acrylic polymeric shell and methods of making such microcapsule. The polymeric shell is prepared from a monomeric blend that includes a mono-functional acrylic monomer and a hyperbranched polyester acrylic oligomer. The methods include a two-stage polymerization process where the monomeric blend is polymerized with an azo-initiator in a first stage polymerization reaction and is subsequently further polymerized with a water soluble initiator in a second stage polymerization reaction.

Overall, the production of acrylic microcapsules via suspension polymerization technique presents a high potential to be explored, specially aiming their incorporation on textiles. Hence, this was the technique selected to encapsulate octadecane. This process of microencapsulation as well as the formulation selected to initiate this study are detailed in the following chapter.

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CHAPTER 3

MICROENCAPSULATION PROCEDURE VIA SUSPENSION POLYMERIZATION

ABSTRACT

This chapter describes the work performed to establish the microencapsulation procedure via suspension polymerization technique. Using octadecane as core material, acrylic microcapsules were prepared using a mixture of three monomers (methyl methacrylate, butyl acrylate and methacrylic acid) and two crosslinkers (ethylene glycol dimethacrylate and pentaerythritol tetraacrylate). Additionally, an thermal initiator, benzoyl peroxide was employed and two stabilizers (polyvinylpirrolidone and poly(vinyl alcohol)) were alternately tested in order to obtain well-defined microcapsules. Different mass ratios of PCM/monomers were also investigated. The prepared microcapsules were fully characterized regarding their chemical composition (by infrared spectroscopy), morphology and size distribution (by scanning electronic microscopy and laser diffraction) and thermal properties (by differential scanning calorimetry and thermogravimetric analysis). Finally, they were compared with industrially produced microcapsules.

At last, a standard experimental procedure was established to successfully produce acrylic shell microcapsules containing octadecane, with suitable properties for thermal energy storage.

3.1 INTRODUCTION

As presented in Chapter 2, there are numerous techniques that allow the microencapsulation of PCMs and an extensive variety of shell materials. Devan Chemicals currently commercializes microcapsules containing PCM composed of melamine-formaldehyde shell. However, to expand its product portfolio and to fill in a market need, particularly the search for new formaldehyde-free products, the company is looking for alternative microcapsules. This was the main motivation of this research, whose the first goal was to implement a new procedure to prepare microcapsules containing PCM, not involving the use of formaldehyde and thus more environmental friendly. As discussed before, in order to achieve this goal, it was decided to prepare acrylic microcapsules through suspension polymerization technique.

Since the desired functionality that is being sought for the textiles is thermo-regulation,

the choice of PCM component is of utmost importance. As it was presented (section 2.1.1), the selected PCM was the octadecane. Besides the core ingredient, other components have to be chosen: the suspension medium, the stabilizer, the monomers, the crosslinker and the initiator.

Water was selected as the suspension medium due to its immiscibility with the octadecane and also because it has low viscosity (allowing an efficient control of reaction temperature) and, most important, it is accessible and the solvent normally used to incorporated the microcapsules into the textile substrates.

The addition of a stabilizer to the continuous phase has the main function of preserving the initial size of the emulsion droplets until the microcapsules are formed. The stabilizer creates a protective layer around the droplet/particle surface. This protective layer acts by a mechanism analogous to steric stabilization and it operates by preventing the approach of the droplets and by avoiding them to touch and aggregate [1,2]. This stabilization can be achieved using macromolecules like amphiphilic block or graft copolymers and homopolymers. In general, a good steric stabilizer is the one that can be well anchored to the surface of the droplets and that provides a thick steric barrier [1,3]. In this work, the first choice of the stabilizer was on the polyvinylpyrrolidone (PVP). PVP was extensively used as stabilizer in the studies of Sanchez-Silva and co-workers [4–6] in order to encapsulate different PCMs through the technique of suspension polymerization, although in only a few cases the authors used acrylic monomers [7,8]. Sodium salt of styrene-maleic anhydride copolymer (SMA) [9–11] and poly(vinyl alcohol) (PVA) [12] are other alternatives as stabilizers to encapsulate octadecane.

Concerning the monomers or the monomers mixture used to prepare the acrylic shell and to encapsulate the hydrophobic core material, these must have low solubility in water (the suspension medium). The monomer selected to be the dominant element of the shell was methyl methacrylate (MMA), due to its chemical and mechanical properties and because it is widely used, easy to handle and inexpensive [13]. PMMA is characterized by a glass transition temperature (T_g) of 105 °C and by a modulus of elasticity of 3300 MPa and hardness of 195 MPa, properties that should provide high mechanical strength to the microcapsules shell and favour the retention and protection of the PCM from the external environment [7,8,13]. Furthermore, PMMA has a relatively good thermal conductivity (0.19 W/ (m K)), which will not restrict the heat transfer of the PCM to the outside and vice-versa [7,8,13]. This monomer was already used as main component to produce acrylic microcapsules and to encapsulate octadecane in different studies of Qui e*t al*. [14,15] and in the work of Shan e*t al*. [9].

In addition to MMA, two other monomers, although in minor percentages were selected: butyl acrylate (BA) and methacrylic acid (MAA). Figure 3.1 illustrates the chemical structure of these monomers.

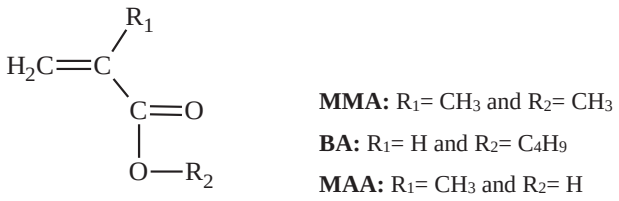

Figure 3.1: Chemical structure of selected monomers: methyl methacrylate (MMA); butyl acrylate (BA); and methacrylic acid (MAA).

The poly(butyl acrylate) is very a flexible polymer at room temperature, presenting a T_g of -54ºC, and it is commonly used in paints, adhesives and coatings [16]. In this work, BA was used essentially to reduce the brittleness of the polymeric shell and therefore to decrease the extent of microcapsule's breakage, especially those that can occur during their incorporation onto the fibres of the textiles. Qui e*t al.* [11,14,16] have already used this monomer to microencapsulate octadecane. In these studies, BA was crosslinked with divinylbenzene and pentaerythritol triacrylate [16] and it was copolymerized with MMA [14] and with butyl methacrylate (BMA) [11].

In contrast to MMA and BA monomers, MAA is a carboxylic acid and it is classified as a hydrophilic monomer (water solubility of 89 g/L at 25 ºC) [17]. This monomer was added to the monomers mixture in order to introduce some reactive groups in the microcapsules shell (carboxyl groups) and to increase the polarity of the mixture. Sánchez-Silva [18] investigated the microencapsulation of PRS® paraffin wax with different monomers, like styrene, MMA, MA, MAA and BA, and using an extensive range of combinations and proportions of these monomers. In their work, copolymeric shells based on MMA, BA and MAA were produced. Nevertheless, the results obtained with this combination seemed not very promising since only microcapsules with low latent heat (with value of around 85 J/g using a core material with 202 J/g) and large sizes (median diameters around 600 μm) [18] were obtained.

In order to improve the mechanical properties of the microcapsules with a denser and with higher thermal resistance, decreasing the permeability and release of the octadecane, it was added crosslinkers to the monomer mixture. The improvement in the thermal resistance of

acrylic microcapsules through the addition of crosslinkers was described by Shan e*t al.* [9]. Thus, in contrast to the work presented by Sánchez-Silva [18], here two crosslinkers were used: ethylene glycol dimethacrylate (EGDMA) and pentaerythritol tetraacrylate (PETRA) (see Figure 3.2). These crosslinkers can react with the monomers mixture (MMA, BA and MAA) creating a polymeric three-dimensional crosslinked network [15].

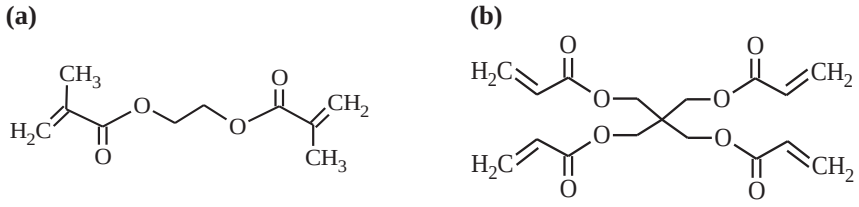

Figure 3.2: Chemical structure of selected crosslinkers (a) ethylene glycol dimethacrylate (EGDMA) and (b) pentaerythritol tetraacrylate (PETRA).

Several studies have been found in the literature about encapsulation of octadecane based on acrylic shells (section 2.2), as far as we know, the combination of these three monomers (MMA, BA and MAA) has not been used to prepare polymeric shells crosslinked with EGDMA and PETRA, aiming for shell robustness for textile type of applications.

Finally, for the suspension polymerization technique, an oil-soluble initiator is required, in order to initiate the reaction inside the oil droplets and ultimately producing the membrane shell of the microcapsules [19]. The trigger used to initiate the polymerization reaction was temperature and thus benzoyl peroxide (BPO), a hydrophobic thermal initiator, seemed appropriate. BPO is a free radical initiator widely used to polymerize acrylic monomers, namely to produce microcapsules [8,9,12].

A schematic representation of the suspension polymerization procedure followed in the present work to produce acrylic microcapsules is shown in Figure 3.3, which consists in the following steps:

- Preparation of ***Solution (1)*** by mixing the monomers, crosslinkers, initiator and core material;

- Preparation of ***Solution (2)*** by dissolving the stabilizer in water;

- Addition of Solution (1) to Solution (2), under mechanical agitation, in order to generate an oil-in-water emulsion;

- The polymerization reaction is initiated by increasing the temperature of the emulsion.

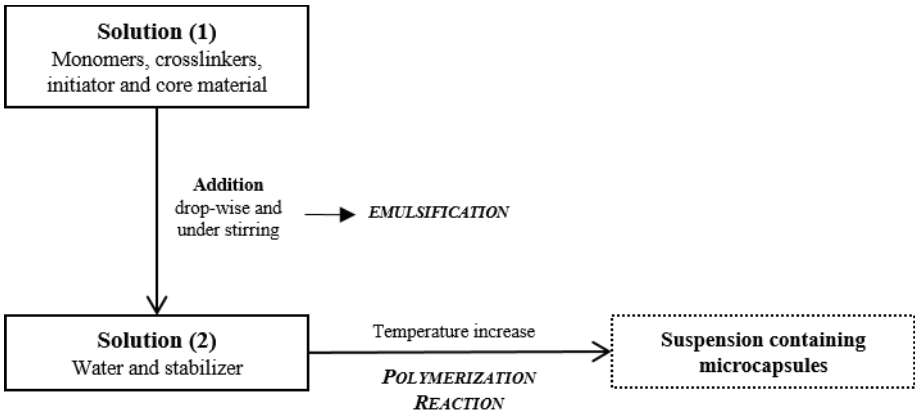

Figure 3.3: Schematic representation of the procedure proposed to produce the acrylic microcapsules via suspension polymerization technique.

In this study, the production of the polymeric shell that creates the microcapsules is characterized by a process called chain reaction polymerization (according to polymerization mechanism) [19]. In this process, the polymeric chain is formed by consecutive linking of monomers at the reactive end of a growing chain. As a consequence, the formed polymer has the same atoms as the monomers in their repeating units [19].

In most of the cases, the monomers require an initiator to start the polymerization reaction. Upon a trigger, this initiator produces a free radical (reactive specie) that, added to a monomer, starts the formation of one polymer chain. As a result, this process can be designated as free radical polymerization. The main reactions of this polymerization mechanism take place in three sequential steps: initiation, propagation and termination, as schematically represented in Figure 3.4 [19,20]. The initiation step involves two reactions: the first one corresponding to the formation of an initiator radical ($R\cdot$) and a second one corresponding to the addition of the initiator radical to a monomer, creating a monomer radical. In propagation, the previous radical reacts with a single monomer molecule and grows through the successive additions of monomer. A radical is continually created during each monomer addition, which leads to for the formation of the macroradical ($M_{i+1}\cdot$). The propagation continues until a reaction terminate this process. This termination can occurs by combination of two radical producing a polymer molecule ($M_{(i+j)}$) and by disproportionation producing two distinct molecules ($M_i + M_j$) [19]. The specific mechanism for the polymerization of the selected acrylic monomers initiated by BPO is represented in Appendix A (Figure A.1).

(a) Initiation

$$I \xrightarrow{k_d} 2\,R\cdot$$

$$R\cdot + M \xrightarrow{k_i} M_1\cdot$$

(b) Propagation

$$M_i\cdot + M \xrightarrow{k_p} M_{i+1}\cdot$$

(c) Termination

$$M_i\cdot + M_j\cdot \xrightarrow{k_t} M_{(i+j)}$$

$$M_i\cdot + M_j\cdot \xrightarrow{k_t} M_i + M_j$$

Figure 3.4: Main reactions of free radical polymerization mechanism, where *I* represents the initiator, *R*· the free radical, *M* the monomers, *M*· the growing chains, $M_{i+1}\cdot$ the macroradical and $M_{(i+j)}$ and $M_i + M_j$ the polymer [19].

The free radical polymerization can be performed through different techniques, such as bulk, solution, emulsion and, the technique described here, the suspension polymerization. Nevertheless, only the heterogeneous methods, like emulsion and suspension polymerization, allow to produce microparticles and to encapsulate active compounds [3].

The aim of the study reported in this chapter is to establish a standard procedure to successfully prepare acrylic microcapsules containing octadecane, via suspension polymerization. For that, a sequence of preliminary tests were carried out changing some experimental parameters and compounds, such as the PCM/monomers mass ratio and the type of stabilizer. The prepared microcapsules were fully characterized and compared with two industrial samples.

3.2 EXPERIMENTAL

3.2.1 Materials

All monomers, methyl methacrylate (MMA), methacrylic acid (MAA) and *n*-butyl acrylate (BA), and all crosslinking agents, ethylene glycol dimethacrylate (EGDMA) and pentaerythritol tetraacrylate (PETRA) were purchased from Sigma-Aldrich. The core material, the octadecane (purity of 97 wt. % and melting onset temperature of about 27 ºC) was received from Devan Chemicals (Belgium). Benzoyl peroxide (75%, contains 25% water, BPO) was

supplied by ACROS. Finally, polyvinylpyrrolidone (Mw = 40 000 g/mol, PVP) and poly(vinyl alcohol) (Mw = 31000 – 50000 g/mol and degree of hydrolysis = 87-89 %, PVA) were purchased from Sigma-Aldrich. All the reagents were used as received.

3.2.2 Microencapsulation procedure

The process designed to microencapsulate octadecane was generically described in section 3.1 and schematized in Figure 3.3. In this section, the procedure followed for the preliminary trials and the corresponding experimental conditions are detailed. Table 3.1 summarizes the recipe, in molar and weight bases, used in the first experiment carried out to microencapsulate the octadecane (PCM-PVP2).

Table 3.1: Recipe for the preparation of acrylic microcapsules containing octadecane, experiment PCM-PVP2.

Experiment	**Monomers**			**Crosslinkers**		**Initiator**	**Stabilizer**	**Core material**
PCM-PVP 2	**MMA**	**BA**	**MAA**	**EGDMA**	**PETRA**	**BPO**	**PVP**	**Octadecane**
	(mol %)			(mol% related to monomers)		(mol% related to monomers)		
	94	5	1	2.5	1.5	0.5		
	(wt. %)			(wt.% related to monomers)		(wt.% related to monomers)	(wt.% in water)	PCM/monomers mass ratio
	93	6	1	5	5	1.2	1	2

Considering molar base, the monomers mixture was composed of 94 mol% of MMA, 5 mol% of BA and 1 mol% of MAA and crosslinkers composed of 2.5 mol% of EGDMA and 1.5 mol% of PETRA (percentages related to the monomers). The lower percentage of PETRA is due to the fact that EGDMA is a crosslinker with two double bonds (C=C) while PETRA is composed by four (as showed in Figure 3.2). Besides the former compounds, BPO was used as thermal initiator and PVP as emulsion stabilizer, as specified in Table 3.1.

This formulation was based on the study of Shan *et al.* [9], which highlighted the importance of the crosslinker addition [9], and on the series of studies of Sánchez-Silva *et al.* [5–8,18] that used BPO as initiator [5–8], PVP as stabilizer [5–8] and the monomers mixture MMA, BA and MAA [18].

Following the described formulation, the suspension polymerization reaction was carried out in a glass reactor (250 mL) equipped with mechanical stirrer, reflux condenser, nitrogen gas inlet tube and immersed in a thermostatic oil bath.

For the synthesis of microcapsules two different solutions were prepared (Figure 3.3). Solution (1) was prepared by mixing the monomers and the crosslinkers and stirring until complete homogenization. The initiator was added afterwards and the solution stirred again. This solution was heated up to 40 ºC and the melted octadecane was introduced. Finally, this mixture was stirred until complete homogenization. This solution was prepared using as base of 10 g of monomers mixture, respecting the proportions listed in Table 3.1.

Solution (2) was prepared by dissolving 1 g of PVP in water (100 mL) and heating until 40 ºC.

Solution (1) was added to Solution (2) drop wise and the mixture emulsified at 6000 rpm (Homogeneizer Polytron PT6000) during 10 minutes. The obtained emulsion was transferred to the reactor, previously heated at 40 ºC, under nitrogen flux and mechanical stirring (300 rpm). After 10 minutes, the temperature was raised up to 80 ºC and the reaction was carried out during 5.5 hours (including with heating process that took about 30 minutes), under nitrogen atmosphere and continuous stirring.

Then the microcapsules were further washed to remove the unreacted monomers, stabilizer and free octadecane. This washing process was carried out with water at 50 ºC and repeated three times. After each washing cycle, the sample was filtered under vacuum to separate microcapsules from water (using a filter paper with pore size of around 2-3 μm). The washed microcapsules were collected and stored as a wet cake (50 - 70% of solid content). A sample of wet cake was further dried in the oven at 40 ºC to remove the water, since some of the characterizing techniques required dry powder.

3.2.3 Characterization techniques

As mentioned before, in order to evaluate the microcapsules properties, the samples were thoroughly characterized regarding their morphology, size, chemical composition and thermal properties, using the following techniques:

Optical microscopy

In order to confirm the formation of microcapsules, after each experiment, the final suspension was visualized by optical microscopy using an optical microscope from Leica, model DM2000.

Scanning electron microscopy

The microcapsules morphology was assessed by scanning electron microscopy (SEM). For that, specimens of microcapsules were diluted using distilled water and placed onto carbon tape in appropriated support. The specimens were dried at room temperature and subjected to a sputtering treatment to deposit a gold nano layer. Micrographs were then obtained by using an electron beam voltage of 15 kV produced by a Tungsten filament with a Leica Cambridge S360 equipment.

Particle size distribution

Particle size distribution was measured by laser diffraction using a Malvern equipment - Mastersizer 2000s. The analyses were performed to specimens of microcapsules, previously dispersed into distilled water. The particle size distribution (calculated in volume) and the corresponding statistical mean values correspond to an average of at least three run measurements per aliquot, 2 up to 3 aliquots were used per specimen.

Fourier transform infrared spectroscopy

Fourier transform infrared (FT-IR) spectra were acquired in the range of 4000-550 cm^{-1} at room temperature, using a Jasco FT/IR-4200 spectrometer, equipped with a Golden Gate Single Reflection Diamond ATR. Data were collected with 4 cm^{-1} spectral resolution and 128 scans. Samples were previously dried in oven at 40 ºC.

Differential scanning calorimetry

Thermal behaviour was studied by differential scanning calorimetry (DSC), in a Netzsch DSC 200 F3 with a cooling unit. Samples were analysed in aluminium crucibles with closed lid. Three thermal cycles were programmed: first the temperature was cooled at 5 ºC/min from 20 ºC to -10 ºC; then it was heated at 5 ºC/min from -10 ºC to 50 ºC; finally, the sample was cooled at 5 ºC/min from 50 ºC to -10 ºC. Isothermals of 3 minutes before each cooling and heating cycle were introduced. Only the second and third cycle that corresponded to heating

and cooling process, respectively, were considered during the DSC curve analyses. Samples' specimens were previously dried in an oven at 40 ºC and a weighting range from 7 to 10 mg was used. DSC analysis was carried out in triplicate and results expressed as average ± standard deviation. The microcapsules PCM content was estimated according to Equation (3.1) [15]:

$$PCM\ content\ (\%) = \frac{\Delta H_{m,\mu caps\ PCM} + \Delta H_{c,\mu caps\ PCM}}{\Delta H_{m,PCM} + \Delta H_{c,PCM}} \times 100 \qquad (3.1)$$

where $\Delta H_{m,\mu capsPCM}$ and $\Delta H_{c,\mu capsPCM}$ are respectively the melting and crystallization enthalpies of microcapsules containing octadecane, and $\Delta H_{m,PCM}$ and $\Delta H_{c,PCM}$ are the melting and crystallization enthalpies of octadecane [15].

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was evaluated using a TA Instruments Q500 equipment, at heating rate of 10 ºC/min, in the range of 25 ºC to 600 ºC and using nitrogen purge flow rate of 100 mL/min. Samples' specimens were previously dried in oven at 40 ºC and a weighting range from 5 to 8 mg was used.

3.3 RESULTS AND DISCUSSION

3.3.1 Microencapsulation procedure: preliminary tests

As described in Table 3.1, a mixture of three monomers (MMA, BA and MAA) was employed in the presence of two crosslinkers (EGDMA and PETRA), to produce the acrylic shell and to encapsulate the octadecane.

Table 3.2 summarizes the preliminary tests highlighting the experimental variables that were modified: the type of stabilizer and the mass ratio of PCM/monomers. These experiments were carried out according to the procedure described in section 3.2.2. Initially, the tests were performed using PVP as stabilizer and a PCM/monomer mass ratio of 2 (PCM-PVP2). Subsequently, this ratio was reduced to unity (PCM-PVP1) and, finally, the stabilizer was replaced by PVA (PCM-PVA1). For comparison purposes and to study the copolymer properties, a blank experiment (B-PVA0) was carried out, following the same procedure as that of sample PCM-PVA1, but without adding octadecane.

Table 3.2: Effect of stabilizer and PCM/monomers mass ratio: preliminary tests.

Sample	Stabilizer	PCM/monomers mass ratio	Morphological characterization
PCM-PVP2	PVP	2	Large agglomerates
PCM-PVP1	PVP	1	Large particles and not individualized
PCM-PVA1	PVA	1	Individual and spherical microparticles
B-PVA0	PVA	0	Individual and spherical microparticles

After each experiment, the unwashed samples were firstly characterized regarding their morphology. Figure 3.5 presents the SEM micrographs corresponding to these samples, where the main observations are:

- Sample PCM-PVP2: it is clear that no individual microcapsules were obtained; instead, large agglomerates can be visualized (Figure 3.5 (a)). This was thought to be the result of a higher PCM/monomers mass ratio used (2), thus in the following experiment this ratio was reduced to half;

- Sample PCM-PVP1: although capsules could be identified, they were not individualized (Figure 3.5 (b)); so, it was decided to change the stabilizer, from PVP to PVA;

- Sample PCM-PVA1: the replacement of PVP by PVA, keeping all the rest unchanged, originated individual and spherical microcapsules, although with rough surface (Figure 3.5 (c)).

- Sample B-PVA0: this experiment was performed without octadecane and it resulted in spherical microcapsules with a smooth shell surface (Figure 3.5 (d)). However, since octadecane was not used, these particles cannot actually be considered "microcapsules", but "microparticles" composed of copolymer.

As a consequence of the results obtained in these initial tests, the PVP stabilizer was permanently replaced by PVA. For the formulation used, PVP was not able to perform its function as stabilizer, contrary to the PVA that originated individual microcapsules. However, as previously mentioned, PVP has been successfully used as stabilizer in acrylic microcapsules to encapsulate PCM, for example by Sanchez-Silva and co-workers [8], although in different conditions (namely with a different PCM). On the other hand, PVA has also been recently used as stabilizer, for example by Al-Shannaq *et al* [12] in the preparation of acrylic microcapsules containing PCM.

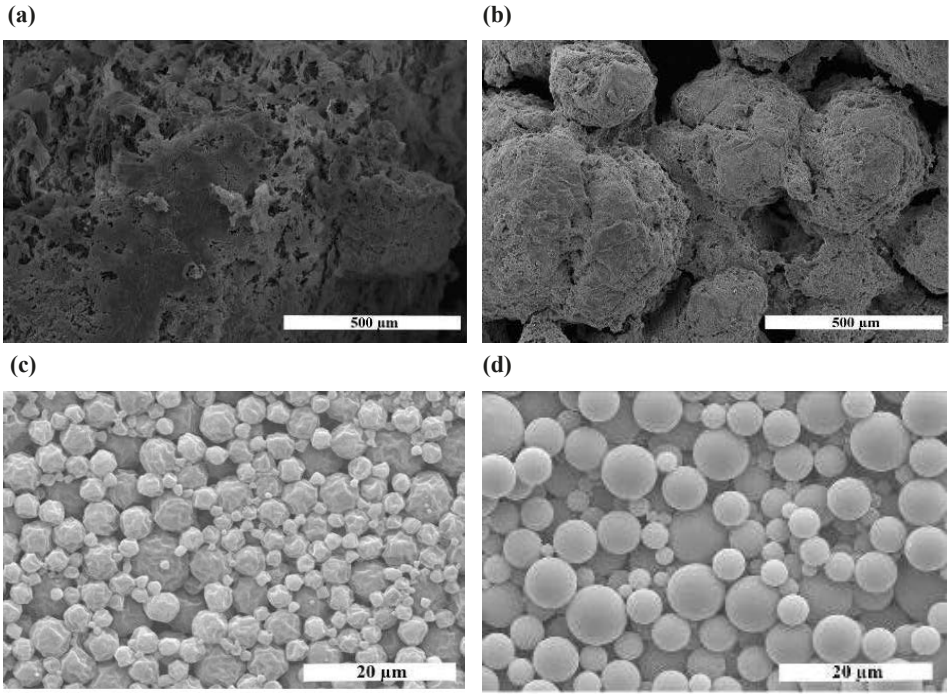

Figure 3.5: SEM micrographs of unwashed samples (a) PCM-PVP2 (magnification x100), (b) PCM-PVP1 (magnification x100), (c) PCM-PVA1 (magnification x2000) and (d) B-PVA0 (magnification x2000).

Given the favourable results of the sample PCM-PVA1, a comprehensive characterization of this sample was carried out, based on three aspects: morphological characterization (SEM and particle sizing); chemical characterization (FT-IR spectroscopy); and thermal performance and stability (DSC and TGA). These measurements were only performed in the washed sample (rather than in the unwashed sample). The idea was to remove any free octadecane and unreacted monomers, but also to investigate if the washing procedure would damage the microcapsules. Additionally, the sample without octadecane (B-PVA0) was also characterized.

a) Morphological characterization

As demonstrated in Figure 3.6 (a), the microcapsules of sample PCM-PVA1 were well preserved after washings. Moreover, the SEM high magnification micrographs also reveal that the microcapsules are composed of a core/shell structure (Figure 3.6 (b)) and that their shell exhibits a rough and wrinkled surface (Figure 3.6 (c)).

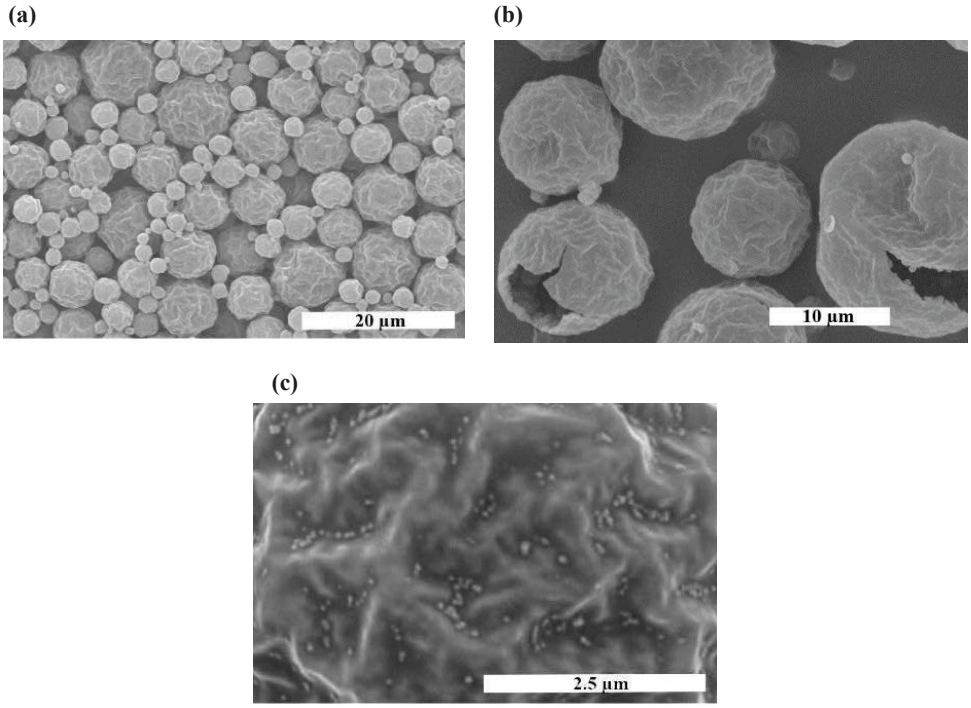

Figure 3.6: SEM micrographs of sample PCM-PVA1 (a) washed sample (magnification x2000), (b) broken microcapsules (sample previously crushed) (magnification x3000) and (c) detail of the shell (magnification x20000).

The mechanism of microcapsules formation has been described by various authors and it is related not only to the polymerization technique, but also to the shell composition and to the core compound properties [9,21]. In suspension polymerization, the shell formation starts at the water-oil droplet interface. As the polymerization reaction proceeds, the monomers are consumed and transferred from the oil phase to the interface, and thus increasing the shell thickness. This mechanism occurs towards the inner side of the microcapsule [21].

Furthermore, the formation of the core/shell structure, clearly visible in Figure 3.6 (b)), was explained according to both thermodynamic and kinetic perspectives by Sánchez-Silva *et al.* [7,8]. According to these authors, the core/shell morphology is thermodynamically favoured when the polarity of the polymer and the core material are distinct. The driving force between them creates a phase separation and produces this core/shell structure [7,8,4]. However, this is not the only factor that determines this structure. For instance, when the polymeric chains do not have time to diffuse to the interface, due to high polymerization rate of monomers and fast polymer formation, this shell structure will not be formed [8].

Sánchez-Silva *et al.* investigated extensively the processes responsible for the core/shell structure formation, using different combinations of acrylic monomers [8]. Nonetheless, they did

not prepare acrylic microcapsules with a well-defined core/shell structure (like sample PCM-PVA1), producing microcapsules with an incomplete phase rearrangement [8]. Later, this structure was successfully obtained for acrylic microcapsules in a series of studies performed by Qiu and co-workers [11,14–16,22,23].

As previously discussed, the microcapsules of sample PCM-PVA1 exhibit a well-defined core/shell structure that, according to the above discussion, justify the microencapsulation procedure adopted in this work. In fact, this structure could have been favoured by the following factors:

- addition of MAA to the monomers MMA and BA: MAA increases the polarity of monomers mixture, thus enhancing the polarity difference between this mixture and the octadecane and helping the phase separation and the copolymer migration to the droplet interface;

- incorporation of BA on the shell composition: this monomer, due to its low T_g, helps the mobility of the polymeric chains that diffuse to the droplet interface;

- creation of the progressive heating during the initial stage of polymerization reaction. Indeed, the emulsion was transferred to the reactor at 40 ºC and afterwards the reaction temperature was increased to 80 ºC. This heating process prevents the drastic increase of reaction temperature that, probably, could avoid a high polymerization rate and favour the core/shell structure formation.

Additionally, the roughness of the microcapsules shell surface (Figure 3.6 (c)) is probably associated to the density variations that occur during their formation. When the monomers react to form the copolymer shell, an increase in density occurs, since the copolymer naturally presents higher density than that of individual monomers [21]. This increase in density and the corresponding volume reduction seems to be responsible for the shell shrinkage and for the production of the noticed rough surface. However, it should be pointed out that density variation is not exclusive of the polymer: the octadecane also changes its density with temperature (its value for solid state is about 0.81 g/cm^3 and for melted state at 80 ºC is 0.69 g/cm^3 [21]). Consequently, after the reaction, when the microcapsules are cooled down from 80 ºC to room temperature, the octadecane volume is expected to reduce the octadecane volume could also be reduced. Many authors describe the combination of these events of density variation as the generation of reserved expansion space in the PCM microencapsulation [9,21,11].

In order to measure the particle size distribution, samples PCM-PVA1 and B-PVA0 (after the washing process) were analysed by laser diffraction. In the literature, it has been mentioned that to incorporate the microcapsules on textile fibres the most convenient particles size should be in the range from 0.5 to 100 µm, in order to avoid negative changes in the substrate properties and thus preserve its original features [24]. Despite this wide size range, in the present work, a mean particle size of about between 5 µm and 15 µm was established as goal, taking as reference an industrial sample used by Devan Chemicals and herein considered a benchmark for comparison (samples described in Section 3.3.3).

The size distribution curves of these samples, in volume basis, are illustrated in Figure 3.7 and the respective values of statistical diameters, as volume mean diameter ($D_{4,3}$) and median diameter D_{50}, together with percentile diameters D_{10} and D_{90}, are listed in Table 3.3. The diameters D_{10}, D_{50} and D_{90} represent the diameter that correspond, respectively, to a percentile of 10^{th}, 50^{th} and 90^{th} of cumulative undersize volume distribution.

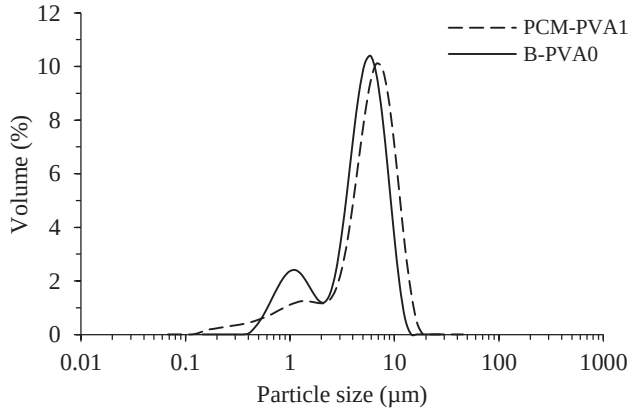

Figure 3.7: Particle size distribution of samples PCM-PVA1 and B-PVA0.

Figure 3.7 shows that a bimodal distribution was obtained for both samples (with one peak much more intense than the other). This result is consistent with the SEM pictures, in which large and small particles are observed. The presence of small microparticles could be ascribed to the process of secondary nucleation, as defined by other authors [7]. This process occurs when a portion of monomers diffuses to the aqueous phase, forming small polymeric microparticles that probably do not contain any core material. This phenomena is favoured by the monomers hydrophilicity as well as by the absence of inhibitors in the aqueous solution [7]. In present procedure, this process could be favoured by the use of MMA as the principal monomer, due to its partial solubility in water (16 g/L at 20 ºC [25]), and also by the absence of inhibitor.

Table 3.3: Statistical diameters of microcapsules size distributions (in volume) presented in Figure 3.7 (values of mean diameter ($D_{4,3}$), D_{10}, D_{50} and D_{90}).

Sample	Mean diameter, $D_{4,3}$ (μm)	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)
PCM-PVA1	6.6	1.4	6.4	11.3
B-PVA0	5.3	1.2	5.3	9.1

As listed in Table 3.3 the ratio between D_{10} and D_{90} is around 10, with sizes that spread from about 1 μm to about 11 μm and with mean diameters around 5 – 6 μm. Additionally, this table shows that size distribution of microcapsules containing octadecane is slightly larger than those of the copolymer microparticles inferring a volume increase through core entrapment of sample PCM-PVA1. In general, besides the presence of the core material, the particle size can be influenced by different parameters, namely: the type and concentration of monomers in dispersed phase; the type and concentration of stabilizer in continuous phase; as well as the stirring conditions for the emulsification and polymerization process [1,8].

b) Chemical characterization

The characterization of the most promising sample obtained in the preliminary tests (PCM-PVA1) also included FT-IR analysis. The analysis was performed not only for this sample but also for all the monomers, for the octadecane and for the microparticles without octadecane (B-PVA0). The obtained spectra are represented in Figure 3.8.

The octadecane is an alkane mostly constituted by methylene groups. Thus, for its spectrum, it is possible to identify two strong peaks at 2911 cm^{-1} and 2847 cm^{-1} that are caused by asymmetric and symmetric C-H stretching vibration of CH_2, respectively. In addition to these two strong peaks, two other peaks must be emphasized: one at 1470 cm^{-1}, attributed to the bending vibration of methylene group, and the other at 716 cm^{-1}, ascribed to the alkane long chain [26].

MMA and BA are esters characterized by one strong peak from C=O stretching vibration, which appears at 1720 cm^{-1} and 1723 cm^{-1} for MMA and BA, respectively. The peaks at 1157 cm^{-1} from MMA and at 1186 cm^{-1} from BA spectra are assigned to the C-O-C stretching vibration of esters. MAA is a carboxylic acid that, contrarily to MMA and BA, presents a broad band around 2930 cm^{-1} ascribed to the O-H stretching vibration. Nonetheless, comparing the

peak from C=O stretching vibration with that of the ester monomers only a small deviation (1688 cm^{-1}) is observed. All these monomers have in common the presence of a double bond C=C, the characteristic peak from its stretching vibration appears around 1635 cm^{-1} [26].

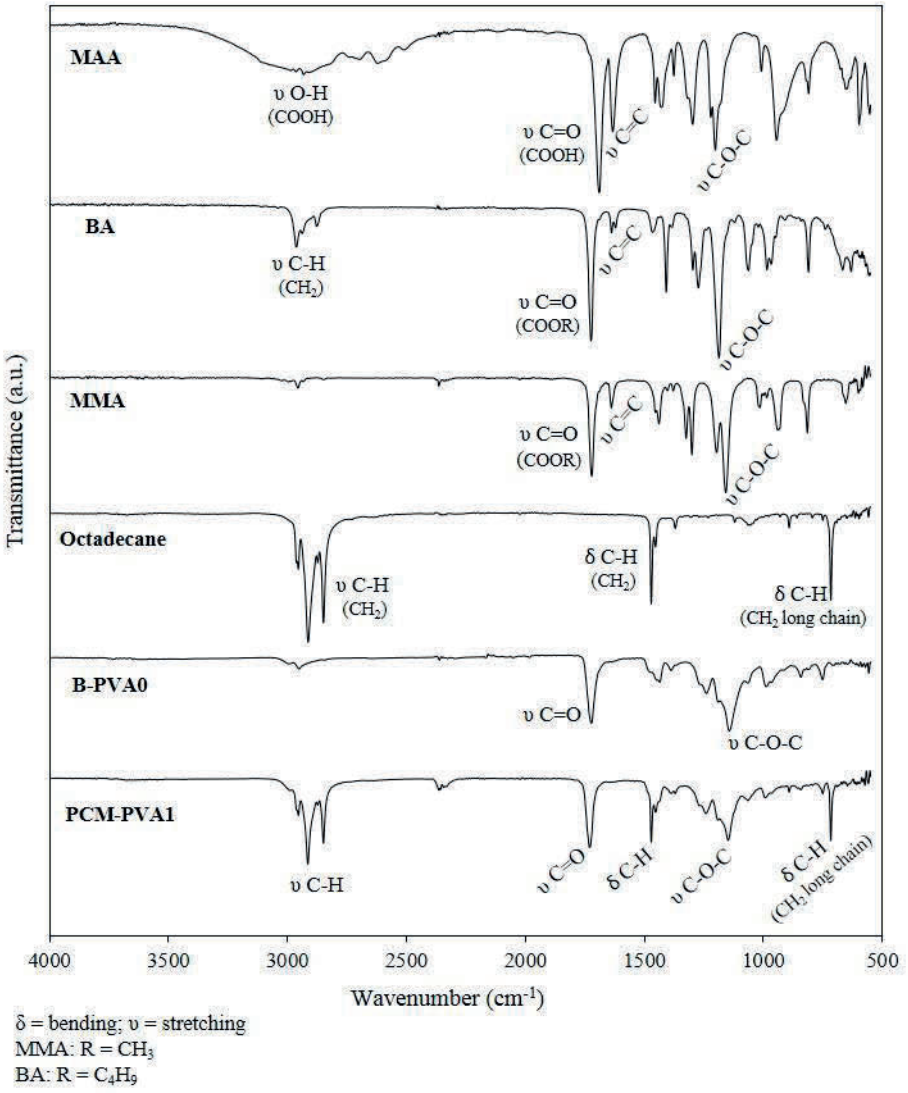

Figure 3.8: FT-IR spectra of monomers (MAA, BA and MMA), octadecane and samples B-PVA0 and PCM-PVA1.

During the polymerization reaction, the double bond C=C presents in the monomers becomes a simple bond to produce the polymer. The absence of this double bond is the change in the chemical structure of all three monomers that allows their differentiation from the polymeric chain. As expected, in the spectra depicted for samples B-PVA0 and PCM-PVA1 this peak does not appear. However, it is not possible to conclude that all the monomers reacted, because the analysed specimens were previously washed and dried and the unreacted monomers could hence be removed.

When the spectrum of microcapsules PCM-PVA1 was compared with those of the monomers and octadecane, it was found that all the main peaks were present, excluding that from the double bond and that from the hydroxyl group from MAA. The absence of the latter is most likely because in the monomers mixture only 1 wt.% of MAA was used.

In conclusion, FT-IR spectroscopy revealed the presence of ester and methylene groups in the sample PCM-PVA1, confirming the existence of an acrylic shell and of octadecane in the produced microcapsules.

c) Thermal characterization

The thermal characterization of microcapsules allows to determine their values of phase change enthalpies and their values of PCM content (see equation 3.1), both quantified by DSC. Moreover, the microcapsules thermal stability through mass degradation upon heat was determined by TGA. In fact, besides the enthalpy capacity of the microcapsules, their stability is also very important because the textile substrates are submitted to high temperatures (around 100-140 ºC) during a few minutes to finalize the incorporation of the microcapsules. Therefore, the estimation of the thermal degradation profile is essential to guarantee the microcapsules are not damaged during this incorporation process.

Figure 3.9 exhibits DSC curves for the samples PCM-PVA1 and B-PVA0 together with a sample of octadecane subject to heating and cooling processes. Although the analyses were performed in triplicate, only one curve is presented in the graph to facilitate comparison. Nonetheless, for each sample the obtained curves profile was always identical. The reproducibility of results is reflected in the values described in Table 3.4, namely in the melting and crystallization enthalpies (ΔH_m and ΔH_c, respectively) and respective onset temperature events (T_{om} and T_{oc}), since they are expressed as average ± standard deviation. In this table, for sample PCM-PVA1, the value of PCM content (calculated according equation (3.1)) is also registered.

Despite the absence of octadecane in sample B-PVA0, these microparticles were also analysed by DSC. The non-appearance of thermal events (see Figure 3.9), naturally means that the thermal events of microcapsules PCM-PVA1 are exclusively resultant from octadecane.

As Figure 3.9 shows, both octadecane and its microencapsulated counterpart exhibited two curves, one endothermic and the other exothermic, respectively for the heating (downwards) and cooling (upwards) processes.

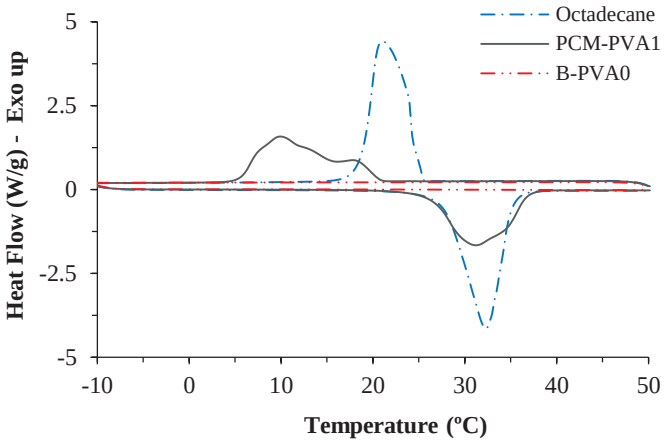

Figure 3.9: DSC curves of octadecane and samples PCM-PVA1 and B-PVA0.

As expressed in Table 3.4, the melting and crystallization onset temperatures (T_{om} and T_{oc}) of octadecane are, respectively, 26.7 ºC and 25.0 ºC at 5 °C/min heating/cooling rate. Comparing these values with those of sample PCM-PVA1, the T_{om} for the melting event are similar for both compounds, while T_{oc} for the crystallization event is considerably lower for the microcapsules (with a value of around 22 ºC). This effect is named supercooling and it is identified by a significant lowering of the crystallization temperature of the core material in the cooling process [27,28]. The microencapsulation of n-alkanes are known for the presence of this effect, being an obstacle for their application as thermal energy storage system [27]. There are many efforts searching for alternatives to avoid this phenomenon, which can include the addition of nucleating agents to different PCMs [27,29]. However, in the present study, this effect was not considered a main constraint and, thus, alternatives to overcome this supercooling effect were not explored.

Table 3.4: Thermal performance (average ± standard deviation) of octadecane and of sample PCM-PVA1 (ΔH_m and ΔH_c: melting and crystallization enthalpies; T_{om} and T_{oc}: melting and crystallization onset temperatures; PCM content was calculated using equation (3.1)).

Sample	**T_{om}** (ºC)	**ΔH_m** (J/g)	**T_{oc}** (ºC)	**ΔH_c** (J/g)	**PCM content** (wt.%)
Octadecane	26.7±0.1	252.3±2.8	25.0±0.1	252.1±3.0	--
PCM-PVA1	26.4±0.2	163.1±9.8	21.7±0.7	165.7±8.7	65.2

Regarding the enthalpies, the values are around 252 J/g for octadecane whereas those of sample PCM-PVA1 are considerably lower (around 163 J/g). This was expected since the microcapsules are composed not only of octadecane, but also of polymeric shell (PCM content is 65.2 wt.%). These values of phase change enthalpies, although satisfactory, need to be improved (trying to reach values around 190 J/g, as the industrial microcapsules presented later in Section 3.3.3).

Thermal stability was evaluated using TGA, for PCM-PVA1 microcapsules as well as for B-PVA0 copolymer microparticles and pure octadecane. The curves of weight loss as a function of temperature are represented in Figure 3.10. Since the global profile of thermal degradation allows to distinguish each stage of weight loss, their derivative curves were not included. Table 3.5 summarizes the most relevant data extracted from the thermoanalytical curves: temperatures corresponding to 5% and 10% of weight loss ($T_{5\%}$ and $T_{10\%}$), the extrapolated onset temperature (T_{on}), which indicates the extrapolated temperature at which the weight loss of each stage of degradation starts, and the resultant weight loss percentage. In general, the thermal resistant temperature of a sample can be defined as initial 5 wt.% weight-losing temperature in TG curve [9,16]. Thus, the value of $T_{5\%}$ was one of the main parameters selected to compare the thermal stability of several samples.

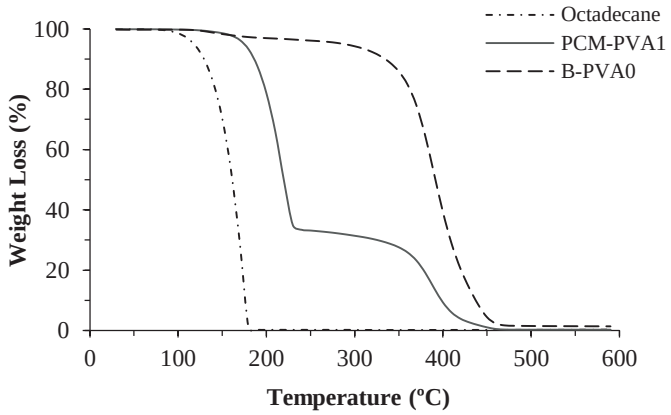

Figure 3.10: TG curves of octadecane and samples PCM-PVA1 and B-PVA0.

The curve of pure octadecane shows that its weight loss occurs in one stage, with T_{on1} of 145 ºC. This profile was originated by octadecane evaporation before flash point (166 ºC) and boiling point (308 ºC) [9,16,30]. As Figure 3.10 shows, the degradation the sample B-PVA0, which was prepared without adding octadecane, also occurs in practically one stage. Like that of octadecane, but at higher temperature (T_{on1} of 357 ºC). However, a small weight loss (around

3wt.%) was observed at the beginning (T_{on1} of 118 ºC), which could be caused by adsorbed water and/or unreacted monomers evaporation.

Regarding sample PCM-PVA1, its thermogram (Figure 3.10) reveals two distinct stages of microcapsules degradation: the first one is originated by the weight loss of octadecane, that diffuses out through the shell membrane and evaporates; and the second one created by the degradation of the polymeric shell [31]. As listed in Table 3.5 this sample presents a T_{on2} value very similar to the temperature obtained for copolymer microparticles (B-PVA0), around 358ºC, suggesting that the presence of octadecane in the microcapsules does not significantly change the thermal degradation of their polymeric shell. On the contrary, higher values were found for T_{on1} of PCM-PVA1 microcapsules compared with octadecane (191 ºC versus 145 ºC) and the same tendency was observed for $T_{5\%}$ and $T_{10\%}$. This difference can be caused by the resistance and protection that the polymeric shell promotes for the octadecane evaporation [31].

Table 3.5: Thermogravimetric data of octadecane and of samples PCM-PVA1 and B-PVA0 ($T_{5\%}$ and $T_{10\%}$: temperatures corresponding to 5% and 10% of weight loss; T_{on1} and T_{on2}: extrapolated onset temperatures of the first and second degradation stage; Weight loss: weight loss (%) in each degradation stage).

Sample	**$T_{5\%}$** (ºC)	**$T_{10\%}$** (ºC)	**1st stage**		**2nd stage**	
			T_{on1} (ºC)	**Weight Loss** (%)	**T_{on2}** (ºC)	**Weight Loss** (%)
Octadecane	117.8	129.4	145.0	99.8	--	--
PCM-PVA1	174.8	186.2	190.8	66.5	358.5	33.1
B-PVA0	285.9	334.5	118.5	3.1	357.4	95.0

These results confirm that octadecane was successfully encapsulated using the suspension polymerization technique and they also demonstrate that PCM-PVA1 microcapsules are stable below $T_{5\%}$ of 170 ºC, thus allowing their incorporation on textile substrates without undergoing thermal degradation.

Furthermore, these preliminary tests allow establishing an experimental procedure to successfully encapsulate octadecane in microcapsules that seems to possess adequate properties for the incorporation onto fibres' surface of textile substrates. In the next section, attempts to increase the PCM amount in order to improve the microcapsules thermal performance are explored.

3.3.2 Influence of PCM/monomers mass ratio

As previously described, the final goal of this work is the incorporation of microcapsules containing octadecane in textile substrates to produce thermo-regulating materials. So, the amount of core that can be encapsulated is of crucial importance. It is well known that a greater amount of encapsulated octadecane leads to microcapsules with better thermal capacity and, consequently, textiles with greater thermal comfort.

In line with the results achieved for PCM-PVA1, tests were performed trying to determine the maximum quantity of octadecane that can be encapsulated using the same formulation as before. These experiments were carried out according to the procedure of microencapsulation described in section 3.2.2, modifying only the PCM/monomers mass ratio, from 1 to 2.5 as listed in Table 3.6. The obtained microcapsules were subsequently characterized before and after the washing process. The success or failure of the experiments (demonstrated by the obtaining or not of individual microcapsules) was also registered in this table. The achieved results for sample PCM-PVA1 are used for comparison.

Table 3.6: Effect of PCM/monomers mass ratio on microcapsules production (unwashed and washed samples).

Experiment	PCM/monomers mass ratio	Unwashed sample	Washed sample
		Presence of individual microcapsules	
PCM-PVA1 *	1.0	Yes	Yes
PCM-PVA1.5	1.5	Yes	Yes
PCM-PVA2	2.0	Yes	Yes
PCM-PVA2.5	2.5	No	No

***** Sample previously presented in section 3.3.1.

a) Morphological characterization

The micrographs of SEM presented in Figure 3.11 reveal the presence of microcapsules in all samples prior to washing, though with a relative broad range of size and different surface structure. When the PCM/monomers mass ratio reached 2.5 (PCM-PVA2.5), the obtained microcapsules were no longer well individualized and their surface appears to be more smooth (Figure 3.11 (d)).

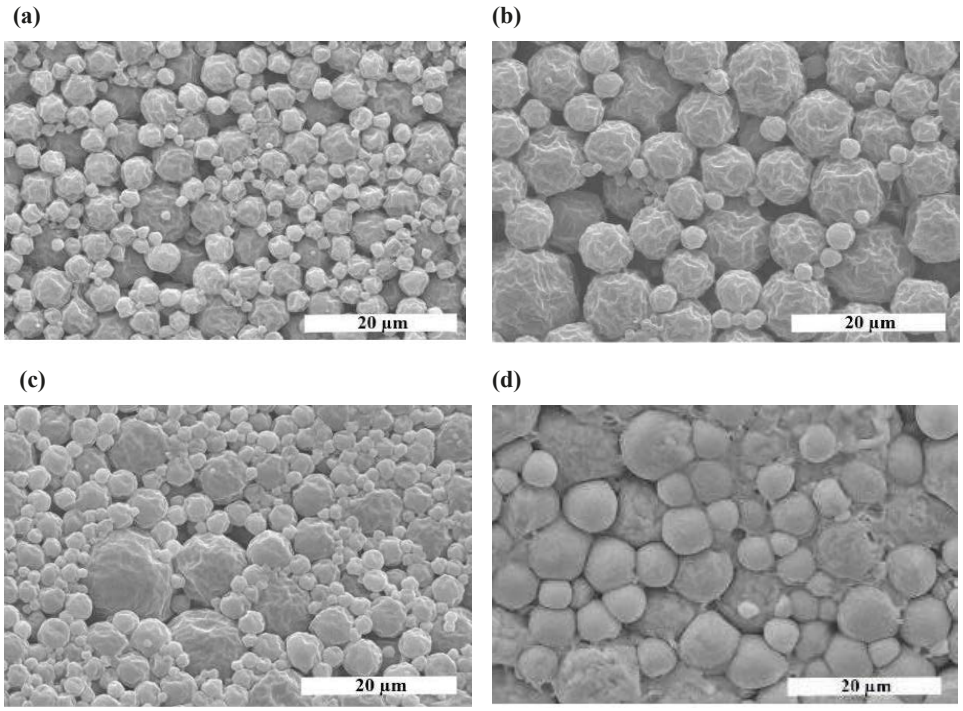

Figure 3.11: Influence of the PCM/monomers mass ratio on microcapsules morphological characteristics. SEM micrographs of unwashed samples: (a) PCM-PVA1 - mass ratio of 1; (b) PCM-PVA1.5 - mass ratio of 1.5, (c) PCM-PVA2 - mass ratio of 2 and (d) PCM-PVA2.5 - mass ratio of 2.5 (magnification x2000). Samples PCM-PVA1 is presented for comparison.

The samples were then washed and further analysed by SEM. As illustrated in Figure 3.12, all the microcapsules preserved their original morphology, except those of sample PCM-PVA2.5 that were damaged. For the latter sample, many shell fragments and free octadecane (which is identified by the charge effect visualized during the SEM analysis) were observed. This result, not observed in Figure 3.11 (d), is probably due to the microcapsules breakage, caused by the vacuum filtration carried out during the washing process. These results revealed that for this core content, the formed acrylic shell is fragile and unable to successfully cover the octadecane. The mass ratio of PCM/monomers should not go beyond 2 to produce individual microcapsules and resistant to the washing process.

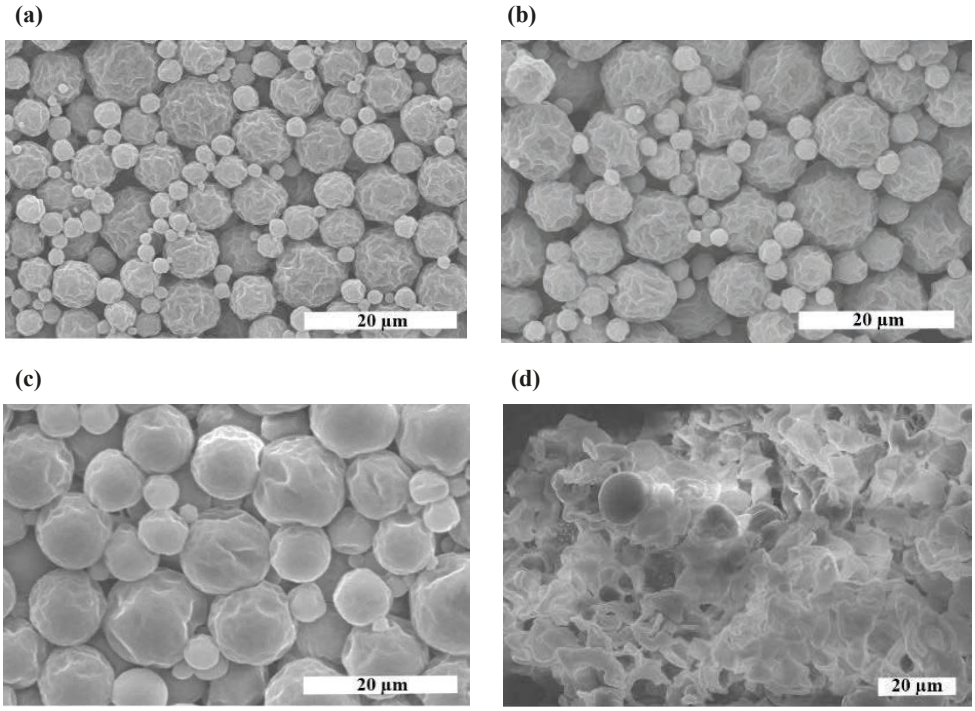

Figure 3.12: Influence of the PCM/monomers mass ratio on microcapsules morphological characteristics. SEM micrographs of washed sample : (a) PCM-PVA1 - mass ratio of 1; (b) PCM-PVA1.5 - mass ratio of 1.5, (c) PCM-PVA2 - mass ratio of 2 (magnification x2000) and (d) PCM-PVA2.5 - mass ratio of 2.5) (magnification x1000). Samples PCM-PVA1 is presented for comparison.

The subsequent characterization tests were only performed for the washed microcapsules. In order to study the effect of increasing the PCM/monomer ratio on particle size, the samples were analysed by laser diffraction, being the results summarized in Figure 3.13 and the corresponding diameter values listed in Table 3.7. The sample PCM-PVA2.5 was not evaluated since, as mentioned, most of their microcapsules were destroyed during the washing procedure.

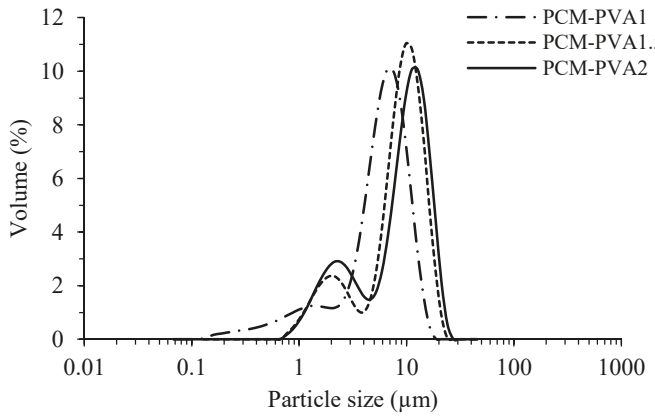

Figure 3.13: Influence of PCM/monomers mass ratio on microcapsules particle size distribution: PCM-PVA1 - mass ratio of 1; PCM-PVA1.5 - mass ratio of 1.5 and PCM-PVA2 - mass ratio of 2.

Once again, the particle size distribution curves show a bimodal distribution (with one peak much more relevant than the other) in agreement with the results observed by SEM. The appearance of the smaller peak is, as previously explained for sample PCM-PVA1, the result of the secondary nucleation process [7].

Table 3.7: Statistical diameters of microcapsules size distributions (in volume) presented in Figure 3.13 (values of mean diameter ($D_{4,3}$), D_{10}, D_{50} and D_{90}).

Sample	Mean diameter, $D_{4,3}$ (µm)	D_{10} (µm)	D_{50} (µm)	D_{90} (µm)
PCM-PVA1	6.6	1.4	6.4	11.3
PCM-PVA1.5	9.4	2.1	9.5	15.9
PCM-PVA2	10.0	2.1	10.2	17.7

The main conclusion that can be withdrawn from these results is the fact that the particle size increases with the rise of the amount of used octadecane. This trend could be induced by the increase in the viscosity of the dispersed phase due to the higher quantity of octadecane, since it is the component with the highest value of viscosity (the viscosity of octadecane is 3.1mPa.s at 40 ºC and that of MMA is 0.6 mPa.s). The presence of a dispersed phase with higher viscosity could originate larger droplets during the emulsification process and, consequently, larger microcapsules [8].

b) Thermal characterization

The DSC data obtained for all samples were also plotted together with those of sample PCM-PVA1 in Figure 3.14, being the relevant data summarized in Table 3.8.

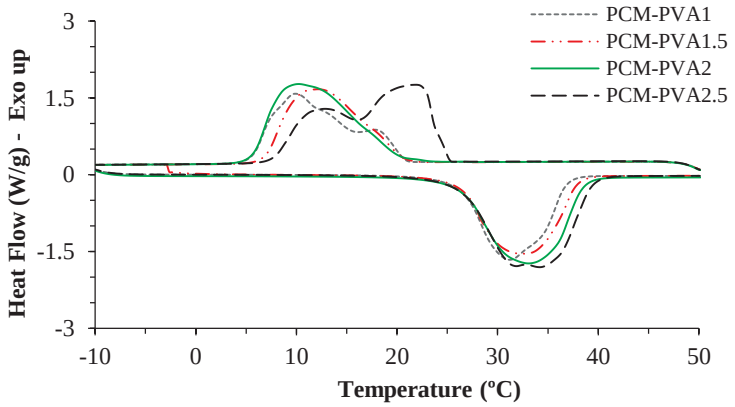

Figure 3.14: Influence of the PCM/monomers mass ratio on microcapsules thermal performance. DSC curves of samples: PCM-PVA1 - mass ratio of 1; PCM-PVA1.5 - mass ratio of 1.5; PCM-PVA2 - mass ratio of 2; and PCM-PVA2.5 - mass ratio of 2.5.

All the tested microcapsules have shown a typical curve profile with two peaks: one endothermic and another exothermic. This profile was only different for sample with the largest octadecane quantity, PCM-PVA2.5. For this sample, the cooling process seems to form two distinct peaks, being one in the temperature range of the octadecane (see Figure 3.9). This result suggest the existence of free octadecane in the analysed sample, as detected by SEM (Figure 3.12).

All the samples, where the octadecane was successfully encapsulated (except PCM.PVA2.5), exhibited values of T_{oc} lower than that of pure octadecane, as shown in Table 3.8, creating the supercooling effect [27,28] (previously discussed for sample PCM-PVA1). The variation of PCM/monomers mass ratio did not have a significant effect on T_{om} and T_{oc}, their values were approximately 27 ºC and 22 ºC, respectively, regardless the PCM content.

Table 3.8: Influence of the PCM/monomers mass ratio on microcapsules thermal performance (average ± standard deviation) (ΔH_m and ΔH_c: melting and crystallization enthalpies; T_{om} and T_{oc}: melting and crystallization onset temperatures; PCM content was calculated using equation (3.1)).

Sample	**T_{om}** (ºC)	**ΔH_m** (J/g)	**T_{oc}** (ºC)	**ΔH_c** (J/g)	**PCM content** (wt.%)
PCM-PVA1	26.4±0.2	163.1±9.8	21.7±0.7	165.7±8.7	65.2
PCM-PVA1.5	26.7±0.2	173.8±3.9	21.9±0.8	175.9±4.9	69.3
PCM-PVA2	26.5±0.3	193.9±3.3	21.5±0.1	196.1±2.3	77.3
PCM-PVA2.5	26.7±0.5	234.2±3.5	25.3±0.1	237.6±2.1	93.5

As expected, the thermal performance of the microcapsules improved with the increase of the PCM/monomers mass ratio. In fact, ΔH_m and ΔH_c values increased with this ratio, which means that the PCM content in the microcapsules actually increased (as last column of Table 3.8 reveals). The highest value found for sample PCM-PVA2.5 (234 J/g of ΔH_m), close to that of octadecane (252 J/g of ΔH_m, see Table 3.4), was already explained by the non-encapsulated octadecane due to the use of an apparently excessive amount of octadecane.

For sample PCM-PVA2 a PCM content of 77.3 wt.% was achieved. This result seems to be very promising since it is similar to the highest values of PCM content described in the literature for the octadecane encapsulation in acrylic microcapsules. Values between 77 - 79wt.% of PCM content were published by Qiu *et al.* [14] for microcapsules based on MMA and BMA [14].

The effect of increasing the octadecane amount on thermal stability of the various samples is presented in the thermoanalytical curves of Figure 3.15. In Table 3.9 the TG data determined from the analysis of these curves are summarized.

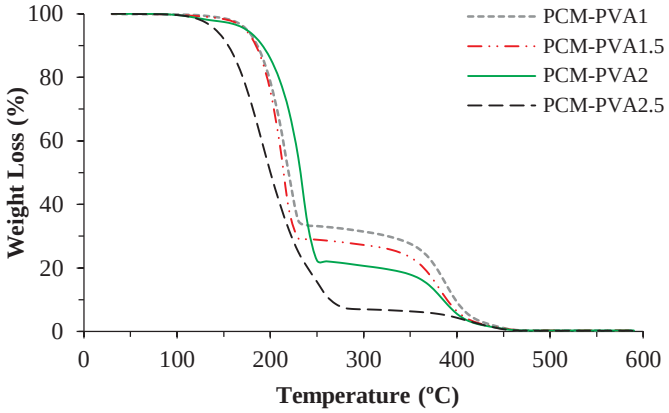

Figure 3.15: Influence of the PCM/monomers mass ratio on microcapsules thermal stability. TG curves of samples: PCM-PVA1 - mass ratio of 1; PCM-PVA1.5 - mass ratio of 1.5; PCM-PVA2 - mass ratio of 2; PCM-PVA2.5 - mass ratio of 2.5.

As Figure 3.15 illustrates, the microcapsules with increasing amounts of octadecane degraded in two stages: one caused by the weight loss of octadecane and the other resultant from the degradation of the polymeric shell. As previously discussed for sample PCM-PVA1, the increase of T_{on1} and $T_{5\%}$ of microcapsules in comparison with pure octadecane is originated by the resistance that the polymeric shell created to the octadecane evaporation [31]. Moreover, as listed in Table 3.9, all produced microcapsules present $T_{5\%}$ values around 170 ºC, except the sample PCM-PVA2.5. This suggest that, for PCM/monomers mass ratios less than 2, the shell creates an identical protection against the octadecane evaporation, regardless the encapsulated octadecane quantity. As for sample PCM-PVA2.5, $T_{5\%}$ was found to be much lower (141ºC), closer to that of octadecane ($T_{5\%}$ of 118 ºC, see Table 3.5), certainly due to the presence of broken microcapsules and non-encapsulated octadecane. This fact emphasizes that the main responsible for the microcapsules thermal stability (reflected on $T_{5\%}$ values) is their polymeric shell.

Regarding the values of T_{on2}, all the samples presented values slightly above 350 ºC with low variation (see Table 3.9). This suggests that, even when the PCM content was increased, the thermal degradation of the copolymer remains invariable.

Table 3.9: Influence of the PCM/monomers mass ratio on microcapsules thermogravimetric data ($T_{5\%}$ and $T_{10\%}$: temperatures corresponding to 5% and 10% of weight loss; T_{on1} and T_{on2}: extrapolated onset temperatures of the first and second degradation stage; Weight loss: weight loss (%) in each degradation stage).

Sample	$T_{5\%}$	$T_{10\%}$	1st stage		2nd stage	
			T_{on1}	Weight Loss	T_{on2}	Weight Loss
	(ºC)	(ºC)	(ºC)	(%)	(ºC)	(%)
PCM-PVA1	174.8	186.2	190.8	66.5	358.5	33.1
PCM-PVA1.5	173.1	184.6	191.0	70.8	351.7	28.9
PCM-PVA2	173.7	191.5	209.8	77.9	357.8	21.8
PCM-PVA2.5	141.0	154.9	153.6	93.0	373.3	6.8

The results of Table 3.9 also reveal that the percentage of weight loss in the first stage increases with the amount of octadecane. As this stage is mainly caused by the weight loss of this component, these results seem to indicate that the addition of more octadecane lead indeed to a larger amount of encapsulated material. These findings are in full agreement with those obtained by DSC.

Finally, it is interesting to compare the percentage of weight loss in this first stage (determined by TGA) with the PCM content calculated from DSC data. For instance, for PCM-PVA2, the first weight loss determined by TGA is 77.9 % (Table 3.9) and the corresponding value of PCM content determined by DSC is 77.3 % (Table 3.8). This full concordance confirms that the weight loss in the first degradation stage corresponds really to the octadecane degradation/evaporation and it should not include the degradation of the shell.

The TGA revealed to be a suitable tool for the characterization of microcapsules containing octadecane, allowing to extract very valuable information. Actually, TGA data has confirmed that the octadecane was successfully encapsulated (except for sample PCM-PVA2.5) and that the microcapsules with the highest amount of encapsulated octadecane (PCM-PVA2) were stable until $T_{5\%}$ of 170 ºC.

The results obtained from the previous morphological and thermal analyses demonstrates that the highest amount of octadecane, that can be used to successfully prepare microcapsules through the implemented procedure, corresponds to the PCM/monomers mass ratio of 2 (sample PCM-PVA2). DSC results show that these microcapsules present a PCM content around 77 wt.% and a ΔH_m value of 194 J/g, whereas the TGA analysis shows that the microcapsules can be incorporated on textile substrates without being degraded by the applied thermal treatment (temperature around 100 – 140 ºC).

3.3.3 Comparison with industrial microcapsules

Finally, and for comparison purposes, two samples of microcapsules available from Devan Chemicals were fully characterized. The selected microcapsules were designated as Wc-PCM28 and Sl-PCM28. These samples are both composed of a melamine-formaldehyde polymeric shell and containing a PCM with a melting temperature peak of around 28 ºC (equivalent to the octadecane used as core material in the present work).

The results obtained from their characterization were compared with those acquired for the acrylic microcapsules containing octadecane presented in the previous study, particularly with sample PCM-PVA2.

a) Morphological characterization

SEM micrographs of these samples are presented in Figure 3.16. Although, they are constituted of individual and spherical particles, samples Wc-PCM28 and Sl-PCM28 exhibit a much smoother shell than sample PCM-PVA2.

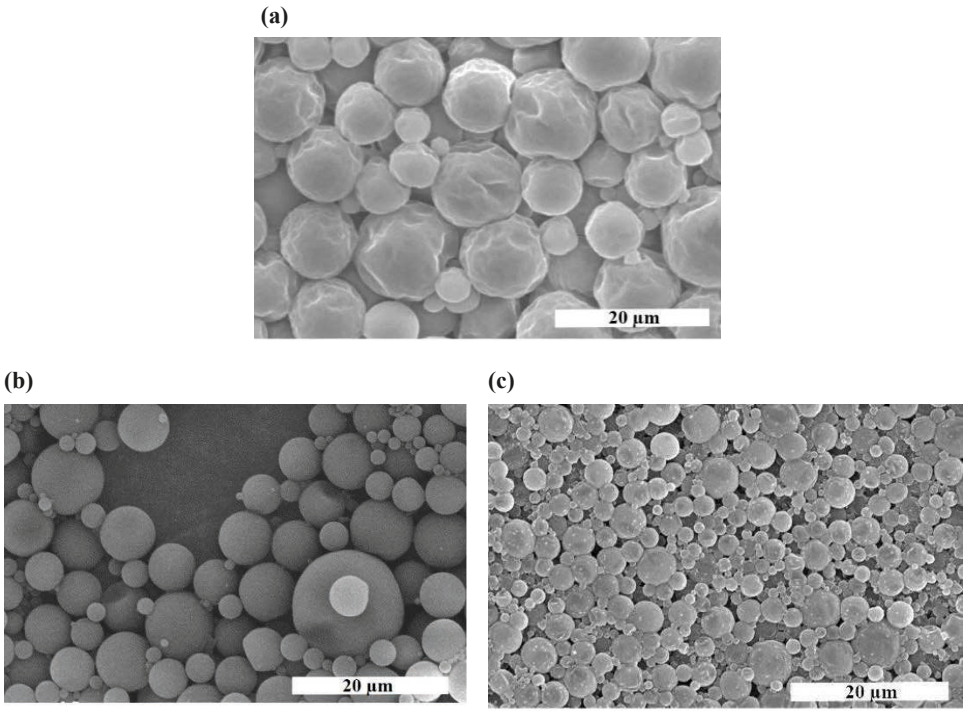

Figure 3.16: SEM micrographs of (a) sample PCM-PVA2, produced in this work, and industrial samples (b) Wc-PCM28 and (c) Sl-PCM28 (magnification x2000).

Regarding the particle size distribution, Figure 3.17 shows that the size distribution of sample Wc-PCM28 is comparable to sample PCM-PVA2. These results are translated in the values presented in Table 3.10. From the diameter values, the only sample that differentiate itself is the Sl-PCM28, due to its much smaller sizes comparing with sample PCM-PVA2 and also Wc-PCM28.

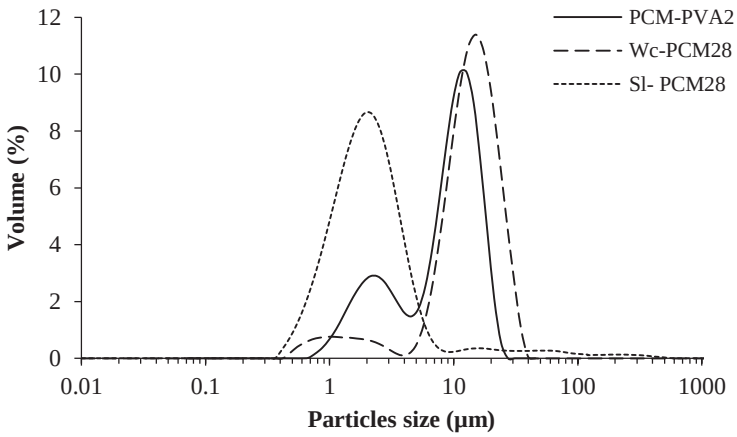

Figure 3.17: Particle size distribution of sample PCM-PVA2, produced in this work, and industrial samples Wc-PCM28 and Sl-PCM28.

Table 3.10: Statistical diameters of microcapsules size distributions (in volume) presented in Figure 3.17 (values of mean diameter, D_{10}, D_{50} and D_{90}).

Sample	Mean diameter, $D_{4,3}$ (µm)	D_{10} (µm)	D_{50} (µm)	D_{90} (µm)
PCM-PVA2	10.0	2.1	10.2	17.7
Wc-PCM28	15.4	6.2	14.8	25.9
Sl-PCM28	2.7	0.9	2.1	5.2

b) Thermal characterization

Like for the sample PCM-PVA2, the thermal properties of industrial microcapsules were evaluated by DSC and TGA. The comparison between their DSC curves obtained for these samples is shown in Figure 3.18.

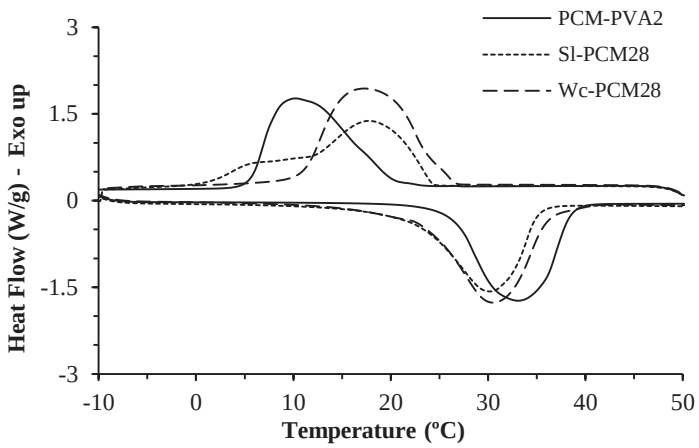

Figure 3.18: DSC curves of sample PCM-PVA2, produced in this work, and industrial samples Wc-PCM28 and Sl-PCM28.

The industrial microcapsules exhibit the typical profile of microcapsules containing PCM: one endothermic peak for heating process; and another exothermic for the cooling process. However, their profile is slightly different from the one of sample PCM-PVA2, as showed in Figure 3.18 and as observed in the data listed in Table 3.11.

Table 3.11: Comparison of thermal performance (average ± standard deviation) of sample PCM-PVA2 and samples Wc-PCM28 and Sl-PCM28 (ΔH_m and ΔH_c: melting and crystallization enthalpies; T_{om} and T_{oc}: melting and crystallization onset temperatures; PCM content was calculated using equation (3.1)).

Sample	**T_{om}** (ºC)	**ΔH_m** (J/g)	**T_{oc}** (ºC)	**ΔH_c** (J/g)	**PCM content** (wt.%)
PCM-PVA2	26.5±0.3	193.9±3.3	21.5±0.1	196.1±2.3	77.3
Wc-PCM28	22.8±1.1	195.1±2.9	25.1±0.0	202.2±3.5	--
Sl-PCM28	21.8±0.4	161.8±5.2	24.4±0.2	167.2±5.2	--

Comparing the onset temperature for the heating and cooling process of microcapsules Wc-PCM28, it was observed that T_{om} is around 23 ºC and T_{oc} is 25 ºC. This temperature behaviour is the inverse of the one previous detected in sample PCM-PVA2, where the value of T_{om} was around 26 ºC and higher than T_{oc} (22 ºC). Thus, contrarily to sample PCM-PVA2, the supercooling effect is not identified in microcapsules Wc-PCM28. Despite minor differences in the onset temperature values, in sample Sl-PCM28 this phenomenon is also absent.

This difference between the industrial microcapsules and the prepared acrylic shell microcapsules was already expected, because in the industrial samples besides the main PCM are used nucleating agents that adjust the phase change temperature of the core material and that supress the effect of supercooling [27].

In these industrial microcapsules, the information about the ΔH_m of the encapsulated PCM are not available, so their PCM content was not calculated. Nevertheless, the comparison of the microcapsules ΔH_m and ΔH_c is possible. For sample PCM-PVA2 and Wc-PCM28 identical values were obtained (ΔH_m values of around 190 J/g), whereas for sample Sl-PCM28 the values were lower (ΔH_m of 160 J/g). These outcomes are in line with the results of microcapsules size, the smallest microcapsules present the lower enthalpy values, due to a small amount of encapsulated PCM (Sl-PCM28) and, in contrast, the largest microcapsules presented the higher enthalpy values (Wc-PCM28).

The thermodegradation profile obtained for both industrial samples are completely different from the one obtained for sample PCM-PVA2. As observed in the weight loss curves represented in Figure 3.19 and as reflected in the values of Table 3.12.

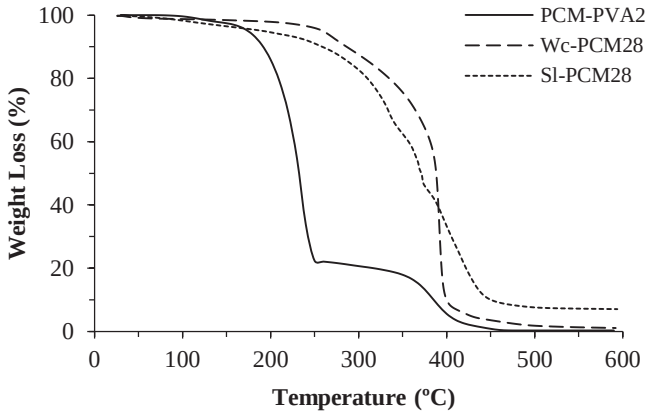

Figure 3.19: TG curves of sample PCM-PVA2, produced in this work; and industrial samples Wc-PCM28 and Sl-PCM28.

Contrary to microcapsules PCM-PVA2, which presents a thermoanalytical curve with two degradation stages (as described in section 3.3.2), both industrial samples presented only one main degradation stage. The thermal properties of a shell based on melamine-formaldehyde are related with its preparation conditions, namely with the molar ratio of melamine and formaldehyde, reaction temperature and pH [32]. Nonetheless, they are characterized by a weight loss around 350 – 400 ºC [32–34], which is consistent with the observed in Figure 3.19. The TG

results showed that these microcapsules present a high thermal stability. It seems that the shell does not allow the weight loss of the encapsulated core material at low temperatures as the acrylic shell microcapsules, appearing only one degradation stage at high temperature (with a percentage of weight loss higher than 90 %). In this weight loss should be included the degradation of the microcapsules shell as well as their core material.

Table 3.12: Comparison of thermal stability of sample PCM-PVA2 and industrial samples Wc-PCM28 and Sl-PCM28 ($T_{5\%}$ and $T_{10\%}$: temperatures corresponding to 5% and 10% of weight loss; T_{on1} and T_{on2}: extrapolated onset temperatures of the first and second degradation stage; Weight loss: weight loss (%) in each degradation stage).

Sample	$T_{5\%}$	$T_{10\%}$	1st stage		2nd stage	
			T_{on1}	Weight Loss	T_{on2}	Weight Loss
	(ºC)	(ºC)	(ºC)	(%)	(ºC)	(%)
PCM-PVA2	173.7	191.5	209.8	77.9	357.8	21.8
Wc-PCM28	259.4	286.7	279.9	97.4	--	--
Sl-PCM28	192.8	259.6	310.4	92.8	--	--

Comparing the thermal stability of both industrial samples, the main divergence is observed at low temperatures, where sample Sl-PCM28 shows a small but continuous weight loss. This behaviour is responsible for the $T_{5\%}$ of 193 ºC of sample Sl-PCM28, which contrast with sample Wc-PCM28 that presents a value around 259 ºC. This initial weight loss could be created by the evaporation of remaining water or other products that are still present. However, for both microcapsules similar values of $T_{10\%}$ were obtained (about 260 ºC - 280 ºC). These samples revealed a much higher thermal stability than the acrylic microcapsules PCM-PVA2 ($T_{5\%}$ of 174 ºC and $T_{10\%}$ of 192 ºC).

Herein, it was determined that sample PCM-PVA2 is equivalent to sample Wc-PCM28, concerning the microcapsules morphology and the values of ΔH_m, while Sl-PCM28 shows a lower particle size and also a lower ΔH_m. Furthermore, both industrial samples presents a much higher thermal stability than the sample prepared in this work. This comparison confirm the potential of the produced acrylic microcapsules to prepared thermo-regulating textiles, since most their properties are in the range of the microcapsules currently used by Devan Chemicals. Additionally, as it will be properly presented in Chapter 5, the characterization of these microcapsules will be completed through their incorporation in textiles. The obtained results will be the base to evaluate the textiles treated with the acrylic microcapsules.

3.4 CONCLUSIONS

This chapter reported the attempts made to find a procedure to prepare acrylic microcapsules via suspension polymerization. The core material selected was octadecane due to its PCM characteristics and suitability for textile applications. During the polymerization a copolymer with three monomers (MMA, BA and MAA) and with two crosslinkers (EGDMA and PETRA) was prepared. Preliminary tests using two stabilizers (PVP and PVA), following the same experimental procedure, led to the conclusion that the PVA was the most adequate stabilizer. SEM analysis revealed that spherical and individual microcapsules were produced in this way, with a well-defined core/shell structure. Their morphological characterization was complemented by particle size analysis, whose curve shows a bimodal distribution with a mean diameter (volume based) of around 7 μm. The characterization of these microcapsules by FT-IR spectroscopy confirmed the presence of octadecane and the formation of acrylic shell.

The thermal performance of these microcapsules was evaluated by DSC, leading to values of ΔH_m around 160 J/g and a PCM content of 65 %. From the thermoanalytical curves, it was possible to differentiate two distinct degradations stages, one originated by the weight loss of octadecane (around 190 ºC) and the other, at higher temperature (360 ºC), formed by the degradation of the polymeric shell. The TG data also suggested that when the PCM was encapsulated, the polymeric shell created a resistance and protection to its evaporation, increasing the degradation temperature.

Once established the microencapsulation procedure that enabled to successfully encapsulate the octadecane, a series of experiments was carried out varying the PCM/monomers mass ratio, in order to maximize the amount of encapsulate octadecane. This study demonstrated that this ratio could be increased up to 2. For the microcapsules produced with this ratio, the PCM content increased to 77 % and the ΔH_m value to 194 J/g, being the mean particle diameter around 10 μm. The thermal analysis performed by TGA demonstrated that these microcapsules were stable below $T_{5\%}$ of 170 ºC.

Comparison with PCM industrial samples led to the conclusion that the microcapsules produced with the recipe/procedure proposed in this work exhibit characteristics similar to those industrially produced (mainly with sample Wc-PCM28), with the advantage of being more environmental friendly (formaldehyde-free product). However, this information must be completed by the results obtained with their incorporation into the textile substrates.

From the above results, it can be concluded that promising results were obtained by using a copolymer of MMA, BA and MAA crosslinked with EGDMA and PETRA, using PVA as stabilizer and a PCM/monomers mass ratio of 2. In addition, it was confirmed that the acrylic shell microcapsules containing octadecane exhibited a thermal performance and stability appropriate for thermal energy storage.

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CHAPTER 4

INFLUENCE OF DIFFERENT REACTION PARAMETERS

ABSTRACT

The influence of different reaction parameters on the suspension polymerization process and on the properties of the obtained microcapsules was evaluated. The implemented experiments were based on the microencapsulation procedure described in Chapter 3. Herein, the initiator type and polymerization temperature were the first parameters to be investigated. Benzoyl peroxide, azobisisobutyronitrile and trigonox 23 were used as thermal free radical initiators and the reaction was performed at different temperatures. Secondly, the effect of the shell composition of microcapsules was assessed, by preparing copolymers of methyl methacrylate, butyl acrylate and methacrylic acid with different monomer proportions. Finally, the influence of the core material was studied, replacing the octadecane by a series of compounds with different chemical nature.

A comprehensive characterization of the microcapsules was undertaken, regarding their chemical composition, morphology and thermal behaviour. In addition, the monomer conversion, as a function of time, for the suspension polymerizations was evaluated. The results demonstrate that the developed encapsulation procedure can be applied to produce microcapsules using all the selected initiators and at different reaction temperatures, including a temperature as low as 40 ºC. Additionally, by using several proportions of monomers, shells with different properties (namely with distinct thermal stability) were produced. Finally, it was demonstrated that the proposed procedure can also be applied to encapsulate other core materials. However, the success of encapsulation, namely the production of the core/shell structure is limited by the core polarity.

In conclusion, microcapsules containing octadecane were successfully prepared using different experimental conditions. The influence of these parameters on the performance of the treated textiles with these microcapsules will be evaluated in Chapter 5.

4.1 INTRODUCTION

In the previous chapter, a standard procedure of suspension polymerization technique was established to microencapsulate octadecane in acrylic based shell. This shell was prepared with a monomers mixture of MMA, BA and MAA crosslinked with EGDMA and PETRA. In order

to produce the microcapsules, an oil-in-water emulsion was prepared using PVA as stabilizer and an octadecane/monomers mass ratio of 2. The polymerization was carried out by using BPO as initiator, with a reaction temperature of 80 ºC during 5.5 hours.

Once established this microencapsulation procedure, attempts were made to study the influence of different reaction parameters, trying to improve not only the properties of the microcapsules, but also the operating conditions. The reaction parameters investigated were:

- the initiator type and polymerization temperature;
- the monomers proportions used in the mixture MMA/BA/MAA;
- the type of core material.

Initiator type and polymerization temperature

As previously described (section 3.1), in free radical polymerization a small concentration of radicals (molecules with an unpaired electron) reacts with monomer molecules by attacking their double bond. The mechanism of initiation is based on the decomposition of an initiator species that generates these radicals. In the present work, only thermal initiators were used, which are decomposed by the temperature increase.

The most important indicator of a thermal initiator activity is its half-life. By definition, half-life is the time necessary to decompose one-half of initiator originally present, at a given temperature. To compare the reactivity or the decomposition rate of different initiators, the temperature at which each initiator has a half-life of 10 hours is one of the most used parameters, the 10 hour half-life temperature. This parameter correspond the temperature at which a 50% of the initiator is consumed in 10 hours – the most reactive (fastest) initiator, at specific temperature, would be the one with the lowest 10 hour half-life temperature [1, 2].

The influence of the initiator type and polymerization temperature was studied, by comparing several experiments undertaken with diverse thermal initiators and at different reaction temperatures. Additionally, it was also intended to follow the reaction involved in the formation of the acrylic microcapsules, through the evaluation of the monomer conversion as a function of time. The ultimate goal was to establish the most adequate experimental conditions to follow the tests.

In order to reach these goals, a series of experiments was conducted employing three thermal initiators:

- BPO, which is a peroxide initiator with a 10 hour half-life temperature of 70 ºC (used in the preliminary tests) [3];

- Azobisisobutyronitrile (AIBN), which is an azo initiator with a 10 hour half-life temperature of 65 ºC [3];

- Trigonox 23 (Trig23) (the trade name of tert-butyl peroxyneodecanoate) that, like BPO, is a peroxide initiator but with a 10 hour half-life temperature of 46 ºC [4].

In the majority of PCM microencapsulation processes via suspension polymerization, either BPO (using styrene [5–7] or acrylic monomers [8–11]) or AIBN (using acrylic monomers [12–16]) were used as thermal initiators. To the best of our knowledge, Trig23 has never been used to encapsulate PCM, neither to produce acrylic microcapsules. This initiator was selected with the intention of using a temperature below 50 ºC, which allows not only to reduce energy consumption but also to encapsulate core materials that degrade at moderate temperature (like probiotics currently used in textile materials). Trig23 was chosen from the existent thermal initiators that present a low initiation temperature (10 hour half-life temperature around 40 - 50 ºC) but also from the ones that are described as suitable to promote free radical polymerization and to react with acrylic monomers [4].

In most of the cases involving PCM microencapsulation based on acrylic polymers, the polymerization temperatures are above 50 ºC, namely when MMA is used as principal monomer [17]. In particular, the processes of suspension polymerization involve temperatures over 70 ºC [9–11,13,18]. Qiu *et al.* [17] studied the influence of the initiator type and the polymerization temperature on the production of microcapsules containing octadecane with MMA based shells. The authors tried to reduce the reaction temperature through the combination of AIBN and redox initiators. However and as final remarks, the authors mentioned that, despite the success in the preparation of microcapsules, their heat capacity and thermal stability were lower than those of microcapsules prepared with AIBN or BPO at 85 ºC. Moreover, to produce the microcapsules by adding the redox initiator, after an initial period of 2 hours at low temperature (between 35 ºC and 55 ºC) the reaction temperature had to be increased to 85 ºC during 4 hours, which is a drawback in their process [17]. In the present work, efforts to reduce the reaction temperature were made by using only a thermal initiator with a low half-life decomposition temperature.

Monomers proportions

Another variable to be investigate was the influence of the shell composition on the suspension polymerization process and on the properties of obtained microcapsules. The goal of this monomer change was also the production of microcapsules with a different shell

composition in order to study their influence on the microcapsules fixation in the textiles and in their washing resistance (as it will be detailed in chapter 5). For that, several experiments were carried out by using the same monomers (MMA, BA and MAA) but with distinct proportions. In the present study, it was intend to understand the effect of increasing:

- the quantity of BA, which from the three monomers is the only one with a low T_g (BA presents a T_g of around -54 ºC, whereas that of MMA is 100 ºC and that of MAA is 228 ºC);

- and the quantity of MAA, which in turn is carboxylic acid with the highest water solubility and hydrophilic degree (MAA presents a water solubility of 89 g/L at 25 ºC [19], MMA of 16 g/L [20] and BA of 2 g/L [21]). In contrast, to the other monomers, MAA presents reactive carboxyl group.

Core material

The study of the influence of the core material was performed replacing the octadecane by other core materials with distinct properties. The main objective is to analyse the encapsulation accomplishment and the eventual changes on the microcapsules morphology, namely on their shell surface, on the formation of the core/shell structure, as well as on the particles size. During the core material selection, only compounds that, like octadecane, do not react with monomers and that present different chemical nature were considered. In order to embrace a wide range of properties, compounds with distinct hydrophilicity degree, molecular weight and chemical structure were selected. However, the key parameter in this selection was the polarity of the core material, since (as discussed in section 3.3.1) the difference in polarity between the core material and the polymer is decisive in the formation of microcapsules with a core/shell structure.

The compounds used to replace the octadecane were: trioctyl trimellitate (TOTM), bis(2-ethylhexyl) adipate (BEHA), dibutyl phthalate (DBP), tributyl 2-acetylcitrate (TBAC) and ethyl phenylacetate (EPA). The main properties of these compounds will be presented later, together with the description of the experimental conditions. It should be mentioned that this selection was not restricted neither to PCMs nor to compounds to be used in textile applications. In fact, some of them are currently employed in Devan Chemicals as core compounds for different purposes, namely as plasticizers that are encapsulated in different shell materials.

4.2 EXPERIMENTAL

4.2.1 Materials

All monomers, methyl methacrylate (MMA), methacrylic acid (MAA) and *n*-butyl acrylate (BA), and all crosslinking agents, ethylene glycol dimethacrylate (EGDMA) and pentaerythritol tetraacrylate (PETRA) were purchased from Sigma-Aldrich. As thermal initiators was used benzoyl peroxide (75%, contains 25% water, BPO) supplied by ACROS, azobisisobutyronitrile (AIBN) purchased from Sigma-Aldrich and trigonox 23 (Trig23) was kindly provided by Companhia Industrial de Resinas Sintéticas, CIRES Lda and it was from Akzo Nobel Polymer Chemistry. The stabilizer poly(vinyl alcohol) (Mw = 31000 – 50000 g/mol and degree of hydrolysis = 87-89 %, PVA) was purchased from Sigma-Aldrich. The octadecane (purity of 97 wt. % and melting onset temperature of about 27 ºC) was received from Devan Chemicals (Belgium). Finally, all the remaining core materials, bis(2-ethylhexyl) adipate (BEHA), tributyl 2-acetylcitrate (TBAC), ethyl phenylacetate (EPA), dibutyl phthalate (DBP) and trioctyl trimellitate (TOTM), were purchased from Sigma-Aldrich. All the reagents were used as received.

4.2.2 Microencapsulation procedure

The new experiments of microencapsulation were performed following the procedure presented in section 3.2.2. However, they were executed at Devan-Micropolis' facilities, instead the laboratories of the Department of Chemical Engineering at University of Coimbra, where the former experiments were conducted. The new experimental setup was different from the one initially used. It was composed of a triple-walled glass reactor with a larger volume capacity (500 mL instead of 250 mL) and equipped with an external circulating heating bath with external temperature probe that allowed an improved temperature control inside the reactor (in the previous experiments, the temperature control was achieved by immersing the single-walled reactor in a thermostatic oil bath).

Thus, the first experiments conducted using this set of equipment, PCM-Bp80 and B-Bp80, were the reproduction of the experiments PCM-PVA2 and B-PVA0 (described in Table 3.2 Chapter 3). The reagents amounts were increased in order to adjust them to the new reactor capacity (25 g of monomers mixture was used instead of 10 g as before), though maintaining the previous proportions. The nomenclature followed to designate to new experiments shows, besides the presence of octadecane, the type of initiator and reaction temperature used in the

experiments procedure and it is the nomenclature adopted in the next section. Thus, the experiment PCM-Bp80 was performed adding octadecane to the monomers mixture (following the recipe of Table 4.1), while experiment B-Bp80 was carried out without this addition.

Table 4.1: Recipe for the preparation of acrylic microcapsules containing octadecane, experiment PCM-Bp80.

Experiment	**Monomer** (wt.%)			**Crosslinker** (wt.% related to monomers)		**Initiator** (wt.% related to monomers)	**PCM/monomers mass ratio**	**Stabilizer** (wt.% in water)
PCM-Bp80	MMA	BA	MAA	EGDMA	PETRA	BPO	Octadecane	PVA
	93	6	1	5	5	1.2	2	1

In Figure 4.1 the new experimental setup is shown, which consists of a triple-walled glass reactor equipped with an external circulating heating bath, a condenser, a nitrogen inlet and an overhead stirrer (with an axial impeller stirrer, four-bladed). All the following experiments were carried out in this new experimental setup.

Figure 4.1: Experimental setup for the production of microcapsules by suspension polymerization available at Devan-Micropolis.

Specific details about microencapsulation procedure have been described in Chapter 3 section 3.2.2. Summarizing, the initiator was dissolved in the monomers and crosslinkers and then the melted octadecane was added. The mixture was heated up to 40 ºC (Solution (1)). This solution was prepared using 25 g of monomers total, respecting the quantities listed in Table 4.1. Solution (2) was prepared by dissolving 2.5 g of PVA in water (250 mL) and heating until

40 ºC. The Solution (1) was emulsified into Solution (2) and the obtained oil-in-water emulsion was transferred to the reactor (previously heated at 40 ºC). After 10 minutes, the temperature was raised to 80 ºC (inside the reactor) and the reaction was carried out under nitrogen atmosphere and mechanical stirring. The obtained microcapsules were washed as described before (section 3.2.2).

4.2.3 Monomer conversion assessment

The monomer conversion as a function of time was monitored via gravimetry. Therefore, at pre-defined periods of time, a sample of approximately 2-3 mL was removed from the reactor, using a syringe, placed in an aluminium dish with known mass and weighed immediately. The dish was positioned in a highly ventilated place to cool the sample and to remove the volatile compounds. The collected samples were dried until constant weight. The monomer conversion percentages were obtained by weighting the dry samples and relating these values with their initial mass and with the total amount of compounds used in the reaction [22,23].

4.2.4 Characterization techniques

The characterization of the microcapsules was performed according to the techniques and procedures described in Chapter 3, experimental section 3.2.3. Their chemical structure was identified by FT-IR spectroscopy, the morphological characterization was performed by optical microscopy, SEM and laser diffraction and, finally, the thermal properties were assessed by DSC and TGA.

4.3 Results and Discussion

The results are grouped according to the parameter studied. Firstly, the experiments carried out in the new experimental setup are presented and compared with the former ones. Subsequently, the influence of the initiator and polymerization temperature is evaluated. Afterwards, the influence of the monomers proportions in the mixture MMA/BA/MAA and of the core material type on the properties of acrylic microcapsules are investigated. For each one of these parameters, the implemented series of experiment is presented and the obtained microcapsules fully characterized.

4.3.1 New experimental setup

The main purpose of replicate experiments PCM-PVA2 and B-PVA0 (with and without octadecane) was to compare the microcapsules prepared in these trials with the ones obtained in the new experimental setup (available at Devan-Micropolis). The new experiments were designated as PCM-Bp80 and B-Bp80, respectively, and they will be used as references for the further experiments.

Characterization of microcapsules

a) Chemical characterization

Figure 4.7 depicts the FT-IR spectra of the replicated samples. As this figure shows, identical spectra were obtained for each pair of experiments (B-PVA0 versus B-Bp80 and PCM-PVA2 versus PCM-Bp80), denoting that all produced samples are composed of a copolymer whose structure presents the same chemical groups. This was expected, since in the new experiments, besides the increase of the reagents amount, no modification in the applied recipe was made.

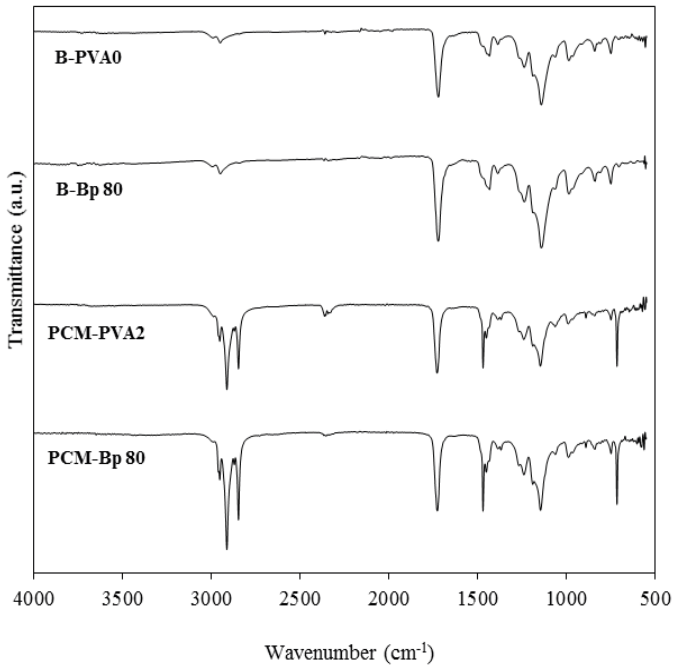


Figure 4.2: Comparison of the FT-IR spectra obtained for the two pairs of experiments (B-PVA0 versus B-Bp80 and PCM-PVA2 versus PCM-Bp80).

b) Morphological characterization

As presented in Chapter 3, the distinction between the microcapsules containing octadecane and the copolymer microparticles (without octadecane) in terms of surface texture is, once again, very clear: the ones with octadecane exhibit a rough shell surface, whereas that of the microparticles is quite smooth (see Figure 4.3). However, comparing the corresponding pairs, no relevant differences were noticed.

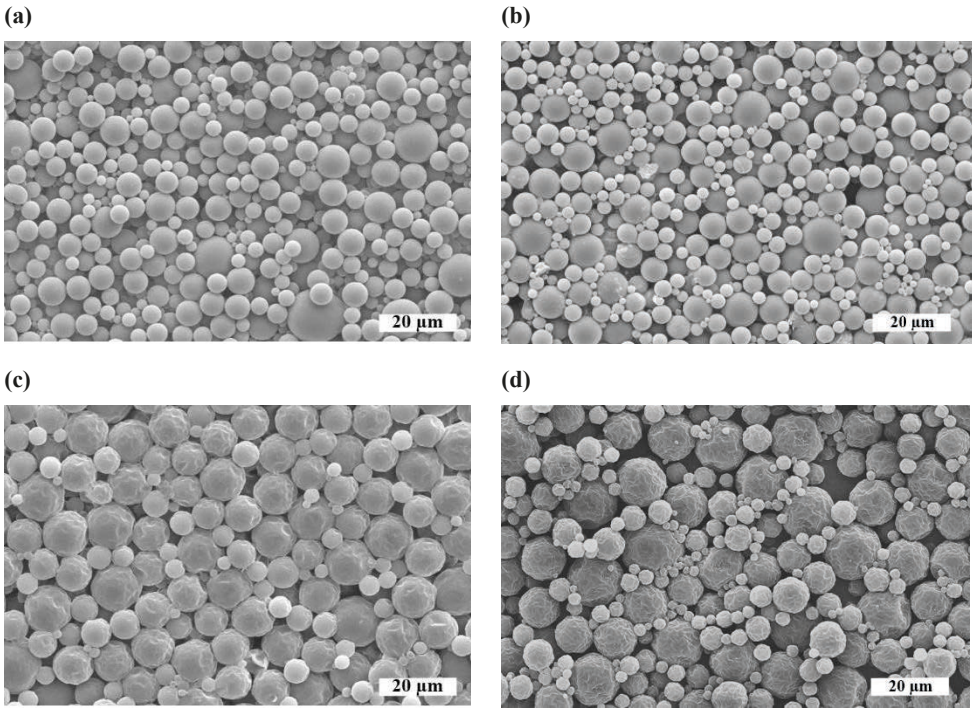


Figure 4.3: SEM micrographs of samples (a) B-PVA0, (b) B-Bp80, (c) PCM-PVA2 and (d) PCM-Bp80 (magnification x1000).

Regarding the results of particle sizing, namely the particle size distribution data (Figure 4.4 (a)) and mean diameters through the values of $D_{4,3}$ (Figure 4.4 (b)), it can be observed that the experiments undertaken in the new experimental setup resulted in relatively larger particles in both cases (with and without octadecane). As it was previously mentioned, to carry out the latter tests and due to the larger reaction vessel, the amount of reagents had to be adjusted by increasing its quantity. Nevertheless, the agitation conditions of the emulsification process carried out to create the oil-in-water emulsion (using a homogenizer at 6000 rpm during 10 minutes) and also the agitation conditions of the reactor during the polymerization process (using a propeller stirrer at 300 rpm) were maintained. In fact the agitation conditions may not have been totally replicated in the new experiments and that can explain the formation of larger droplets and, consequently, microcapsules with larger diameters.

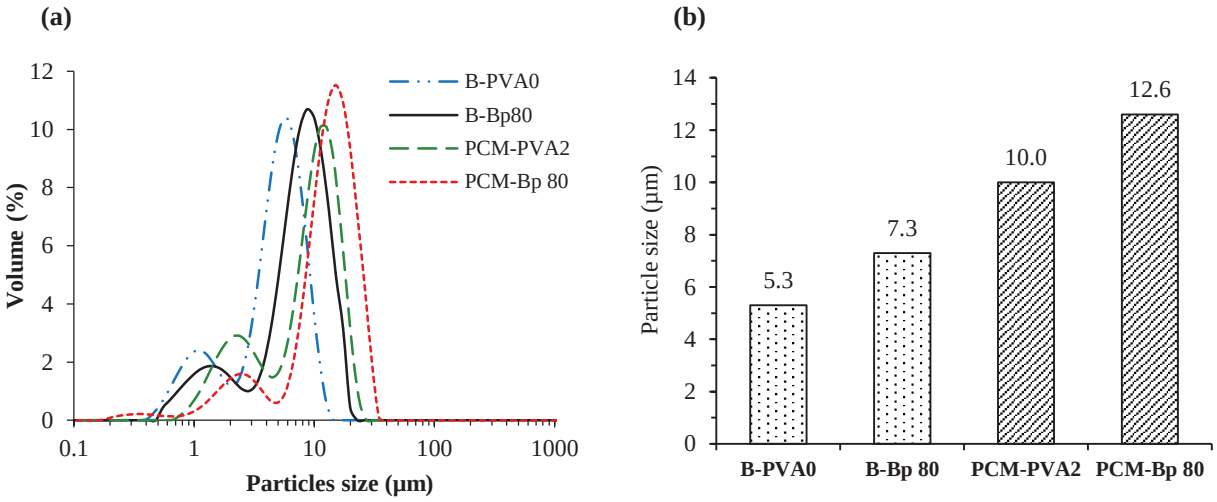


Figure 4.4: Comparison of (a) particle size distribution curves and (b) values of $D_{4,3}$ obtained for the two pairs of experiments.

c) Thermal characterization

Herein, in order to facilitate the discussion, only the most relevant results are compared. The complete data is available in Appendix B, Tables B.1 and B.2. The values of ΔH_m and PCM content evaluated by DSC and the values of $T_{5\%}$, T_{on} and weight loss evaluated by TGA are summarized in Table 4.2. Despite the similar curve profiles obtained by DSC and by TGA (see Figure B.1 in Appendix B), some deviations between the parameters of the corresponding pairs are detected in this table.

As observed, although sample PCM-Bp80 is the replicate of PCM-PVA2, its PCM content is lower (77.3% for PCM-PVA2 against 69.3% in PCM-Bp80). The values of PCM content depends on the relative quantity of octadecane with respect to the total quantity of the sample (octadecane and copolymer) (see equation (3.1)). The theoretical value of PCM content in these microcapsules should be 64.5 % (value calculated using the mass of octadecane and the mass of monomers plus crosslinkers and following the recipe of Table 4.1). According to the definition of PCM content, a value lower than the theoretical could indicate that not all the octadecane was encapsulated, being removed during the microcapsules washing. On the other hand, a higher value could reveal that not all the monomers reacted and an amount of copolymer smaller than the theoretical was formed. Nevertheless, the final properties of the microcapsules, namely their PCM content, are most likely influenced by these two factors. Thus, considering the experiments PCM-PVA2 and PCM-Bp80, it was observed that the PCM content is, in both cases, higher than the theoretical value. This suggests that, despite the possible presence of

some free and residual octadecane, not all the monomers and crosslinkers used in formulation were able to react and form the copolymer. Additionally, as in sample PCM-Bp80 the value of PCM content becomes closer to the theoretical value than in PCM-PVA2, it is possible that in experiment PCM-Bp80 a highest production of copolymer has been occurred. This higher production of copolymer should be reflected in a higher production of polymeric shell in the microcapsules and, probably, also in a higher production of small microparticles composed of only copolymer.

These results obtained in batch PCM-Bp80 could be a consequence of the changes made in the experimental setup (namely the use of a new reactor equipped with an external circulating heating bath) that promoted a higher polymerization efficiency (reducing the quantity of unreacted monomers and their release as well as increasing the formed polymer).

Table 4.2: Thermal properties of the two pairs of experiments, determined by DSC (ΔH_m: melting enthalpy (average ± standard deviation) and PCM content) and by TGA ($T_{5\%}$: temperature corresponding to 5% of weight loss; T_{on1} and T_{on2}: extrapolated onset temperature; and weight loss).

Sample	**ΔH_m** (J/g)	**PCM content** (wt.%)	**$T_{5\%}$** (ºC)	**1st stage**		**2nd stage**
				T_{on1} (ºC)	Weight Loss (%)	**T_{on2}** (ºC)
B-PVA0	---	---	285.9	118.5	3.1	357.4
B-Bp80	---	---	278.3	126.7	1.9	345.5
PCM-PVA2	193.9 ± 3.3	77.3	173.7	209.8	77.9	357.8
PCM-Bp80	174.4 ± 0.9	69.3	181.2	199.7	70.2	351.6

Concerning TGA results, for the values of $T_{5\%}$ of the microcapsules containing octadecane, sample PCM-Bp80 shows a value 7.5 ºC higher that PCM-PVA2. This higher value suggests a greater thermal resistance for sample PCM-Bp80 due to a higher resistance of the microcapsules shell to the octadecane evaporation, probably caused by a thicker or denser shell. Moreover, regarding the values of weight loss, some differences are also detected (see Table 4.2). PCM-PVA2 presents a weight loss in the first degradation stage of around 78%, while that of PCM-Bp80 is about 70%. Once, this stage is mainly originated by the octadecane weight loss, these results suggest that in sample PCM-Bp80 a highest amount of polymer is prevailing. This observation is consistent with the discussed above for the DSC results.

Summing up, the changes in the experimental setup (a larger reactor equipped with a improved heating control system) resulted in some differences in the produced microcapsules. From the new experiments, microcapsules with a slight larger size are detected and a higher production of copolymer during the suspension polymerization seems to be achieved. Additionally, a small reduction in the value of ΔH_m (around 175 J/g instead of 194 J/g) was observed, nevertheless its value can still be considered satisfactory. TGA results confirmed that the obtained microcapsules were still stable until 170 ºC ($T_{5\%}$).

All the following experiments were carried out in this new experimental setup, being the results obtained in experiments B-Bp80 and PCM-Bp80 the base of comparison in the study of the different reaction parameters. These parameters are going to be properly discussed in the following sections.

4.3.2 Influence of the initiator type and polymerization temperature

The series of experiments to study the influence of the type of initiator was initiated by performing experiences using different initiators at their 10 hour half-life decomposition temperature: BPO at 70 ºC, AIBN at 65 ºC and Trig23 at 48 ºC (Table 4.3). Subsequently, the influence of temperatures was also evaluated for some of them: 80 ºC for BPO, as already used in previous experiments, and 40 ºC for Trig23. Concerning the latter, it should be stressed that no information is available regarding the use of this initiator to prepare acrylic microcapsules. So, it was found interesting to test its performance at lower temperatures and perform experiments without the encapsulation of octadecane.

Table 4.3 summarizes the main differences between these experiments, emphasizing the parameters that were modified: the type of thermal initiator (presenting the respective half-life temperature of 10 hours and 1 hour [2–4]), the reaction temperature and the addition or not of octadecane. For these experiments, the monomer conversion profiles were determined and the microcapsules produced were fully characterized as described in section 4.2.

Table 4.3: Series of experiments carried out to study the influence of initiator type and reaction temperature, presenting the modified parameters: thermal initiator, reaction temperature and addition of octadecane [2–4].

Experiment	**Initiator**			**Reaction Temperature** (ºC)	**Addition of octadecane**
	Type	***Half-life temperature*** (ºC)			
		10 hour	*1 hour*		
PCM-Bp80 *	BPO	70	91	80	Yes
PCM-Bp70	BPO	70	91	70	Yes
PCM-Aibn65	AIBN	65	81	65	Yes
PCM-Trig48	Trig23	46	64	48	Yes
PCM-Trig40	Trig23	46	64	40	Yes
B-Bp80 *	BPO	70	91	80	No
B-Trig48	Trig23	46	64	48	No
B-Trig40	Trig23	46	64	40	No

***** Samples previously presented

Besides searching for the most suitable experiments, regarding not only the type of initiator but also the temperature and time of reaction, this work also attempts to acquire additional information about the suspension polymerization reaction. In fact, the knowledge of the kinetic parameters is crucial for a detailed understanding of chemical processes as well as the industrial implementation of the developed procedure.

Monomer conversion curves

Figure 4.5 shows the comparison between the monomer conversion curves of experiments carried out with the three initiators at respective 10 hour half-life decomposition temperatures: 70 ºC when using BPO (PCM-Bp70), 65 ºC when using AIBN (PCM-Aibn65) and 48 ºC when using Trig23 (PCM-Trig48). The conversion-time curves obtained for these experiments are next to each other, which means that the monomers conversions occurred at a similar rate for these conditions. Nonetheless, the value of the final conversion achieved for experiment PCM-Aibn65 is slightly lower than the others (92 % for PCM-Aibn65 instead of around 97 % for the other two).

Additionally, it was observed that the monomer conversion only started after around 30 minutes, which correspond to the induction period of the reaction (i.e., time during which no observable change occurs in the chemical reaction [24]). Nevertheless, despite this constant

induction period, for experiment PCM-Bp70, PCM-Aibn65 and PCM-Trig48 the set-point temperatures were reached after around 30, 25 and 7 minutes, respectively (all the experiments started at 40 ºC)

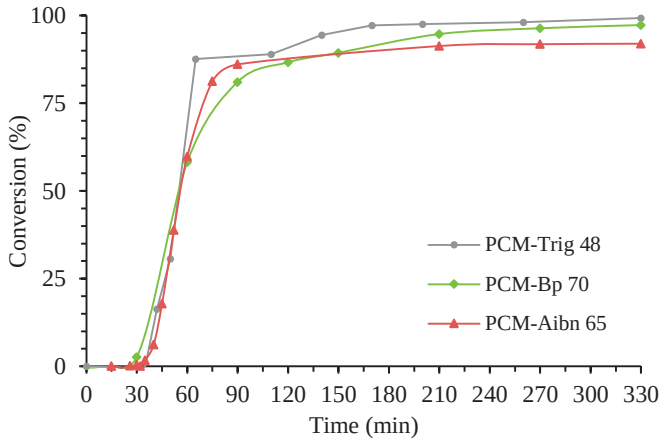


Figure 4.5: Monomer conversion as a function of time for the suspension polymerization with BPO at 70 ºC, AIBN at 65 ºC and Trig23 at 48 ºC (the respective 10 hour half-life temperature, see Table 4.3).

The effect of the reaction temperature on the monomer conversion of suspension polymerization carried out using BPO at 70 ºC and 80 ºC can be observed in Figure 4.6 (a) and when using Trig 23 at 40 ºC and 48 ºC in Figure 4.6 (b). For both initiators, the slopes of the conversion-time curves increase as the reaction temperature increases, denoting a faster polymerization rate. This effect is particularly notorious for the initiator Trig23. The monomer reaction of experiment PCM-Trig48 started after 40 minutes, reaching 95 % of conversion after approximately 2.5 hours, while for PCM-Trig40, the reaction was initiated only after 2.5 hours and a monomer conversion of 97 % was reached only after 6 hours. This was somehow expected since for a polymerization at higher temperature, the half-life of the thermal initiator is lower and its initiation activity is higher (see Table 4.3). For instance, BPO has a half-life of 10 hours at 70 ºC and a half-life of 1 hour at 91 ºC [2,3]. Moreover, in a specific microenvironment, when the thermal initiator presents a high initiation rate (i.e. highest formation of free radicals), it will be responsible for a faster monomer conversion [25].

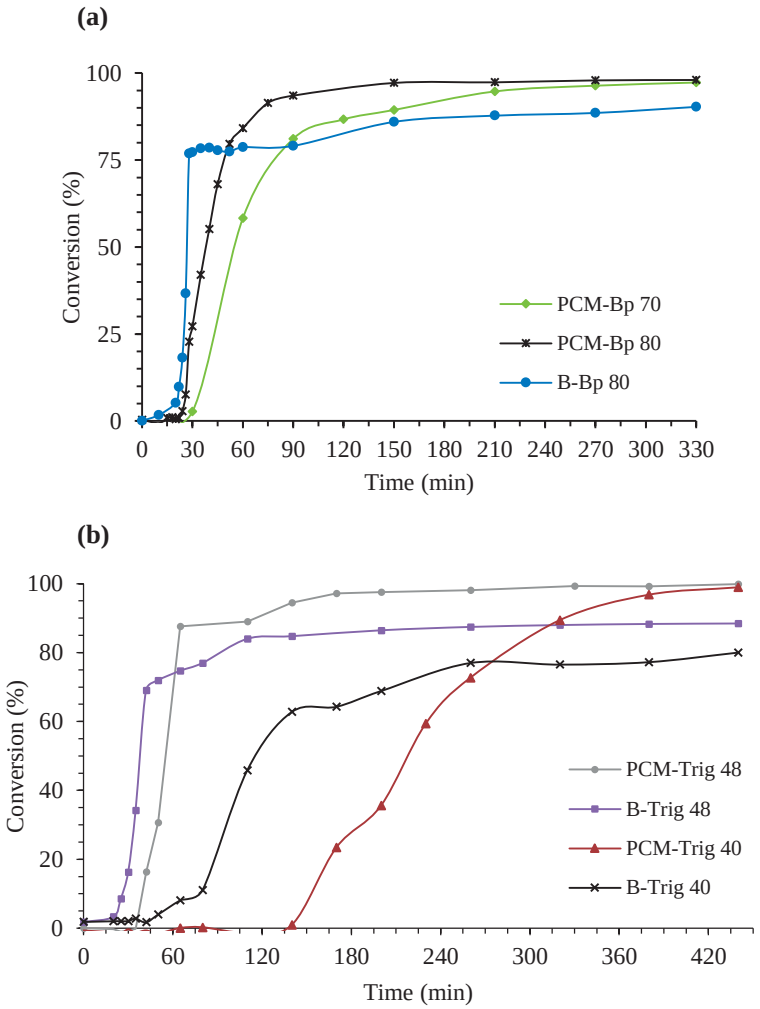


Figure 4.6: Monomer conversion as a function of time for the suspension polymerization with (a) BPO at 70 ºC and at 80ºC in the presence of octadecane and with BPO at 80ºC in the absence of octadecane; and (b) Trig23 at 48 ºC and at 40ºC in the presence and absence of octadecane (up to 7.5 hours). See Table 4.3 for details.

Regarding the effect of the presence of octadecane in the suspension polymerization with both initiators, it is clear that in the absence of octadecane the reaction rate is faster, presenting a small induction period, and the final monomer conversion is lower than when octadecane is present. The shorter induction period is easily detected when comparing, experiment B-Trig40 with PCM-Trig40: the monomer conversion started after 50 minutes instead of 2.5 hours. As previously mentioned, in the suspension polymerization technique, the polymeric shell is formed by free radical polymerization. Therefore, its reaction rate depends on the microenvironment and on the local monomer concentration where the free radicals are produced and where the initiation takes place [26,22]. In the absence of octadecane, the concentration of the monomers and crosslinkers within the dispersed phase is higher (the phase where the initiators

is present), originating a fast polymerization rate (Figure 4.6). Additionally, the lower final conversion that occurs in the experiments carried out without octadecane could be caused by a higher evaporation rate of monomers in the polymerization reaction, probably because in the absence of octadecane, the monomers could evaporate more easily.

Summarizing, the above results show that the initiator type and the reaction temperature greatly influence the monomer conversion curves as function of time. For the investigated thermal initiators, and as expected, it was demonstrated that the monomer conversion rate increased with the rise of the reaction temperature. Despite the differences observed between the experiments, all of them exhibit high rates of monomer conversion (except for experiment PCM-Trig40), reaching final conversions above 90 %. These figures also suggest that the percentage of initiator used in these tests is adequate and thus, in the next experiments, its quantity will be maintained. Finally, this work reveals that it is possible to prepare microcapsules using reaction temperatures of 40 ºC, despite the lower monomer conversion. This is particularly important for processes involving the microencapsulation of thermo-sensible core materials.

Characterization of microcapsules

a) Chemical characterization

The FT-IR spectra of microcapsules containing octadecane are presented in Figure 4.7. To facilitate the comparison, the main peaks of sample PCM-Bp80 are highlighted. In this spectrum, the presence of the characteristic peaks from octadecane and from the acrylic shell were identified. The two strong peaks at 2913 cm^{-1} and 2847 cm^{-1} are assigned to asymmetric and symmetric C-H stretching vibration of CH_2, which should be predominantly originated by the presence of octadecane. Also from octadecane, the peak at 1470 cm^{-1}, ascribed to the bending vibration of methylene group, and the peak at 716 cm^{-1}, attributed to the alkane long chain, are detected. From the acrylic polymer, more specifically from the ester group, the strong peak at 1728 cm^{-1} from C=O stretching vibration and the band at 1190 cm^{-1} for its C-O-C stretching vibration are easily identified. The characteristic peak that is only present in the monomers, corresponding to the stretching vibration of double bond C=C (normally appears around 1635 cm^{-1}), was not noticed in this sample PCM-Bp80 [27].

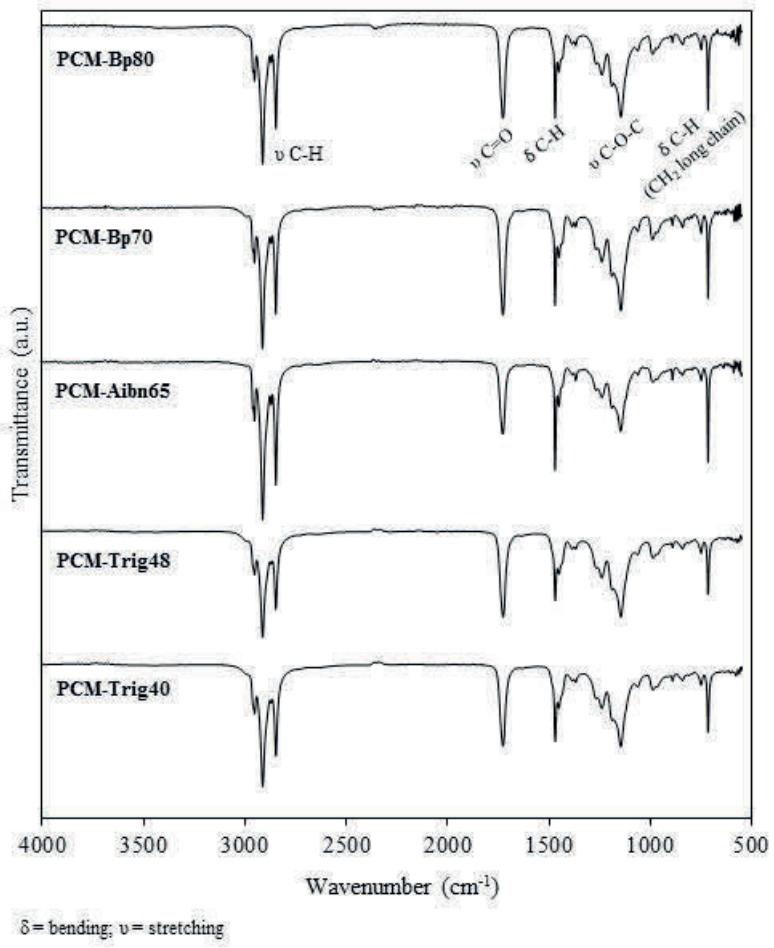


Figure 4.7: FT-IR spectra of samples prepared with several initiators and at different reaction temperature, samples PCM-Bp80, PCM-Bp70, PCM-Aibn65, PCM-Trig48 and PCM-Trig40. Experiments listed in Table 4.3.

Comparing the spectra represented in Figure 4.7, it can be observed an identical pattern for all of them, comprising the characteristic peaks formerly identified. This fact confirms the presence of octadecane and the production of the acrylic shell as well as the absence of unreacted monomers. Finally, these results do not show any dependence of initiator type and/or reaction temperature.

Similar conclusion can be withdrawn from the FT-IR spectra corresponding to the experiments performed without octadecane, which exhibit the same profile of sample B-Bp80 (see Figure B.2 in Appendix B).

b) Morphological characterization

The SEM analyses confirmed that all experiments conducted in the presence of octadecane originated spherical microcapsules of different sizes and with a rough shell surface. In Figure 4.8, as an example, the micrograph obtained for sample PCM-Trig40 is compared with the one obtained for sample PCM-Bp80 (previously presented). Even corresponding to a completely different monomer conversion curves, similar morphologies were obtained (see other micrographs in Appendix B, Figure B.3).

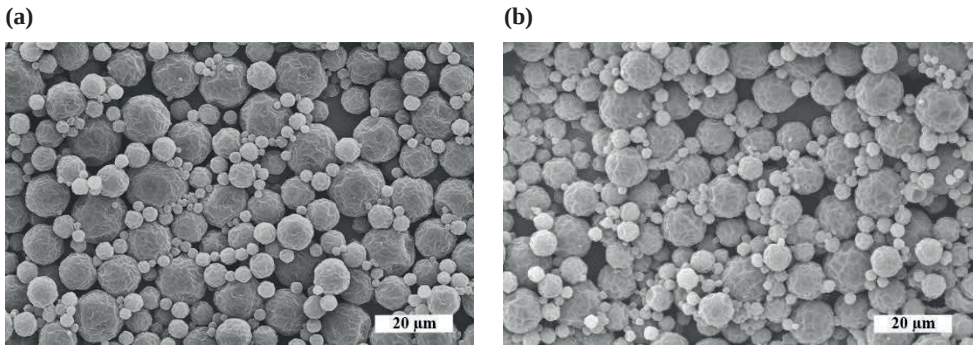


Figure 4.8: SEM micrographs of samples (a) PCM-Bp80 and (b) PCM-Trig40 (magnification x1000).

The experiments performed without octadecane also produced spherical microparticles but with smooth surface. This structure is illustrated in Figure 4.9, where like in the figure above, the micrograph obtained for sample B-Trig40 is compared B-Bp80 (see sample B-Trig48 in Figure B.4 Appendix B).

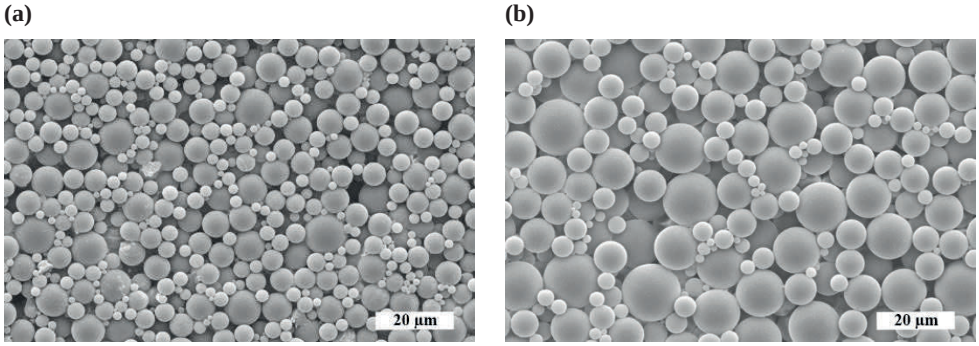


Figure 4.9: SEM micrographs of samples (a) B-Bp80 and (b) B-Trig40 (magnification x1000).

A bimodal particle size distribution was detected for all the samples with and without octadecane (Figure B.5 in Appendix B). This bimodal distribution profile was already discussed in section 3.3.1 (the production of the smaller microparticles is attributed to the process of

secondary nucleation [28]). Thus, the changes in the kind of initiator do not seem to alter this phenomenon.

In Figure 4.10, the values of mean diameters ($D_{4,3}$) determined for all specimens can be compared (the complete particle size analysis is available in Appendix B, Table B.3). From these figure, it is clear that the initiator type and/or the temperature do not affect much the size of the microcapsules. Additionally, this series of experiments also confirms that the presence of octadecane is responsible for the particle size increase (discussed in section 3.3.1).

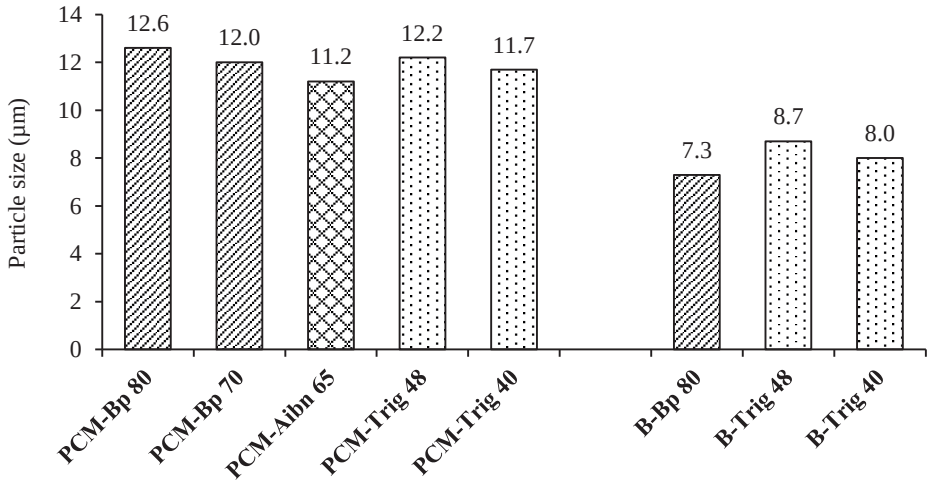


Figure 4.10: Influence of initiator type and polymerization temperature on the particle size (mean diameter - $D_{4,3}$), experiments listed in Table 4.3. Samples PCM-Bp80 and B-Bp80 are represented for comparison.

To sum up, for the implemented experiments (similarly to the FT-IR data), the effect of initiator type and reaction temperature was not relevant in the morphological parameters of the produced microcapsules.

c) Thermal characterization

As in the previous section, only the most relevant data from DSC and TGA will be presented here (supplementary information is gathered in Appendix B, in Figures B.6 and B.7 and also in Tables B.4 and B.5). For the DSC curves, the samples produced with the different initiators exhibit the same curve profile: one endothermic peak (downwards) for the heating process and one exothermic peak (upwards) for the cooling process. Also in the TG curves of microcapsules containing octadecane the typical degradation pattern was confirmed – a thermoanalytical curve with two distinct degradation stages: the first stage produced by the weight loss of octadecane that diffuses out from the microcapsules and evaporate; and the

second one originated by the polymeric shell degradation (as extensively discussed in section 3.3.1). In Table 4.4 the most significant values of these results are summarized.

Table 4.4: Influence of initiator type and polymerization temperature on thermal properties, determined by DSC (ΔH_m: melting enthalpy (average ± standard deviation) and PCM content) and by TGA ($T_{5\%}$: temperature corresponding to 5% of weight loss; T_{on1} and T_{on2}: extrapolated onset temperature; and weight loss). PCM-Bp80 and B-Bp80 results are also listed for comparison.

Sample	ΔH_m (J/g)	PCM content (wt.%)	$T_{5\%}$ (ºC)	1st stage		2nd stage
				T_{on1} (ºC)	Weight Loss (%)	T_{on2} (ºC)
PCM - Bp80 *	174.4 ± 0.9	69.3	181.2	199.7	70.2	351.6
PCM - Bp70	178.1 ± 8.8	71.1	172.4	190.1	70.8	347.7
PCM - Aibn65	207.8 ± 7.6	82.6	175.5	195.2	80.2	361.8
PCM - Trig48	181.1 ± 5.3	72.2	172.2	188.4	69.7	354.4
PCM - Trig40	183.5 ± 4.6	73.1	168.5	184.4	71.4	361.3
B - Bp80	---	---	278.3	126.7	1.9	345.5
B - Trig48	---	---	280.2	103.9	2.3	344.0
B - Trig40	---	---	284.0	99.4	2.7	344.2

* PCM-Bp80: sample previously presented

From the analysis of this table, it is obvious that the influence of the initiator type and temperature is, one again, not very relevant. With the exception of sample PCM-Aibn65 that exhibits the highest ΔH_m (above 200 J/g) and PCM content (around 83 %), as well as the highest value of weight loss in the first degradation stage (around 80 %). Additionally, this sample also presents the lowest final monomer conversion, near 92%, while the other samples containing octadecane showed values around 97 % (Figure 4.5). This lower monomer conversion could be responsible for a reduction of the quantity of produced copolymer and for an increase in the percentage of octadecane of the sample (the unreacted monomers are removed during the microcapsules washing or drying process). However, this may not be the only cause for the smaller production of copolymer. Indeed, the properties of the initiators can also be associated to this behaviour. As mentioned before, from the three initiators, the AIBN is the only azo initiator that, compared to BPO, has higher water solubility (350 mg/L at 25 ºC for AIBN [29] versus 9.1 mg/L for BPO [30]). Thus, for AIBN, more free radical can be produced in the aqueous phase, which probably react with the monomers that diffuse from the dispersed phase instead of react in the droplet interface to form the shell of the microcapsules.

The value of 83 % of PCM content and 208 J/g of ΔH_m obtained for sample PCM-Aibn65 appears to be an excellent result of heat storage capacity. However, as mentioned above, these results seems to reveal the lower formation of copolymer. Therefore, it will be very important to check the performance these microcapsules when incorporated on textile substrates. Nonetheless, it should be pointed out that, contrary to the results of Li *et al.* [25], who were not able to prepare well-defined microcapsules based on styrene and acrylic monomers using AIBN at the range of temperatures from 65 ºC to 80 ºC [25]. Here, the octadecane was successfully encapsulate using this initiator at a reaction temperature of 65 ºC.

In conclusion, the study of the influence of initiator type and polymerization temperature revealed that, with the exception of sample PCM-Aibn65, the tested conditions did not have a significant influence on the morphology of the microcapsules, PCM content or thermal stability. However, the monomer conversion curves showed some major differences. The results of monomer conversion as a function of time confirm the importance of the reaction temperature and of the half-life decomposition temperature of the thermal initiator when using the developed microencapsulation procedure. All the microcapsules containing octadecane, presented in these section, were incorporated onto textile fibres and their performance studied (Chapter 5).

As a result, it was decided to continue using the BPO as thermal initiator and 80 ºC as the reaction temperature. Indeed, this temperature corresponded to the fastest polymerization rate and it did not compromise the thermal performance of the microcapsules containing octadecane. As for the reaction time, it was decided to shorten the reaction to 3.5 hours. Since for these conditions, the monomer conversion curve (Figure 4.6 (a)) shows that the conversion value tend to stabilize after around 2 hours and this reaction time seems to guaranty a high monomer conversion. Moreover, although not discussed in this section, the decision to continue to use BPO at 80 ºC to perform the following experiments was also based on the results from the impregnation tests, where the microcapsules PCM-Bp80 revealed the best thermo-performance.

4.3.3 Influence of the monomers proportions

This study follows the work presented in the previous section, where the type of initiator and the reaction temperature and time were established. Once defined these parameters, the following step was to test different monomers proportions (MMA, BA and MAA) in the

monomer mixture, preserving the crosslinkers quantities (5 wt.% EGDMA and 5 wt.% PETRA relative to the total weight of monomers).

Table 4.5 lists the percentages of each monomer used this new series of experiments. The formulation of PCM-Bp80 (Table 4.1 – 93 wt.% of MMA; 6 wt.% of BA; and 1 wt.% of MAA) was taken as starting point. Since the MMA is the dominant component of the monomers mixture, it was decided to decrease its quantity to 85 wt.% and then to 75 wt.%, either by increasing the amount of BA or by increasing the amount of MAA. To reach these MMA percentages:

- the BA was firstly increased to 14 wt.% and, subsequently, to 24 wt.%, maintaining the amount of MAA (experiment BA**14**-MAA1 and BA**24**-MAA1);

- alternatively, the MAA was increased to 9 wt.% and then to 19 wt.%, maintaining the amount of BA (experiment BA6-MAA**9** and BA6-MAA**19**);

An additional experiment was performed keeping the highest percentages of BA and MAA (24 wt.% and 19 wt.%, respectively) and, naturally, decreasing MMA (experiment BA**24**-MMA**19**). Finally, two experiments using only MMA (MMA100) and BA (BA100) were carried out. The experiment using MAA as the only monomer can not performed, due to the high water solubility of this monomer (89 g/L at 25 ºC [19]). The developed procedure of suspension polymerization is not adequate to produce microcapsules using a monomers mixture miscible with water, since the oil-in-water emulsion could not be formed.

Table 4.5: Series of experiments carried out to study the influence of monomers proportions.

Experiment	**Monomers**		
	MMA (wt.%)	BA (wt.%)	MAA (wt.%)
PCM - Bp80 *	93	6	1
BA14 - MAA1	85	**14**	1
BA24 - MAA1	75	**24**	1
BA6 - MAA9	85	6	**9**
BA6 - MAA19	75	6	**19**
BA24 - MAA19	57	**24**	**19**
MMA100	**100**	0	0
BA100	0	**100**	0

* PCM-Bp80: sample previously presented (monomers mixture of MMA/BA/MAA with 93/6/1 wt.%)

For all these experiments, the monomer conversion-time curves obtained during the suspension polymerization were explored and the properties of the microcapsules studied. Finally, it should be mentioned that the microcapsules produced with different monomers proportions will be further incorporated into the textiles in order to evaluate their performance.

Monomer conversion curves

The effect of the monomers proportions was initiated by analysing the curves of monomer conversion as a function of time (Figure 4.11), like in the above section.

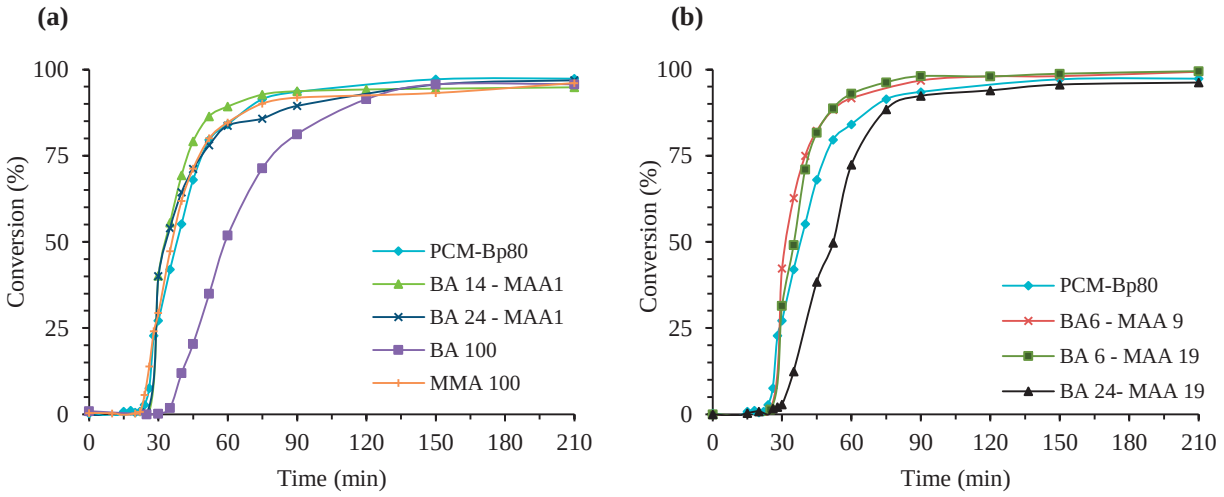


Figure 4.11: Monomer conversion as function of time for the suspension polymerization carried out with different monomers proportions: (a) experiments increasing the amount of BA and with 100 wt.% of MMA; (b) experiments increasing the amount of MAA. The experiment PCM-Bp80 (monomers mixture of MMA/BA/MAA with 93/6/1 wt.%) is plotted in both graphs for comparison. See Table 4.5 for details about their composition.

When the monomer conversion curves of homopolymers (experiment BA100 and MMA100) is compared, a distinct profile is observed (see Figure 4.11 (a)). The suspension polymerization performed with 100 % of BA exhibits the lower conversion rate. This result was not the one initially expected, since the coefficient propagation rate of BA is higher than MMA [23,31]. In general, the reaction kinetics in suspension polymerisation shows good agreement with bulk phase kinetics [32]. However, in this study, besides the monomers, crosslinkers and the initiator, the octadecane is also present in the dispersed phase, which can act as a diluent and change the reaction kinetic [32]. Additionally, this behaviour can be also influenced by the different affinity of the monomer and the octadecane or by different solubility of BPO in MMA and in BA.

Concerning the remaining experiments represented in Figure 4.11 (a), an identical profile to that of sample MMA100 was identified. Even the curve profile of the sample in which the amount of BA was increased up to 24 wt.% (experiment BA24-MAA1) is similar. Most likely, because the variation on the monomers proportions was not different enough to create a distinct curve profile.

As for Figure 4.11 (b), a tendency to slightly increase the rate of reaction as the proportion of MAA increases was observed. The coefficient propagation rate of MAA is higher than that of MMA [33] and, thus the obtained behaviour was the one expected. Moreover, it is described that in suspension polymerization the water solubility of monomers is one of the factors that can affect the kinetics of the reaction [34] and, here, the MAA is the monomer that present highest water solubility.

From all the copolymers, the higher quantity of BA (24 wt.%) and of MAA (19 wt.%) was used in experiment BA24-MAA19. In this case, the monomer conversion curve seems to show the influence of these two monomers (see Figure 4.11 (b)). In this experiment BA24-MAA19, the polymerization rate is slower than that of BA6-MAA19 (due to its higher amount of BA and lower of MMA) and it is faster than that of BA100 (due to the presence of MAA and MMA).

In general, despite the small changes on the monomer conversion curves profile of these experiments, all of them present a high final conversion (around 95 - 98 %) after 3.5 hours.

Characterization of microcapsules

a) Chemical characterization

The chemical characterization through FT-IR spectroscopy was also implemented. However, considering that the monomers (MMA, BA and MAA) were always the same and only their proportion was changed, significant differences between the several spectra are not expected. From the three monomers, the only one that exhibits a distinct characteristic peak is MAA, since it is a carboxylic acid (which shows a broad band at 2930 cm^{-1} attributed to the O-H stretching vibration - see monomers spectra in Figure 3.9 section 3.3.1). Therefore, besides the confirmation of the presence of acrylic shell and of octadecane, it was also searched for the presence of OH group in order to confirm an acrylic shell with a different composition, specifically in the microcapsules prepared with the highest amounts of MAA (sample BA6-MAA19 and BA24-MAA19).

In Figure 4.12, FT-IR spectra of the samples corresponding to the most significant differences in monomers mixtures are represented (see remaining spectra in Figure B.8 Appendix B). For all them, a configuration identical to that of sample PCM-Bp80 was identified. The peak assignments of these spectra are similar to those obtained for the pure octadecane and the respective acrylic microcapsules, as stated in section 3.3.1. Even in the spectra of sample BA6-MAA19 and BA24-MAA19 (prepared with highest amount of MAA) the obtained patterns are identical and only a slight difference around the wavenumber of 3500 cm^{-1} - 3000 cm^{-1} is observed (see enlargement in Figure 4.12). However, it is difficult to confirm that this difference is originated by the peak corresponding to O-H stretching vibration of the MAA due to its higher amount. If present, the characteristic peak of MAA can also be overlapped with the peak ascribed to C-H stretching vibration of octadecane (that appears between 2900 cm^{-1} - 2850 cm^{-1}). Accordingly, through FT-IR spectroscopy analysis, it is not possible to confirm differences between the compositions of the polymeric shells. Nevertheless, the presence of octadecane and of acrylic microcapsules is identified.

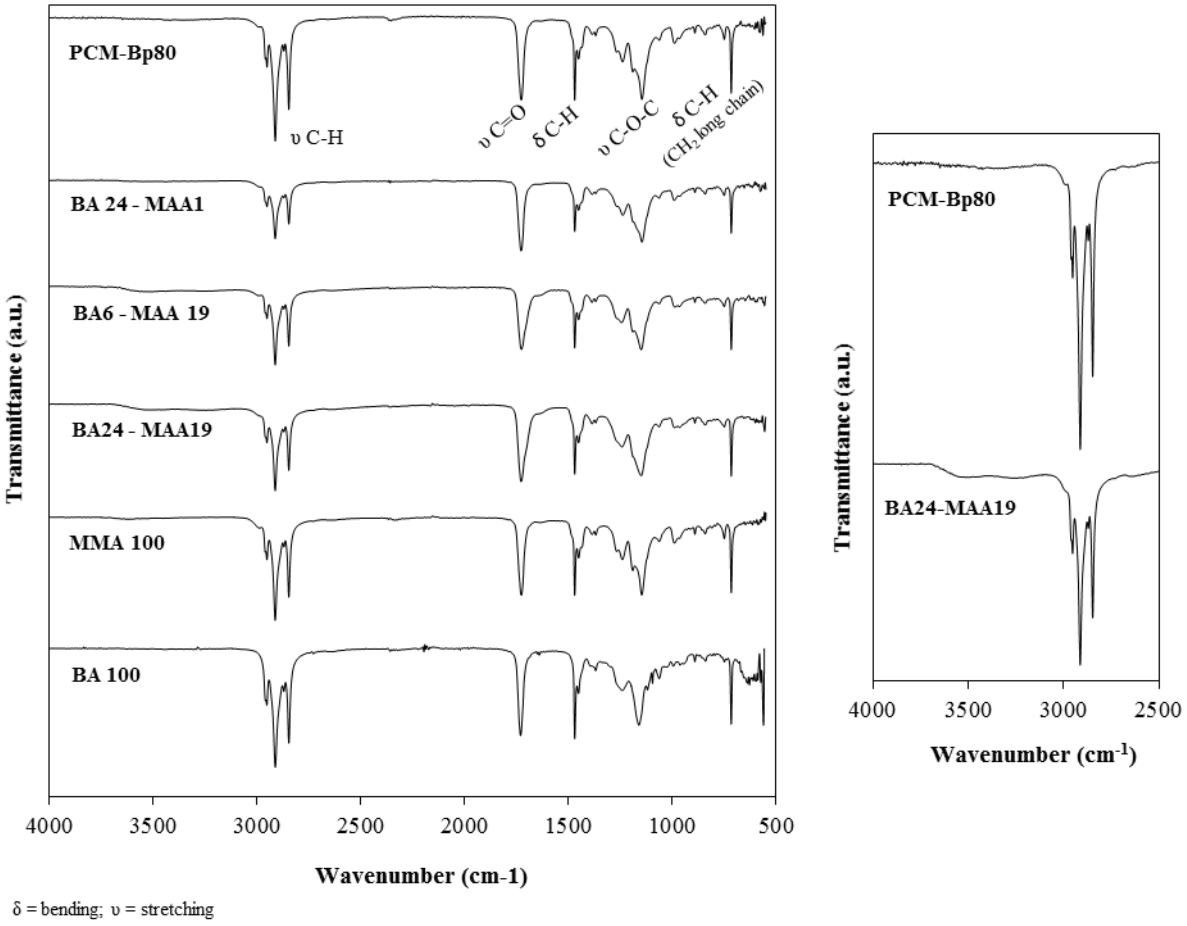


Figure 4.12: Influence of monomers proportions on the FT-IR spectra, experiments listed in Table 4.5. Spectrum of sample PCM-Bp80 (monomers mixture of MMA/BA/MAA with 93/6/1 wt.%) is represented for comparison.

b) Morphological characterization

The morphological analysis, performed by SEM, shows that in most of the cases spherical microcapsules with a rough surface were produced, similar to sample PCM-Bp80 (Figure 4.13 (a)). Their structure is illustrated in Figure 4.13 (b) and (c) for sample BA24-MAA19 and MMA100, respectively (additional micrographs are presented in Figure B.9, Appendix B). The only exception, as Figure 4.13 (d) illustrates, was attained for sample BA100, prepared with only BA crosslinked with EGDMA and PETRA. This result was already expected, since the T_g of the homopolymer of BA is very low (-54ºC), which confers to the obtained microcapsules very flexible shells that easily collapse during the SEM analysis, due to the applied vacuum.

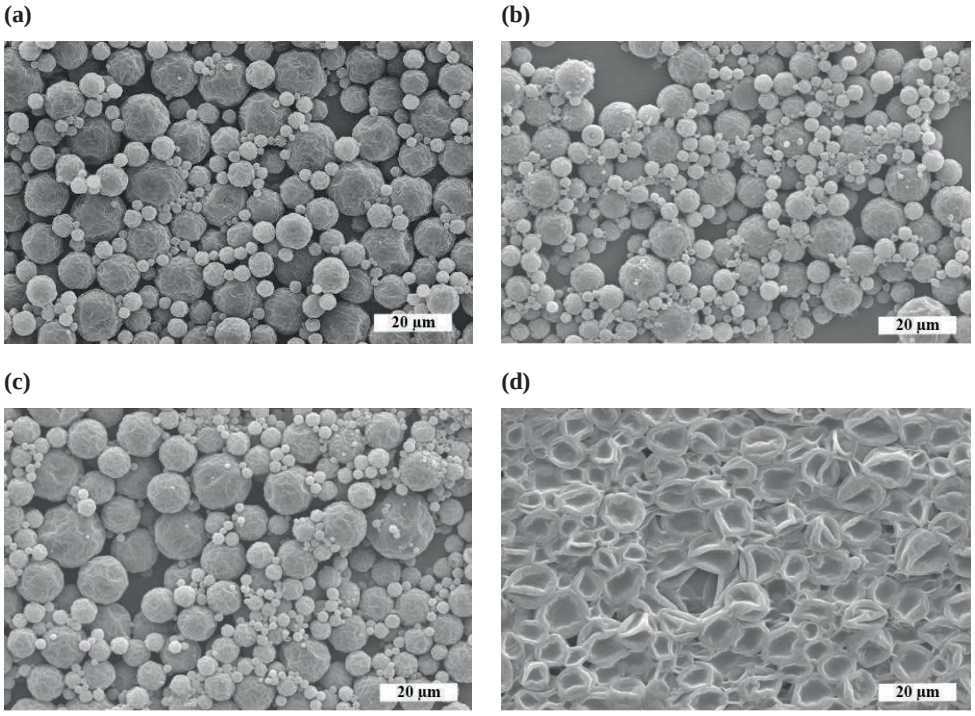


Figure 4.13: SEM micrographs of microcapsules prepared with different monomers proportions. Samples: (a) PCM-Bp80; (b) BA24-MAA19; (c) MMA100 and (d) BA100 (magnification x1000). See Table 4.5 for details.

In order to complement this morphological characterization, particle size analysis was performed and the obtained values of mean diameter ($D_{4,3}$) are depicted in Figure 4.14. Additionally, as illustrated in Figure B.10 Appendix B, all the samples exhibited identical bimodal size distributions, similar to that of sample PCM-Bp80.

The values of the $D_{4,3}$ are mostly around 11 - 12 µm, corresponding the smallest size to the microcapsules prepared with the highest quantity of MAA and lowest quantity of BA (BA6-

MMA19), while the largest size was obtained for the microcapsules with 100 % of BA (BA100), around 20 µm. However, when the amount of BA was fixed, it was observed that with the increase of MAA the mean diameter decreased from 12.6 µm in sample PCM-Bp80 (1 wt.% of MAA), to 11.4 µm in BA6-MAA9 (9 wt.%) and, finally, to 10.2 µm in BA6-MAA19 (19 wt.%). Sanchez *et al.* [9] also described this trend of microcapsules size when MAA was added to the mixture of MMA and MA. The authors suggest that the decrease in particle size could be caused by the reduction in the interfacial tension between the dispersed and the water phase, which MAA monomer provides due to its carboxyl group [9]. Additionally, Qiu *et al.* [14] described that the hydrophilic nature of the polymeric shell, attained by the presence of a carboxyl group, usually causes a greater stability of the polymer droplet in the encapsulation process, leading to a decrease in coalescence of the polymer droplets and, therefore, an improved dispersion of the microcapsules with a hydrophilic nature shell [14,35].

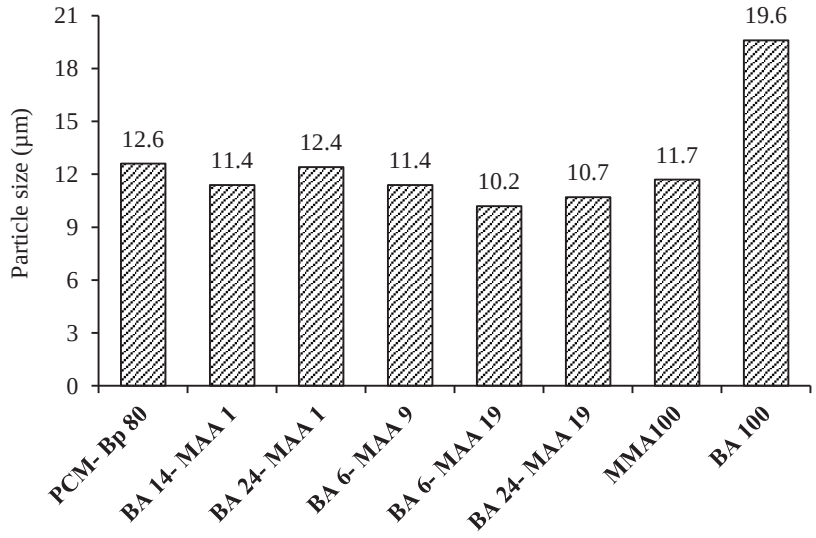


Figure 4.14: Influence of monomers proportions on the particle size ($D_{4,3}$), experiments listed in Table 4.5. Samples PCM-Bp80 (monomers mixture of MMA/BA/MAA with 93/6/1 wt.%) is represented for comparison.

The much larger mean diameter obtained for BA100 could be triggered by the lower hydrophilic nature of this monomer, compared with the MMA and MAA, which probably creates the opposite effect than that of the monomer MAA (described above). Nevertheless, in the microcapsules prepared by increasing the amount of BA (BA14-MAA1 and BA24-MAA1), this tendency in the particles size was not detected.

c) Thermal characterization

The summary of thermal analysis presented in Table 4.6 reveals that all the enthalpy values achieved by DSC are quite similar, whereas the thermal stability achieved by TGA are distinct (supplementary information in Table B.7 and B.8 Appendix B). In fact, for all the samples, values of ΔH_m and PCM content around 175 J/g and 70 wt.% were achieved, respectively. These results suggest that, despite the relevant changes in the microcapsules composition, the relation between the amount of encapsulated octadecane and the formed copolymer is identical. The DSC curves that originated the values listed in this table presented the characteristic profile of the microcapsules PCM-Bp80 (see Figure B.11 in Appendix B).

Table 4.6: Influence of monomers proportions on thermal properties, determined by DSC (ΔH_m: melting enthalpy (average ± standard deviation) and PCM content) and determined by TGA ($T_{5\%}$: temperature corresponding to 5% of weight loss; T_{on1} and T_{on2}: extrapolated onset temperature; and weight loss).

Sample	ΔH_m (J/g)	PCM content (wt.%)	$T_{5\%}$ (ºC)	1st stage		2nd stage
				T_{on1} (ºC)	Weight Loss (%)	T_{on2} (ºC)
PCM -Bp80 *	174.4 ± 0.9	69.3	181.2	199.7	70.2	351.6
BA14 - MAA1	173.7 ± 0.9	69.4	165.9	185.8	68.0	362.9
BA24 - MAA1	176.3 ± 6.6	70.4	164.5	183.6	69.3	366.0
BA6 - MAA9	180.5 ± 3.1	72.2	204.4	222.8	70.4	379.3
BA6 - MAA19	180.0 ± 2.8	72.0	222.5	240.4	69.9	384.2
BA24 - MMA19	176.5 ± 1.0	70.7	197.0	214.5	68.4	377.7
MMA100	184.8 ± 5.6	73.9	175.5	193.8	73.3	355.9
BA100	167.4 ± 9.1	67.8	136.4	134.6	65.7	371.1

* PCM-Bp80: sample previously presented (monomers mixture of MMA/BA/MAA with 93/6/1 wt.%)

Regarding the thermal stability of the microcapsules containing octadecane, themoanalytical curves with slightly different profiles were obtained (see Figure 4.15). In Figure 4.15 (a) are represented the TGA data obtained for the microcapsules prepared by increasing the amount of BA in the monomer mixture, together with sample MMA100. In Figure 4.15 (b) are shown the data obtained for the microcapsules produced by increasing the amount of MAA.

As previously mentioned, the microcapsules prepared in the experiment BA100 presented a very flexible shell that collapsed during the SEM analysis. These microcapsules also present a very low thermal stability, as observed by the considerable differences from all the other

samples (see Figure 4.15 (a) and Table 4.6). This sample exhibits a $T_{5\%}$ of around 135 ºC, whereas for the microcapsules PCM-Bp80 a temperature of 180 ºC was reached. This behaviour is probably caused by an easier evaporation of the octadecane across their shell, due to its flexibility. Property that is related with the low T_g that characterizes the BA (-54ºC for its homopolymer).

In Figure 4.15 (a), it is also observed that, when the monomers mixture of experiment PCM-Bp80 was changed by increasing BA and reducing MMA, the thermal stability of the produced microcapsules is reduced. This is probably due to the same effect as the one mentioned above for sample BA100, although with a much lower impact. The increase of BA amount seems to induce a decrease in the stiffness of the microcapsules and originate a weight loss at lower temperatures. Even so, for the experiments BA14-MAA1 and BA24-MAA1 values of $T_{5\%}$ around 165 ºC were obtained, which still permit their incorporation in textiles.

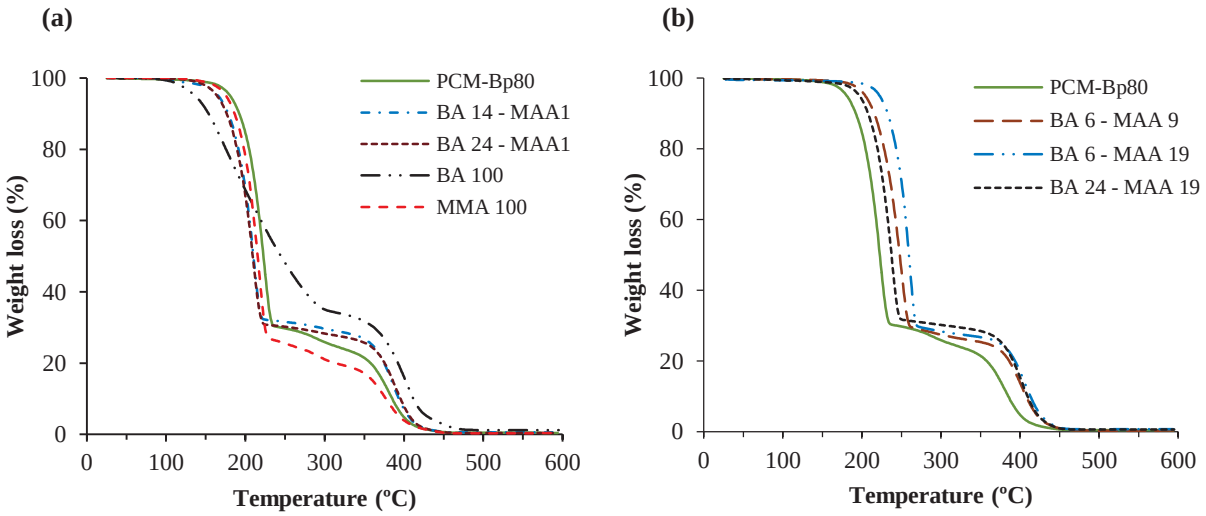


Figure 4.15: Influence of monomers proportion on thermal stability. TG curves of (a) microcapsules prepared increasing the amount of BA and microcapsules MMA100; and (b) microcapsules prepared increasing the amount of MAA. Samples PCM-Bp80 (monomers mixture of MMA/BA/MAA with 93/6/1 wt.%) is plotted for comparison.

When the amount of MAA on the monomers mixture was increased, the thermal stability of the microcapsules was improved, as depicted in Figure 4.15 (b). The values gathered in Table 4.6 show that the $T_{5\%}$ of sample PCM-Bp80 increase from around 180 ºC, to 204 ºC for sample BA6-MAA9 and to 223 ºC for sample BA6-MAA19. Contrary to BA, MAA is a monomer with a high T_g (228 ºC) that seems to be responsible for the formation of microcapsules with high thermal resistance. As a result, these microcapsules are composed of a shell that creates a higher resistance and protection to the octadecane evaporation with the temperature increasing.

Additionally, for sample BA24-MAA19, a $T_{5\%}$ of 197 ºC was determined. The degradation profile of this specimen should have the contribution of both effects described for BA and MAA. Nevertheless, $T_{5\%}$ is even higher than the value of sample PCM-Bp80 (that was 180 ºC).

Concerning the values of the weight loss (Table 4.6), in general, percentages around 70 % in the first degradation stage were obtained for all the samples, regardless the values of $T_{5\%}$ and degradation profile.

With the results obtained through TGA, it was confirmed that the changes in the monomers mixture produced microcapsules with a different shell composition. Despite the lower thermal stability of samples BA14-MAA1 and BA24-MAA1, all the new microcapsules containing octadecane present thermal properties suitable for their incorporation into textile substrates (except BA100). Nevertheless, it should be pointed out that their thermal stability should be as higher as possible, to guaranty a good performance during the incorporation on the textile fibres.

The study of the influence of the monomers proportion used in the mixture MMA, BA and MAA showed that, even with the applied modifications, the procedure established to encapsulate octadecane can be implemented to produce well-defined microcapsules. However, despite the similarity between their chemical structure (identified by FT-IR), morphology and PCM content, it was prepared microcapsules with different shell properties as confirmed by TGA. Once more, these new samples were incorporated into the textiles in order to verify which monomers mixture present a better performance during the incorporation process as well as a better resistance to the washing process.

4.3.4 Influence of the core material

In order to investigate if the developed encapsulation procedure is valid for other core materials, the octadecane was replaced by different compounds. These compounds were: trioctyl trimellitate (TOTM), bis(2-ethylhexyl) adipate (BEHA), dibutyl phthalate (DBP), tributyl 2-acetylcitrate (TBAC) and ethyl phenylacetate (EPA). In Table 4.7 are listed the experiments carried out in this study, together with some properties of the selected core materials. These experiments were performed following the recipe of experiment PCM-Bp80, described in Table 4.1, section 4.2.2, changing only the core material.

Among the core material selection criteria is the compound solubility in water and, consequently, its polarity. For a specific compound, the partition coefficient between water and an immiscible organic solvent (normally n-octanol) is directly related to its polarity and water

solubility. Thus, the logarithm of n-octanol/water partition coefficient (log $P_{o/w}$) was used as a quantitative measure of the hydrophilic character and, consequently, of the polarity [36]. This coefficient is also presented in Table 4.7 and the core materials are listed in descending order of log $P_{o/w}$ and, consequently, in ascending order of polarity (except the octadecane).

Table 4.7: Influence of the core material type: values of molecular weight (M_w), logarithm of n-octanol/water partition coefficient (log $P_{o/w}$), melting temperature and viscosity (at 40 ºC) of the tested materials [37, 38].

Sample	**Core material**	**M_w** [37]	**log $P_{o/w}$** [38]	**Melting point** (ºC) [37]	**Viscosity** (mPa.s)
PCM-Bp80 *	Octadecane	254.5	8.5	28	3.1
TOTM-Ac01	Trioctyl trimellitate	546.8	11.3	-43	74
BEHA-Ac01	Bis(2-ethylhexyl) adipate	370.6	6.8	-70	5.9
DBP-Ac01	Dibutyl phthalate	278.3	4.6	-35	n. a.
TBAC-Ac01	Tributyl 2-acetylcitrate	402.5	3.5	-80	n. a.
EPA-Ac01	Ethyl phenylacetate	164.2	2.1	-29	n. a.

* Sample previously presented

With this work, it was not only aimed to study the effect of the core material on the encapsulation process and on the properties of microcapsules, but also to prove the potential of the developed suspension polymerization procedure to encapsulate different compounds for diverse end applications.

Characterization of microcapsules

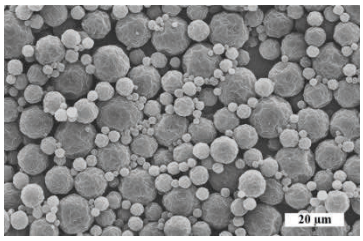
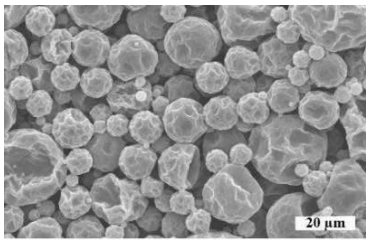
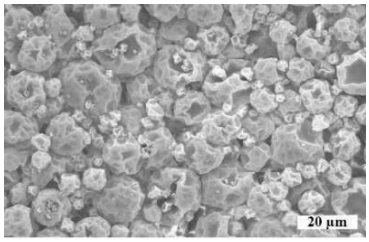
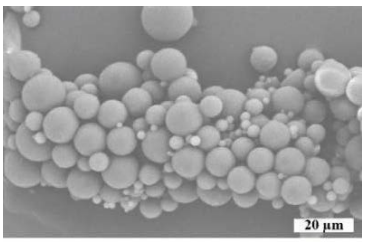
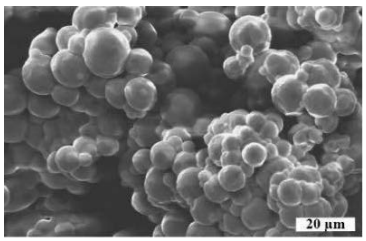
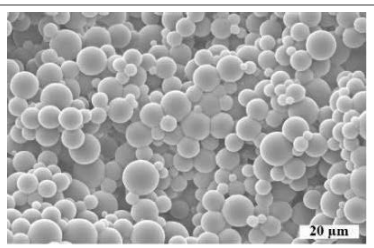
In contrast with the samples described in the previous sections and taking into account that all these experiments were performed using the same recipe as that of PCM-Bp80 (maintaining the chemical composition of the acrylic shell), their FT-IR spectra were not found relevant and thus they are not presented here. The properties of the obtained microcapsules were evaluated through morphological and thermal characterization.

a) Morphological characterization

After each experiment, the obtained suspension was analysed in order to confirm the formation of microcapsules and/or to detect the presence of agglomerates and of free core material. Contrary to the samples prepared with octadecane, in some of these experiments the presence of non-encapsulated core material was observed. Thus, some remarks about the

unwashed as well as washed samples are presented in Table 4.8. The washing process was performed as described in section 3.2.2, but here using ethanol as the washing solvent, instead of hot water. The microcapsules PCM-Bp80 has also been considered for comparison purposes.

Table 4.8: Results of the encapsulation of different core materials: unwashed samples and washed samples (images acquired by SEM, magnification x1000).

Sample	Unwashed sample	Washed sample	
PCM-Bp80	- Homogeneous suspension with individual microcapsules	- Individual and spherical microcapsules - Rough and irregular surface	
TOTM-Ac01	- Homogeneous suspension with individual microcapsules	- Individual and spherical microcapsules - Irregular surface with larger concavities	
BEHA-Ac01	- Homogeneous suspension with individual microcapsules	- Individual and spherical microcapsules - Irregular surface with larger concavities	
DBP-Ac01	- Small agglomerates - A thin layer of free oil at the surface of the reaction medium was observed	- Small agglomerates - No traces of free oil - Microcapsules with smooth shell	
TBAC-Ac01	- Large agglomerates	- Large agglomerates - Oil at the surface of the microcapsules seems to be present - Microcapsules with smooth shell	
EPA-Ac01	- Small agglomerates - A thin layer of free oil at the surface of the reaction medium was observed	- Without visible agglomerates - No traces of free oil - Microcapsules with smooth shell	

The main features of the produced samples can be summarized as follows:

- for samples TOTM-Ac01 and BEHA-Ac01, structures similar to those of PCM-Bp80 were obtained (spherical microcapsules with a rough surface). However, as illustrated by the SEM micrographs, these microcapsules present larger concavities. For both samples, as for the microcapsules containing octadecane, the analysis by SEM confirmed the presence of a core/shell structure. Figure 4.16 (a) shows a broken microcapsule of BEHA-Ac01 in a larger magnification.

- samples TBAC-Ac01, DBP-Ac01 and EPA-Ac01 present some agglomerates together with free core material. Their microcapsules are constituted by a smooth surface (identical to those of sample B-Bp80 prepared without octadecane, see Figure 4.9 (d)). The observation of agglomerates and free core material in some specimens, even after the washing process, suggest low encapsulation efficiency or an excessive amount of core material. Additionally, the smooth shell found for these samples could indicate that microcapsules with a core/shell structure were not formed. This fact was confirmed by the SEM analysis of their cross-sections, as illustrated in Figure 4.16 (b). This suggests that, if present, the core compound was not really enclosed by a shell but dispersed in a polymeric matrix.

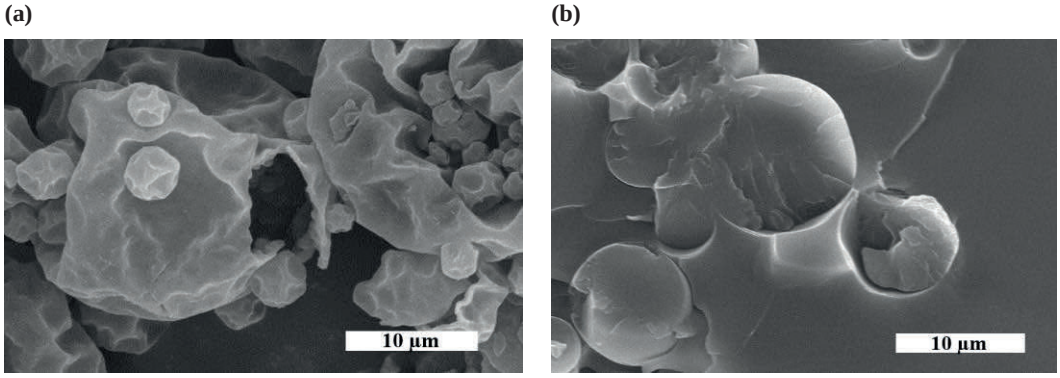


Figure 4.16: SEM micrographs of (a) broken microcapsule of BEHA-Ac01 (the sample was previously crushed) and (b) cross-section of microcapsules EPA-Ac01 (the sample was previously fixed in an epoxide matrix [39] and then broken in liquid nitrogen) (magnification x3000).

Based on the properties of the core materials (Table 4.7), the analysis of these results suggest that compounds possessing low polarity (higher values of log $P_{o/w}$) form a core/shell structure, similar to that of sample PCM-Bp80, whereas those with lower log $P_{o/w}$ do not exhibit this structure. As discussed in section 3.3.1, the formation of core/shell structure requires a

difference between the polarity of monomers and the core material [9]. For the applied monomers mixture, the log $P_{o/w}$ values of its monomers are: 1.3 for MMA [20]; 2.3 for BA [21] and 0.9 for MAA [19]. Therefore, in the case of samples TBAC-Ac01, DBP-Ac01 and EPA-Ac01 (corresponding to the core materials with higher polarity and log $P_{o/w}$ values inferior to 4.6) the driving force between the polarity of the monomers and the core is not, probably, sufficient to promote their phase separation. This result seems to imply that the core polarity has a key influence on the microencapsulation mechanism (independently, for example, of its molecular weight).

As before, the morphology studies were complemented by particle size analysis. It should be pointed out that the samples TBAC-Ac01 and DBP-Ac01 exhibit many agglomerates, even after the washing step, and thus they were not considered for particle sizing assessment. The size distribution curves of samples TOTM-Ac01, BEHA-Ac01 and EPA-Ac01 are presented in Figure 4.17, together with sample PCM-Bp80. The corresponding values of mean diameter (the value of $D_{4,3}$) and percentile diameters (D_{10}, D_{50} and D_{90}) are registered in Table 4.9.

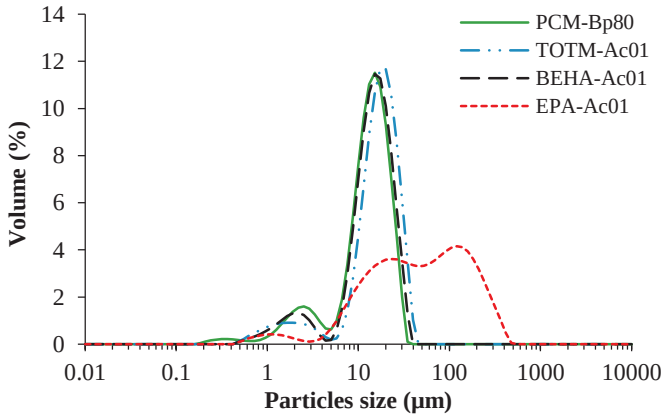


Figure 4.17: Influence of core material on the particle size distribution, sample TOTM-Ac01; BEHA-Ac01 and EPA-Ac01 (PCM-Bp80 was represented for comparison).

Likewise sample PCM-Bp80, the samples TOTM-Ac01 and BEHA-Ac01 present a bimodal size distribution, with a small peak revealing the existence of small particles. The latter are attributed, as mentioned before, to the process of secondary nucleation, confirming that this phenomenon is not directly related with the type of core material. EPA-Ac01 showed a much broader size distribution with three peaks not very clear, which can be a consequence of agglomeration.

Analysing now the values of Table 4.9, it can be seen that the mean particle sizes varied with the type of core material. Furthermore, the average particle size may be related to the viscosity of the different materials: a higher core viscosity leads to larger microcapsules. As Table 4.7 shows, the viscosity decreases from TOTM, to BEHA and to PCM, while their mean diameter also decreases. Sample EPA-Ac01 is not included in this analysis since its size distribution could be masked by the presence of agglomerates.

Table 4.9: Influence of core material on the values of mean diameter ($D_{4,3}$), D_{10}, D_{50} and D_{90}.

Sample	**Mean diameter, $D_{4,3}$** (µm)	**D_{10}** (µm)	**D_{50}** (µm)	**D_{90}** (µm)
PCM-Bp80	12.6	2.6	12.5	21.3
TOTM-Ac01	18.1	3.8	18.1	30.6
BEHA-Ac01	15.8	3.1	15.4	26.6
EPA-Ac01	86.5	9.2	50.3	218.9

b) Thermal characterization

The thermal properties of the sample prepared using the different core materials were only evaluated by TGA (Figure 4.18 and Table 4.10). Regarding these results, it was thought more convenient to divide the TG curves in two groups: those that resulted in microcapsules with a well-defined core/shell structure, samples TOTM-Ac01, BEHA-Ac01 and PCM-Bp80, and the corresponding core materials (Figure 4.18 (a)); and those where this structure was not identified, samples DBP-Ac01, TBAC-Ac01 and EPA-Ac01, together with their core materials (Figure 4.18 (b)).

As expected, TG curves profiles revealed that all pure compounds present only one stage of weight loss, while the microcapsules exhibited two stages. The only degradation stage visualized for the several pure core materials present an analogous profile to that of octadecane. However, for each core a different range of degradation temperature was determined (see Table 4.10). In the case of the microcapsules, and as already noted, the first stage is originated by the weight loss of core material whereas the second one results from the degradation of the polymeric shell.

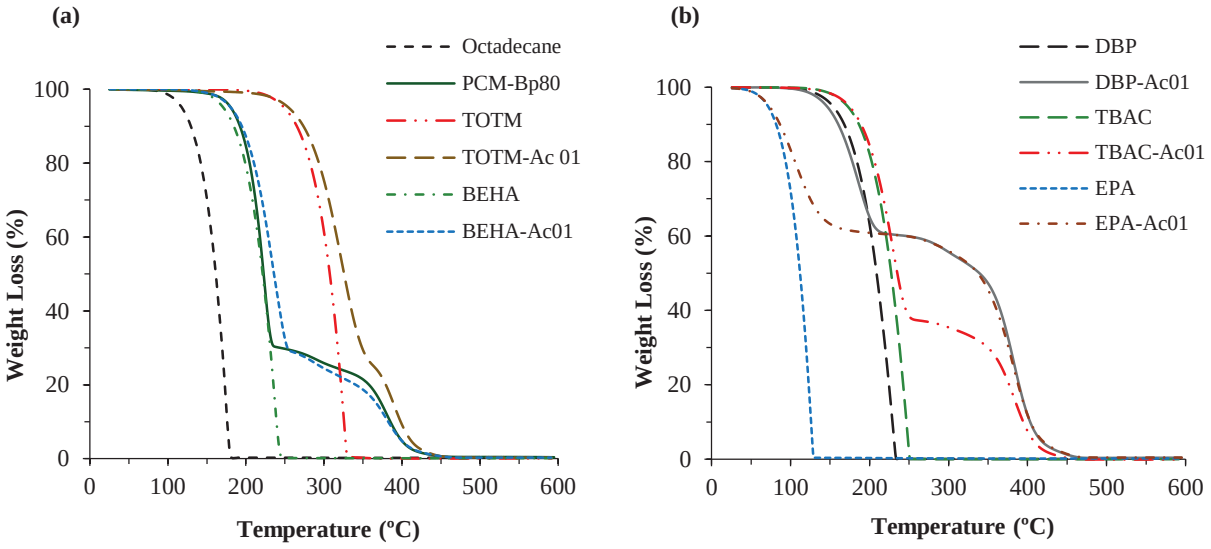


Figure 4.18: TG curves of pure core materials and respective microcapsules, (a) for the core octadecane, TOTM and BEHA and (b) for the core DBP, TBAC and EPA.

Comparing the values of $T_{5\%}$ and $T_{10\%}$ of pure TOTM and BEHA with the corresponding values of their microcapsules (TOTM-Ac01 and BEHA-Ac01), it was observed that the degradation temperature of these pure compounds is slightly lower than that of the microcapsules, around 10 ºC (see Table 4.10). The same trend was found for PCM-Bp80, although the temperature difference was much larger (around 60ºC). Unlike PCM-Bp80, for the samples TOTM-Ac01 and BEHA-Ac01 the shell of the microcapsules is not capable of creating additional protection to their core degradation, probably due to higher degradation temperatures of TOTM and BEHA. In fact, pure TOTM and BEHA show a $T_{5\%}$ of 248.9 ºC and 171.1 ºC, respectively, whereas that of octadecane is only 117.8 ºC.

Additionally, in the TG curve of sample TOTM-Ac01, the end of the first degradation stage is not as clear as that of sample BEHA-Ac01 and PCM-Bp80. Nonetheless, their percentages of weight loss can be considered identical, varying between 70.2% for PCM-Bp80 and 74.4% for TOTM-Ac01. These results can suggest that the quantities of encapsulated core material are identical.

Table 4.10: Thermogravimetric data of microcapsules prepared with different core materials ($T_{5\%}$ and $T_{10\%}$: temperatures corresponding to 5% and 10% of weight loss; T_{on1} and T_{on2}: extrapolated onset temperatures of the first and second degradation stage; Weight Loss: weight loss (%) in each degradation stage).

Sample	$T_{5\%}$	$T_{10\%}$	1st stage		2nd stage	
			T_{on1}	Weight Loss	T_{on2}	Weight Loss
	(ºC)	(ºC)	(ºC)	(%)	(ºC)	(%)
PCM	117.8	129.4	145.0	99.8	--	--
PCM-Bp80	181.2	192.2	199.7	70.2	351.6	29.3
TOTM	248.9	265.4	288.9	99.7	--	--
TOTM-Ac01	254.8	273.6	279.5	74.4	375.5	25.1
BEHA	171.1	184.8	202.0	99.9	--	--
BEHA-Ac01	180.6	195.0	200.1	71.2	354.0	28.5
DBP	153.1	167.8	184.7	99.9	--	--
DBP-Ac01	145.3	160.7	150.4	39.5	347.9	60.1
TBAC	171.5	186.9	207.6	99.9	--	--
TBAC-Ac01	173.6	189.6	193.1	62.8	352.2	37.2
EPA	71.1	82.0	97.7	99.4	--	--
EPA-Ac01	72.7	86.9	72.1	38.3	340.6	61.1

The second group of TG curves, corresponding to pure DBP, TBAC and EPA and respective microcapsules, are represented in Figure 4.18 (b). As mentioned before, for these microcapsules the core/shell structure was not formed and free oil was detected in the samples, even after the washing procedure. The difference between the $T_{5\%}$ of these pure compounds and the respective values for the microcapsules are quite small (between 1 ºC and 2 ºC), which could indicate that the shell does not create resistance to core weight loss.

Regarding their percentage of weight loss in the first stage, corresponding to the core degradation, it is clear that their values are much smaller than those of the samples of the previous group, ranging from 38 % to 63 %. These smaller results showed that some of the oil initially used was not encapsulated (as visualized in the unwashed samples) and/or was removed during the washing process. In fact, TGA results confirm the presence of the core compound in these samples but, it is not possible to know if the detected core material is really entrapped in the polymeric matrix or it is simply adsorbed and free at their surface shell.

Summing up, the replacement of octadecane by other core materials originated different types of microcapsules with distinct properties, leading to the conclusion that the core material type highly affects the encapsulation success, the microcapsules size as well as their thermal properties. Microcapsules with a well identified core/shell structure were only obtained for systems with the core materials with low water solubility and polarity (i.e. log $P_{o/w}$ values higher than 5). Therefore, considering that the formation of the core/shell structure improve the encapsulation efficiency of the core material, these results suggest that the core material polarity restrict the use of the developed microencapsulation procedure.

4.4 CONCLUSIONS

In this chapter, the modification of different experimental conditions of the suspension polymerization procedure is described. These changes aimed to explore and, eventually, improve the process of encapsulation as well as to obtain microcapsules with enhanced properties.

Based on the results of Chapter 3, all the microcapsules were prepared by using MMA, BA and MAA as monomers, EGDMA and PETRA as crosslinkers, PVA as stabilizer and using the core/monomers mass ratio of 2. However, these experiments were carried out in a new experimental setup (available at Devan-Micropolis and that is composed of a larger reactor equipped with an external circulating heating bath), being the obtained microcapsules compared with ones prepared at University of Coimbra. Microcapsules containing octadecane were successfully prepared using these new conditions. Nevertheless, a larger diameter in the microcapsules and a lower ΔH_m were identified.

The study of the influence of the initiator type and polymerization temperature revealed that the polymerization reaction using the three selected initiators (BPO, AIBN and Trig23) at respective 10 hours half-life temperature present identical monomer conversion rates and that, as expected, with the increase of the reaction temperature the polymerization rate also increases. Additionally, it was also demonstrated that the presence of octadecane decreases the reaction rate. Therefore, it was found out that the time-monomer conversion profile was influenced by the initiator type, the reaction temperature and also by the presence or absence of octadecane. Despite the variations in the monomer conversion profiles, the microcapsules exhibited only slight differences between them with respect to morphology and thermal properties. In general,

the microcapsules showed a ΔH_m around 175 J/g, a PCM content of 70 % and $T_{5\%}$ around 170 ºC, being the mean particle diameter around 12 µm. These characteristics make them suitable to incorporate into the textiles, as detailed in the next chapter. From these results, it was decided to continue to use BPO as thermal initiator and to carry out the reactions at 80 ºC but only during 3.5 hours.

The shell composition was investigated by preparing copolymers of MMA, BA and MAA with different monomers proportions. Herein, it was shown that the rates of suspension polymerization performed by using a monomers mixture with increasing amounts of BA are slower than those with increasing amounts of MAA or MMA. The produced microcapsules presented a similar characteristics identified by FT-IR, SEM and DSC. Nonetheless, the particle size showed a little dependency on the monomer formulation. Additionally, the thermal analysis carried by TGA revealed that the shells composed of higher amounts of BA present low thermal stability ($T_{5\%}$ of 136 ºC), whereas the shells with higher amounts of MAA present greater stability (reaching $T_{5\%}$ of 223 ºC). These differences demonstrated the formation of microcapsules with distinct acrylic shells.

Finally, the procedure selected to encapsulate octadecane was applied to different core materials. Here, it was confirmed that the compound polarity highly affects the microcapsule structure: compounds with lower polarity (about log $P_{o/w} > 4.6$) resulted in microcapsules with a well-defined core/shell structure; whereas for higher polarities this structure was not identified. Moreover, some relationship between particle size and core viscosity was found: core materials with higher viscosity lead to larger microcapsules.

The overall results showed that acrylic microcapsules can be prepared by suspension polymerization following the proposed procedure and using a variety of thermal initiators, reaction temperatures, monomers proportions and core materials. As a result, a wide range of microcapsules were prepared that apparently exhibit adequate characteristics to be incorporated into textile materials. The final decision about the most adequate to be incorporated onto the fibres in order to produce thermo-regulating textiles, will be taken in the following chapter.

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CHAPTER 5

INCORPORATION OF MICROCAPSULES INTO TEXTILE SUBSTRATES: CHARACTERIZATION AND PERFORMANCE

ABSTRACT

This chapter deals with the incorporation into woven substrates of acrylic shell microcapsules containing octadecane, which were obtained using different reaction conditions (as discussed in the previous chapter). These microcapsules were impregnated on the surface of polyester and cotton fibres using the technique of padding. SEM and DSC were used to investigate the response of the different microcapsules to the impregnation process, namely to the pressure of the rolls applied in the foulard as well as their thermo-performance. The textiles were subsequently submitted to a washing process and characterized, once again, to evaluate the microcapsules washing resistance. Additionally, two types of industrial microcapsules were submitted to the same tests for comparison purposes.

The acrylic shell microcapsules revealed a similar performance to that of the industrial microcapsules, with the added value of being a formaldehyde-free product. Moreover, the washing tests suggested that the shell composition is a decisive parameter with regard to the washing resistance. It was demonstrated that the presence of carboxyl groups in the microcapsules shell favour their fixation onto the textile fibres.

5.1 INTRODUCTION

The knowledge on the microcapsules performance after their incorporation into the textile substrates is of utmost importance in the context of this work. This performance will determine the ability to successfully produce thermo-regulating functional materials. As described in section 2.1.3, microcapsules containing PCMs can be incorporated in a variety of substrates, like home textiles (e.g. mattress ticking and bed linen), footwear, technical textiles, apparel or even in substrates of foam (normally used to produce mattresses and pillows). In all these materials, the microcapsules cannot be broken during the process of incorporation and they need to be well fixed in order to avoid their release.

In the present study, it was aimed to produce textile substrates with thermo-regulating properties but also obtain substrates capable of preserve these properties after several cycles of washing, through a high fixation of microcapsules on the textile fibres. Therefore, the acrylic microcapsules prepared using different reaction parameters (fully characterized in the previous chapter) were impregnated onto the surface of textile fibres and their resistance to the washing

process was tested. Additionally, in order to detect the behaviour of these microcapsules in distinct substrates, two types of fabrics were selected:

- a woven composed of 100 % cotton, whose the main component is cellulose (reaching a value of around 95 %), a polysaccharide with a linear chain of β(1→4) linked D-glucose (see Figure 5.1 (a)) [1, 2].

- a polyester woven of 100 % poly(ethylene terephthalate) (PET) (see Figure 5.1 (b)), a semi-aromatic copolymer that can be prepared through the reaction of polycondensation of terephthalic acid with ethylene glycol. This is the predominant polyester used for the textile fibres production [3,4].

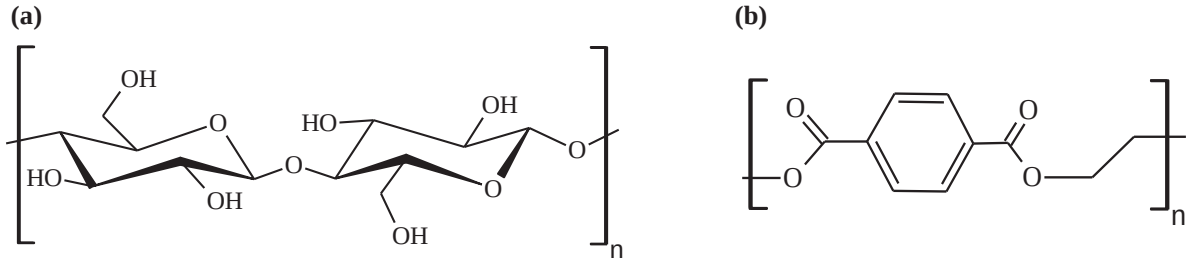

Figure 5.1: Chemical structure of (a) cellulose and (b) poly(ethylene terephthalate) (PET).

In this work, the microcapsules were impregnated into the textile substrates using the technique of padding and using the current technology of Devan Chemicals [5,6]. As described before, this technology promotes the microcapsules fixation onto the textile fibres without using binders. This patented methodology is based on the production of microcapsules with reactive groups in their shell, in order to form durable bonds with the functional groups of the textile fibres, and based on the addition of a bi-functional coupling agent to react with the microcapsules and with the fibres [5,7].

The composition of the finishing formulation was supplied by Devan Chemicals, being one of the formulations presently used to incorporate microcapsules containing PCM in the selected fabrics of polyester and cotton woven. The implemented procedure consisted of applying this formulation (in which are included, among others, the microcapsules and coupling agent) using a foulard and a nip roll pressure of 4 bar (the pressure normally used as standard in industrial environment). To finish this process, the impregnated substrates were submitted to a drying and curing stage using the temperature of 140 ºC. Details about the finishing formulation will be given further on (section 5.2.3) together with a detailed description of microcapsules impregnation procedure.

As already mentioned, to impregnate the microcapsules into the fabrics a coupling agent was used. For this work, an organosilane compound with two distinct reactive groups: one epoxide group and three methoxy groups was selected (named as CoupA01). According to the chemistry of these reactive groups, they can react either with the groups present in the textile fibres (represented in Figure 5.2 as route (1)) or with the groups availables in the microcapsules shell (Figure 5.2 - route (2)).

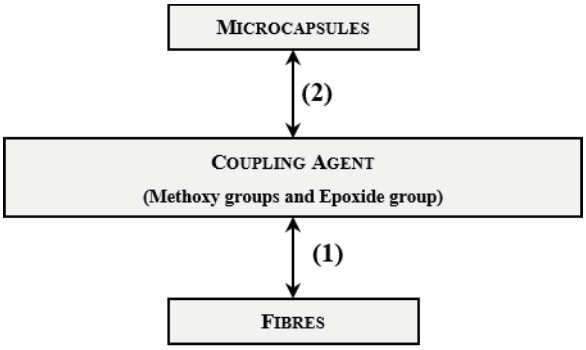

Figure 5.2: Interactions of the coupling agent (CoupA01) with the microcapsules and with textile fibres.

One of the selected substrates was the cotton, which is mainly composed of cellulose that, in turn, is composed of a large number of hydroxyl groups (see Figure 5.1 (a)). Consequently, these hydroxyl groups (Cell – OH) can probably be attached covalently to the methoxy or epoxide groups of CoupA01. To study their possible reactions, the methoxy groups of this coupling agent are the first to be considered. Thus, when CoupA01 is added to the aqueous suspension of microcapsules and the pH adjusted (acid pH), its methoxy groups are quickly hydrolysed with water to form silanol groups (Si – OH), as represented in Figure 5.3 [8].

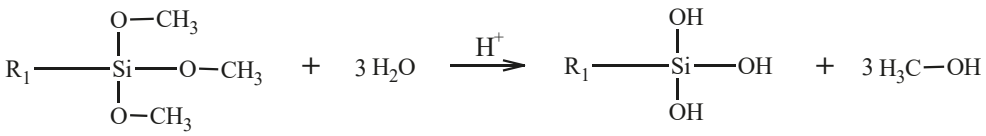

Figure 5.3: Hydrolysis of methoxy groups of CoupA01 in the presence of water (acid pH).

The silanol in the hydrolysed CoupA01 can be adsorbed on the surface of the cellulose fibres by creating hydrogen bonding to the hydroxyl groups of fibres or even by forming covalent linkages through the process of condensation, which occurs by thermal activation (this

reaction is thermally activated during the curing step of the impregnation process) (see Figure 5.4 (a)) [8,9]. Simultaneously, as CoupA01 is a trifunctional alkoxysilane, the silanol groups can also condense with each other to produce oligomeric structures and forming siloxane linkages (Si – O – Si) [8,10]. Thus, considering that the silanol groups can react with the fibres and with itself, a three dimensional network can be formed, as exemplified in Figure 5.4 (b).

The kinetics of hydrolysis and condensation reactions of the silanol groups are affected by the structure of the organic part of the silane and by the reaction medium and conditions (temperature, pH, concentration, amount of water and catalyst) [8]. These issues were considered in the impregnation process and, consequently, for all the experiments the same procedure was carried out. Maintaining the pH correction (the finishing formulation pH was adjusted to 4.5 after the CoupA01 addition) and maintaining the drying and curing steps (the fabrics were put in an oven at 140 ºC during 4 minutes), as further described in section 5.2.2.

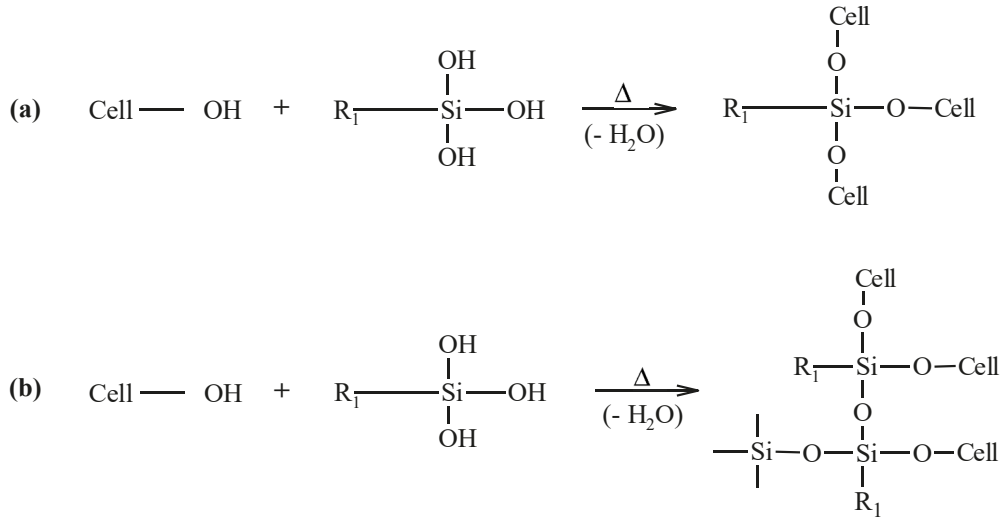

Figure 5.4: Chemical reactions between the hydroxyl group of cellulose and the silanol group (a) considering that the silanol groups react only with the cellulose fibres and (b) considering that the silanol groups react with the cellulose fibres and with itself [4, 9].

In addition, the interactions between the hydroxyl groups of cellulose and the epoxide ring of coupling agent are also investigated. Typically, one hydroxyl group can act as a nucleophile agent, reacting with the epoxide through a nucleophilic substitution. Thus, considering that the hydroxyl groups of cellulose are available to react with the epoxide groups of CoupA01, their chemical reaction can form a ether linkage by different routes (as represented in Figure 5.5) [11,12].

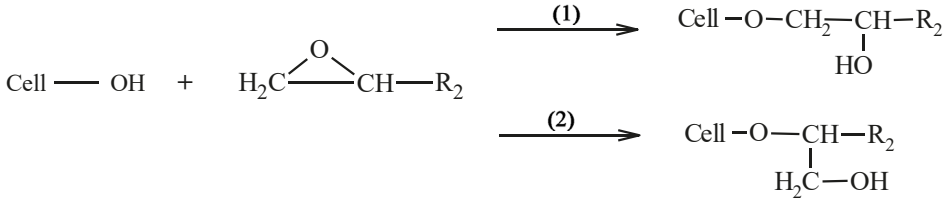

Figure 5.5: Chemical reaction between the hydroxyl group of cellulose and the epoxide ring of coupling agent [11].

In contrast with cotton, which present large number of hydroxyl groups, the polyester is basically a non-reactive substrate that presents ester links along the PET chains. Besides, in a low quantity, this polyester can also contain two distinct chain ends: a hydroxyl end group resulting from the diol (ethylene glycol); and a carboxyl end group resulting from the aromatic diacid (terephthalic acid) [13,14]. Thus, these groups, if available, can react with the coupling agent in the course of impregnation process, favouring the microcapsules fixation on the polyester fibres. So, the possible chemical reaction between hydroxyl end group of polyester and the CoupA01 are analogous to the one formerly described for the OH groups of cellulose. Therefore, to complete this study, only the reactions between the carboxyl end group of polyester and the reactive groups of the CoupA01 are described bellow.

Carboxylic acids are known to react with many functions, namely with epoxide ring [10]. Nevertheless, the reaction between the carboxyl group and methoxy group seems not be favourable and, consequently, it was not discussed here. Concerning the interaction between the carboxyl groups and the epoxide ring, their chemical reaction is represented in Figure 5.6. Here, two possible routes of reaction are represented: the α-addition to the carbon atom of the methylene group and the β-addition to the carbon atom of CH groups [10]. Several catalysts have been successfully used to catalyse this reaction, namely: tertiary amines, tertiary amine salts and metallic complexes [10]. In the present study, a tertiary amine was added. In this chemical reaction, as for the reaction of the hydroxyl groups of cellulose, the carboxyl group can also act as a nucleophile reacting with the epoxide ring via nucleophilic substitution. Nevertheless, here a ester linkage is formed [10,11].

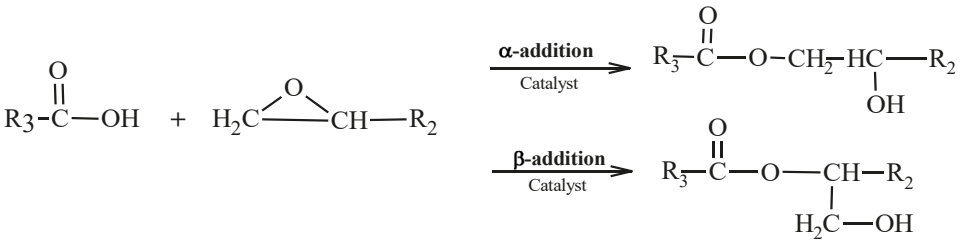

Figure 5.6: Chemical reaction between the carboxyl end group of polyester and the epoxide ring of coupling agent (α- and β-addition) [10].

To complete the description of the coupling agent role on the process of incorporation, especially on the fixation of microcapsules in the fabrics, the interaction between the selected coupling agent (CoupA01) and the acrylic shell microcapsules need to be also studied (route (2) in Figure 5.2). Although, this topic will be only discussed after the presentation of the results for the treated textiles and together with their results of microcapsules washing resistance.

In sum, the viability of the acrylic shell microcapsules to produce textile substrates with thermo-regulating properties is investigated in this chapter. The several microcapsules containing octadecane (described in the former chapter) were impregnated into polyester and cotton woven fabrics. In the first place, it was intended to verify the microcapsules performance in the impregnation process and, afterwards, to study of microcapsules resistance to the washing process.

5.2 EXPERIMENTAL

5.2.1 Materials

Two types of woven fabric, 100 % polyester (composed of PET) with 170 g/m ^{2} and 100% cotton with 185 g/m^2, were selected as textile substrates. All reagents used into the finishing formulation: thickener, stabilizer, softener, catalyst, coupling agent and citric acid were received from Devan Chemicals (Belgium).

5.2.2 Incorporation of microcapsules into textile substrates

Microcapsules were incorporated into textile substrates by implementing the technique of padding and following a standard procedure and a finishing formulation supplied by Devan-Micropolis. This procedure is normally applied with its microcapsules with PCM and using the same type of fabrics (polyester and cotton woven). This process was performed at laboratory scale, reproducing the industrial conditions.

All microcapsules were impregnated in the fabrics through the same procedure and using a finishing formulation with a microcapsules concentration of 40 g/L. This formulation was prepared in two steps:

- Preparation of *Solution 1*. This solution (50 mL) was prepared by dispersing the microcapsules in water through mechanical stirring and, after complete dispersion, adding the remaining components listed in Table 5.1 (Thick01, Stab01, Soft01 and Cat01). Thus, despite water and microcapsules, this solution contains a thickener and a stabilizer, which main function is to increase the stability of the microcapsules dispersion and to avoid a fast phase separation. Besides, a softener was also used, which presents as only function to increase the softness of treated textiles. These three compounds do not react with the fibres or with coupling agent. Finally, a catalyst was added, in this case a tertiary amine that contributes to activate the reaction of the coupling agent (epoxide groups) with the textile fibres, as described in section 5.1.

- Preparation of finishing formulation. This formulation (200 mL) was prepared with *Solution 1*, coupling agent (CoupA01, previously described in section 5.1) and water, obtaining a microcapsules concentration of 40 g/L. After the stirring of this dispersion, the pH was adjusted to 4.5 using citric acid.

Table 5.1: List of components used to prepare *Solution 1*.

Function	**Compounds**
	Microcapsules
	Water
Thickener	Thick01
Stabilizer	Stab01
Softener	Soft01
Catalyst	Cat01

The textile substrates (25 cm x 50 cm samples) were completely immersed into the finishing formulation and squeezed at 4 bar using a horizontal padding mangle of pneumatic type (RAPID foulard, model P-B0, from Labortex CO., Ltd) (see Figure 5.7). Finally, in order to perform the drying and curing stages, the impregnated fabrics were placed in an oven at 140ºC during 4 minutes.

Figure 5.7: Laboratory horizontal foulard from Devan - Micropolis.

The amount of finishing formulation picked up by the textile substrate is usually expressed as a percentage of the dry textile weight (untreated textile). In this study, this quantity was designated "wet pickup" (WPU) and it was calculated according Equation (5.1) [15].

$$WPU\ (\%) = \frac{weight\ of\ formulation\ picked\ up}{weight\ of\ dry\ textile} \times 100$$

$$= \frac{weight\ of\ wet\ textile - weight\ of\ dry\ textile}{weight\ of\ dry\ textile} \times 100 \qquad (5.1)$$

5.2.3 Textiles washing process

After the incorporation of microcapsules into fabrics, a segment of each treated fabric was washed in order to test the microcapsules washing resistance. The washing program was established from the procedure type 6A (40 ºC) based in EN ISO 6330:2002, which is defined for woven and knit fabrics. Thus, in order to follow this procedure, the washing cycles were performed using solid laundry detergent (ECE Non Phosphate Detergent (A) from SDC

Enterprises Ltd) in the presence of 2 kg ballasts and implementing a washing program of 85 minutes, at 40 ºC and with 1000 rpm for torsion. These tests were carried out in a washing machine Ariston - Hotpoint, model ARXF125. The defined washing conditions are equivalent to 5 cycles of normal washing (5W). The washed substrates were subsequently dried at room temperature.

5.2.4 Characterization techniques

Scanning electronic microscopy

For SEM observation, fabric's specimens were placed onto carbon tape in an appropriated support and, before the analysis, they were subjected to a sputtering treatment to deposit a gold nano layer. Micrographs were then obtained by using an electron beam voltage of 15 kV produced by a Tungsten filament with a Leica Cambridge S360 equipment. SEM analyses were performed in both unwashed and washed textile substrates.

Differential scanning calorimetry

The thermo-performance of textile substrates was studied by DSC, in a *Netzsch DSC 200 F3 with a cooling* unit. Fabric's specimens were analysed in aluminium crucibles with closed lid. As for the microcapsules analysis, a program with three thermal cycles was used: firstly the temperature was decreased at 5 ºC/min from 20 ºC to -10 ºC; then heat was supplied at 5 ºC/min from -10 ºC to 50 ºC; finally, the sample was cooled at 5 ºC/min, from 50 ºC to -10 ºC. Isothermals of 3 minutes before each cooling and heating cycle were implemented. Each analysis was carried by using three small pieces of fabric, collected from three different positions in the treated specimen, with total weights ranging from 7 to 10 mg. Each fabric was analysed in triplicate and the results were expressed as average ± standard deviation. This study was performed in both unwashed and washed textile substrates.

The microcapsules retention for each fabric after the washing cycle was estimated according to Equation (5.2).

$$Microcapsules\ retention\ (\%) = 100 - \left(\frac{\Delta Hm_{\ unwashed} - \Delta Hm_{washed}}{\Delta Hm_{\ unwashed}} \times 100\right) \qquad (5.2)$$

Where the $\Delta Hm_{unwashed}$ and ΔHm_{washed} are the melting enthalpy obtained for unwashed and washed fabrics, respectively.

5.2.5 Data treatment

Figure 5.8 summarizes the sequence of operations followed in the work described in this chapter. It should be noted that the impregnation of microcapsules onto textile fibres started by using the industrial samples (Wc-PCM28 and Sl-PCM28) since there are more know-how for these materials. Moreover, their results were taken as reference in order to evaluate the performance of acrylic microcapsules containing octadecane (presented in Chapter 4). These microcapsules were prepared to study the influence of different types of initiator and polymerization temperature and the influence of the monomers proportions of mixture MMA, BA and MAA.

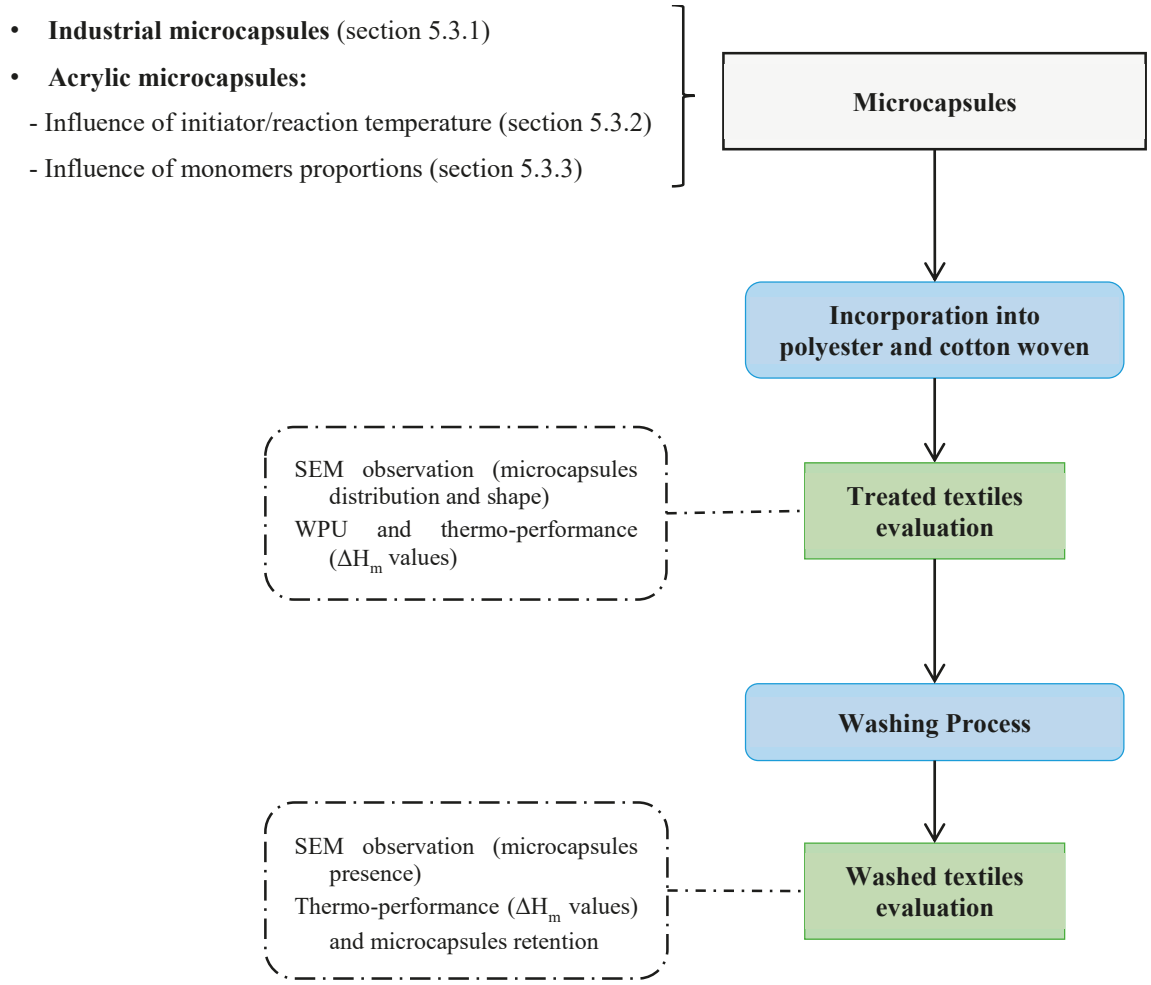

Figure 5.8: Sequence of the operations followed in the work presented in this chapter.

The microcapsules were impregnated into distinct fabrics (polyester and cotton woven) and in each sample, the value of WPU was determined. In general, this value is associated to the amount of microcapsules that is incorporated in the fabrics, since it results from the quantity of finishing formation absorbed by them.

The response to the microcapsules incorporation into both types of substrates was assessed by SEM and DSC. SEM observations enable to determine the microcapsules capacity to resist to the roll pressure as well as their distribution throughout the substrate, while the DSC analysis allows to evaluate the textile thermo-performance (through the values of enthalpy).

As mentioned before, in this work, the study of microcapsules washing resistance is also intended. Therefore, the techniques of SEM and DSC were also used to characterize the textiles after the 5 cycles of normal washing (5W) and to calculate the percentage of microcapsules retention (based on the values of enthalpy and through the equation 5.2). Furthermore, in the following chapter, for the microcapsules that exhibit better washing resistance after 5W, the washing cycles were extended to 25 cycles of normal washing (25W).

5.3 RESULTS AND DISCUSSION

Herein, the results obtained with the incorporation of the industrial microcapsules are firstly presented, describing the treated polyester and cotton based woven in parallel. Then, the treated fabrics with the microcapsules prepared with different types of initiator and polymerization temperature and, afterwards, with the ones prepared with different monomers proportions were studied.

5.3.1 Industrial microcapsules

In section 3.3.3, the characterization of industrial microcapsules was described. As mentioned there, these the two types of selected microcapsules differ mainly in their particle size distribution and in their enthalpy values:

- sample Wc-PCM28 presents a ΔH_m of about 195 J/g and a $D_{4,3}$ of 15 µm;
- sample Sl-PCM28 exhibits a ΔH_m of about 160 J/g and a $D_{4,3}$ of 3 µm.

Characterization of treated textiles

a) Scanning electron microscopy observation

Before the SEM observations of treated woven fabrics, the untreated samples were analysed. These substrates differ not only in their chemical nature (polyester versus cotton), but also in the fabric structure and fibres rearrangement (see Figure 5.9). For the cotton woven the yarns are thinner and closer together (presenting a more tight structure) than for the polyester woven. Moreover, it was also detected that the fabric of cotton is slightly thinner than the polyester.

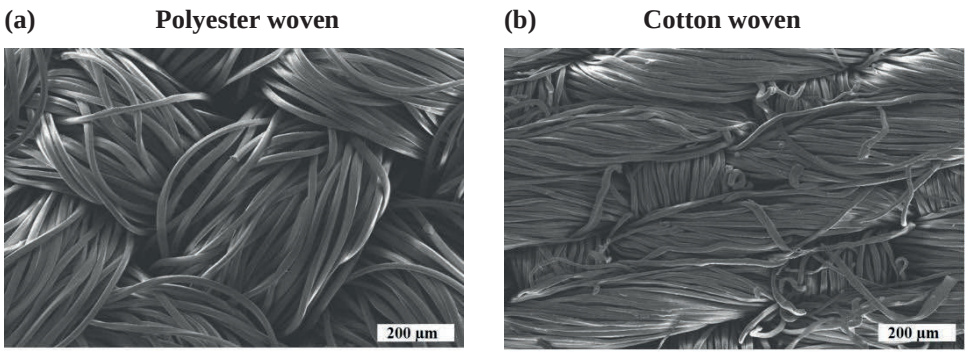

Figure 5.9: SEM micrographs of untreated woven fabric: (a) polyester fibres and (b) cotton fibres (magnification x100).

The SEM micrographs of textiles impregnated with the microcapsules Wc-PCM28 and Sl-PCM28 are presented in Figure 5.10 (a and b) and Figure 5.10 (c and d), respectively. As these figures illustrate, the main difference between these pairs of figures are related to the size of the microcapsules (being the particles sizes of sample Sl-PCM28 much smaller than those of sample Wc-PCM28). Moreover, and besides some degree of deformation in microcapsules Wc-PCM28, the presence of broken microcapsules was not detected. The breakage of microcapsules during their incorporation into the textile substrates should be avoided, since it will allow the octadecane release and, consequently, it will produce treated textiles with inferior thermo-performance. This breakage can occur during the process of padding, due to the rolls pressure applied in the foulard, or later during the washing of the textiles.

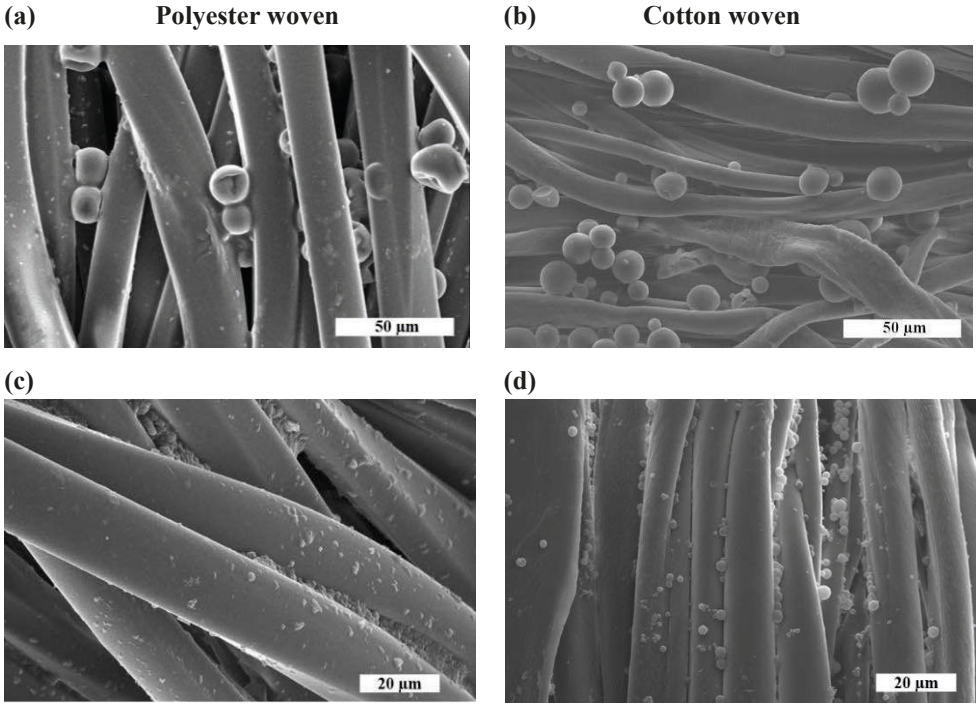

Figure 5.10: SEM micrographs of treated woven: microcapsules Wc-PCM28 on (a) polyester and (b) cotton fibres (magnification x600); and microcapsules Sl-PCM28 on (c) polyester and (d) cotton fibres (magnification x1000).

b) Thermo-performance

The DSC curves of treated fabrics with industrial microcapsules Wc-PCM28 and Sl-PCM28 (see Figure 5.11) denote two distinct peaks: one endothermic for the heating process and one exothermic for the cooling process, as the DSC curves of the corresponding microcapsules (Figure 3.18). Table 5.2 summarizes the values of ΔH_m calculated from these curves, together with the percentages of WPU (estimated by equation (5.1)).

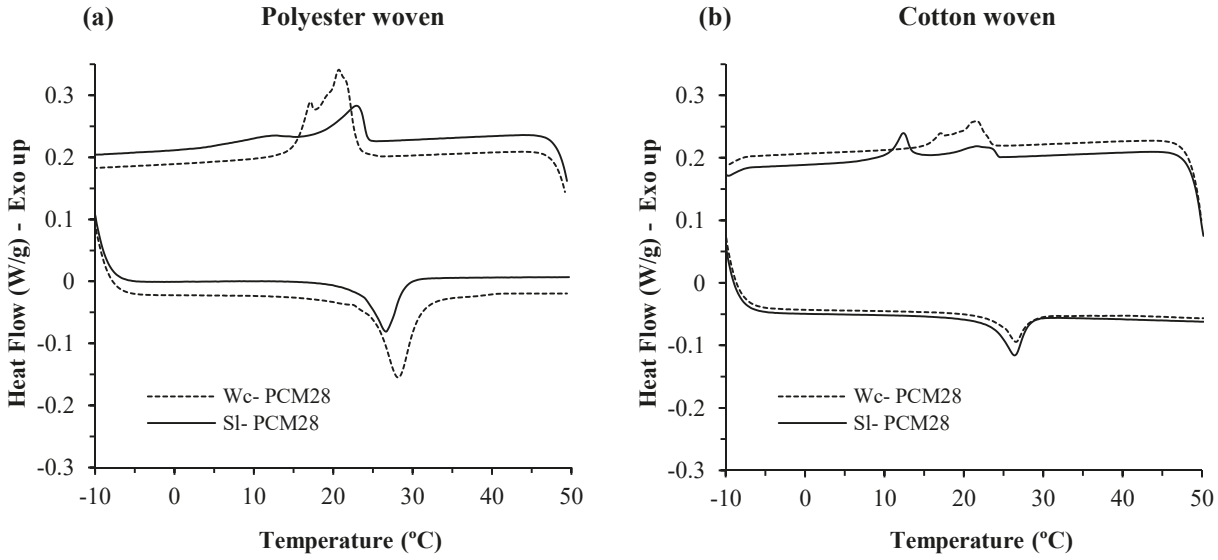

Figure 5.11: DSC curves of treated woven with industrial microcapsules: (a) polyester and (b) cotton woven.

Regarding the percentages of WPU (see Table 5.2), it is clear that these values are very similar for both types of microcapsules, being quite dependent upon the type of substrate. In fact, the values obtained for the cotton woven are approximately half of those for polyester (value of about 50% versus 90%). This is most certainly a consequence of the differences between both substrates, especially the distinct fabric structure that was described before (Figure 5.9). The thinner and closer together yarns of the cotton woven seems to allow a lower retention of finishing formulation.

As expected and in line with the values of WPU, the highest values of ΔH_m were achieved for treated polyester woven (see Table 5.2): ΔH_m was 8.4 J/g for polyester woven with microcapsules Wc-PCM28, whereas for cotton the value was only 1.9 J/g. Nevertheless, the proportion between the WPU values of both fabrics and the corresponding ΔH_m was not maintained. For microcapsules Wc-PCM28, the ΔH_m of treated cotton woven was significantly lower than one half of the ΔH_m of polyester woven. Probably due to the different chemical nature of the fibres (which can promote different affinity with the microcapsules) but, most likely, due to the distinct rearrangement of the textile fibres, in which the cotton yarns with less space between them could promote a lower distribution of the larger microcapsules in the interior of fabric substrate.

Table 5.2: Values of WPU (calculated using equation (5.1)) and thermo-performance (values of ΔH_m) of polyester and cotton woven treated with industrial microcapsules.

Microcapsules	**Treated polyester woven**		**Treated cotton woven**	
	WPU (wt.%)	**ΔH_m (**J/g)	**WPU** (wt.%)	**ΔH_m (**J/g)
Wc-PCM28	88.7	8.4 ± 1.3	49.5	1.9 ± 0.1
Sl-PCM28	88.1	4.5 ± 0.1	48.5	1.3 ± 0.1

Comparing the ΔH_m for the same substrate, it is found that the fabrics with microcapsules Sl-PCM28 present much lower values than those with Wc-PCM28. These results are in agreement with the values of ΔH_m obtained for the microcapsules before their impregnation (sample Wc-PCM28 have a ΔH_m of 195 J/g and Sl-PCM28 of 160 J/g). Besides, the distinct values of ΔH_m, also their particles sizes are expressively different (sample Wc-PCM28 present a $D_{4,3}$ of around 15 µm and Sl-PCM28 of 3 µm). This different size will also promote distinct behaviours during the impregnation process. Thus, the results suggest that the thermo-

performance of treated fabrics is a consequence of these two factors: the microcapsules ΔH_m and their mean diameter.

In sum, for the established finishing formulation and for both types of industrial microcapsules, the treated polyester woven showed values of ΔH_m between 8.5 and 4.5 J/g, whereas the cotton showed values between 1.9 and 1.3 J/g. The high reduction of ΔH_m for treated fabrics compared with microcapsules was already expected. Since, during the process of padding only a low quantity of microcapsules is impregnated into the fabrics. Additionally, the former results suggest that the quantity of impregnated microcapsules is also associated with other factors, such as: the characteristic of the fabrics (like the rearrangement of yarns and fibres, its chemical nature and its WPU); the properties of the microcapsules (like their ΔH_m and their particles sizes); and also the concentration of microcapsules in the finishing formulation. Due to these numerous variables and in order to allow an adequate comparison of the described results with the ones obtained for the acrylic samples, in all the following experiments the microcapsules concentration as well as the type of fabrics were maintained.

As the microcapsules were successfully incorporated onto the polyester and cotton fibres, the next step was to subject the treated fabrics to the washing process and perform the same characterization as above.

Characterization of textiles after washing process

a) Scanning electron microscopy observation

Comparing SEM micrographs of washed polyester and cotton woven (Figure 5.12) with the corresponding unwashed samples (Figure 5.10), it seems that in the case of the sample Wc-PCM28 a large amount of microcapsules was removed, being mainly retained those inside of the fabric. As for the microcapsules Sl-PCM28, this effect does not seem to be so clear. As expected, with the washing, the microcapsules preferably removed were the ones with larger diameter and the ones distributed on the surface of the fabric, which are the microcapsules more accessible to the mechanical action of the washing process. These results suggest that the particle size is an important property regarding the microcapsules washing resistance.

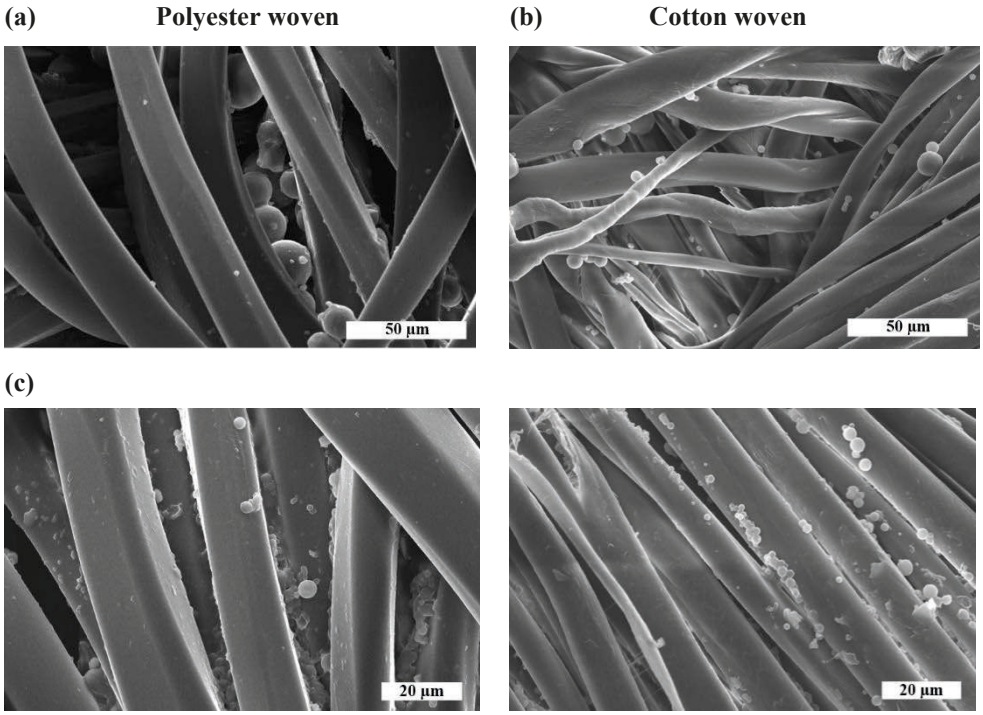

Figure 5.12: SEM micrographs after washing process (5W) of treated woven: microcapsules Wc-PCM28 on (a) polyester and (b) cotton fibres (magnification x600); and microcapsules Sl-PCM28 on (c) polyester and (d) cotton fibres (magnification x1000).

b) Thermo-performance

As explained in section 5.2.4, the retention of microcapsules after the washings can be calculated from the ΔH_m values of the unwashed and washed fabrics. These values have been plotted in Figure 5.13, for both fabrics and microcapsules types. The microcapsules retention should not be analysed independently of the ΔH_m values and that is why the retention values were also plotted in this figure. Nonetheless, more important than a high value of microcapsules retention is a high value of ΔH_m, since it is the latter that reflects the thermo-performance of a textile.

Figure 5.13 shows that the washing process removes microcapsules from both treated fabrics, with a different impact depending upon the type of microcapsules and of substrate.

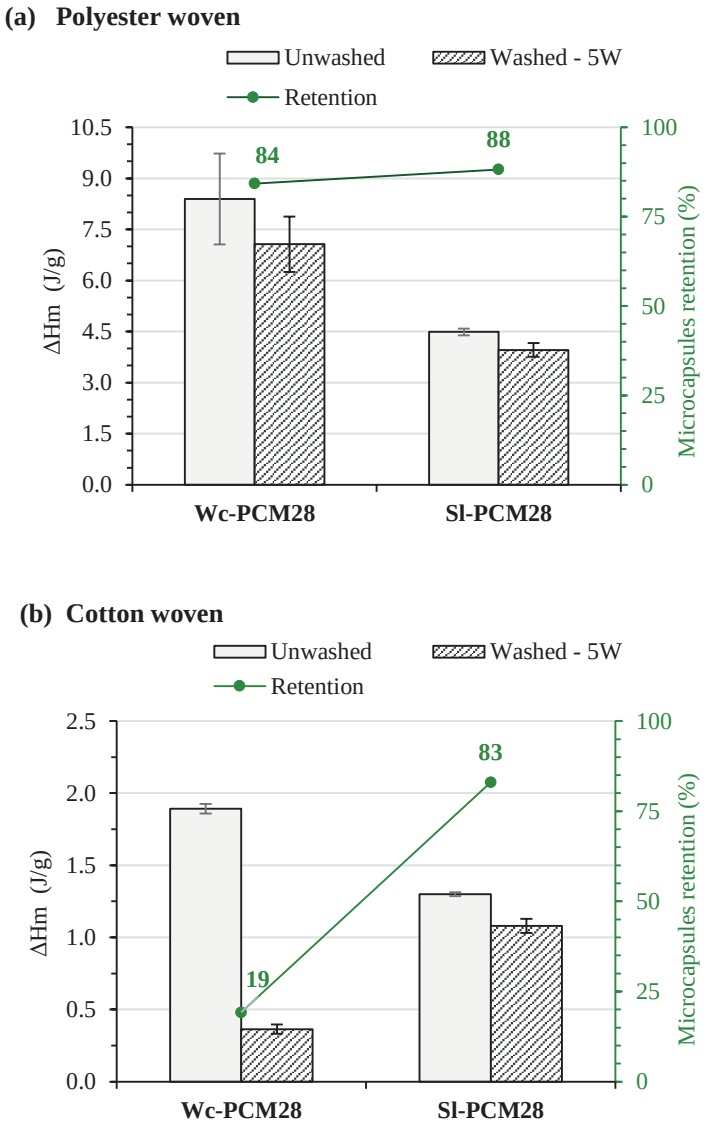

Figure 5.13: Thermo-performance (values of ΔH_m) of unwashed and washed (5W) (a) polyester woven and (b) cotton woven with industrial microcapsules and corresponding percentage of microcapsules retention (calculated using equation (5.2)).

For the polyester woven (Figure 5.13 (a)), the percentage of retention for microcapsules Wc-PCM28 are lower than those of Sl-PCM28. For cotton woven (see Figure 5.13 (b)), the same tendency was observed, but with a large difference between both microcapsules types. As the main difference between these two microcapsules is the particle size distribution, these results suggest that the higher removal of microcapsules Wc-PCM28 is originated by their larger size (as the SEM results seemed already to suggest).

Comparing the percentage of retention for similar microcapsules type, for polyester with sample Wc-PCM28 the value of retention was around 84 % (Figure 5.13 (a)), while for cotton

the value was only 19 % (Figure 5.13 (b)). This difference between the polyester and cotton woven could be explained by the different structure of the fabrics and the distinct chemical composition of the fibres.

Concerning the different structure of both fabrics (presented in Figure 5.9), the results of microcapsules retention suggest that the structure of fabric composed of polyester favours the fixation of microcapsules (increasing their resistance to the washing process) more than the one composed of cotton. Nevertheless, as this tendency of low retention is the common behaviour of fibres composed of cotton, independently of their structure (results given by the company using these microcapsules), this performance should be also influenced by their chemical composition. In order to associate the composition of the fibres (polyester and cotton) and the washing durability of the microcapsules, and since a coupling agent was used during the impregnation process, the interactions between the textile fibres and this coupling agent have been studied. The generic reactions between them were previously described in section 5.1.

Thus, regarding the different chemical composition of the fibres, the increased retention of microcapsules Wc-PCM28 found for the polyester seems counter-intuitive. Since cotton (cellulose) presents a large number of hydroxyl groups in their chemical structure and the polyester is basically a non-reactive substrate. Nevertheless, and despite the absence of reactive groups in the main chain, it can considered that this polyester (PET) contains two distinct end groups: a hydroxyl and a carboxyl end group (as discussed in section 5.1). The possible reactivity of these groups with the coupling agent can help to justify the fixation and stability of the microcapsules on the surface of polyester fibres. On the other hand, the low microcapsules retention for cotton woven could be probably explained by a high formation of hydrogen bonds within and between cellulose molecules [2]. These attractive forces could reduce the formation of new linkages between the cellulose fibres (hydroxyl groups) and the coupling agent, reducing the fixation of microcapsules in the fabrics.

For microcapsules Sl-PCM28, only a small difference between the retention of the polyester and cotton woven is observed. This behaviour seems to be result of the chemical composition of the textile fibres but, mostly, result of the smaller particle size of these microcapsules and the tightly structure of the cotton fabric. These features probably reduce the impact of the mechanical action of the washing process, increasing the microcapsules retention. However, despite the high values of microcapsules retention of these samples, their performance is far from the ideal due to the low ΔH_m values.

As mentioned before, the results acquired by the incorporation of these industrial microcapsules into polyester and cotton woven fabrics are used as reference for the study of the acrylic shell microcapsules.

5.3.2 Microcapsules prepared with different initiators and polymerization temperature

In this section, a similar study to that carried out with the industrial microcapsules is presented, but using the microcapsules that were prepared with different initiator and/or reaction temperatures (described in section 4.3.2). The tested samples were:

- microcapsules PCM-Bp80 and PCM-Bp70 prepared using BPO as initiator at 80 ºC and 70 ºC, respectively;

- microcapsules PCM-Aibn65 prepared using AIBN as initiator at 65 ºC;

- microcapsules PCM-Trig48 and PCM-Trig40 prepared using Trig23 as initiator at 48ºC and 40 ºC, respectively.

These samples exhibit ΔH_m values of around 175 J/g and $D_{4,3}$ of 12 µm, with exception of sample PCM-Aibn65 that showed a ΔH_m of 208 J/g. Microparticles B-Bp80 (prepared without octadecane) were also incorporated onto the polyester and cotton fibres for comparison purposes.

Characterization of treated textiles

a) Scanning electron microscopy observation

Figure 5.14 shows the SEM micrographs of fabrics with microcapsules PCM-Bp80. In the images with lower magnification (Figure 5.14 (a and b)), the distinct structure of the polyester and cotton woven, previously discussed, is clearly noticed. From these pictures, it is also clear that there is no agglomeration of microcapsules along the fabrics. Figure 5.14 (c and d) (images at higher magnification) exhibits spherical and well-shaped microcapsules with only a small number of them broken, particularly on fabric's surface.

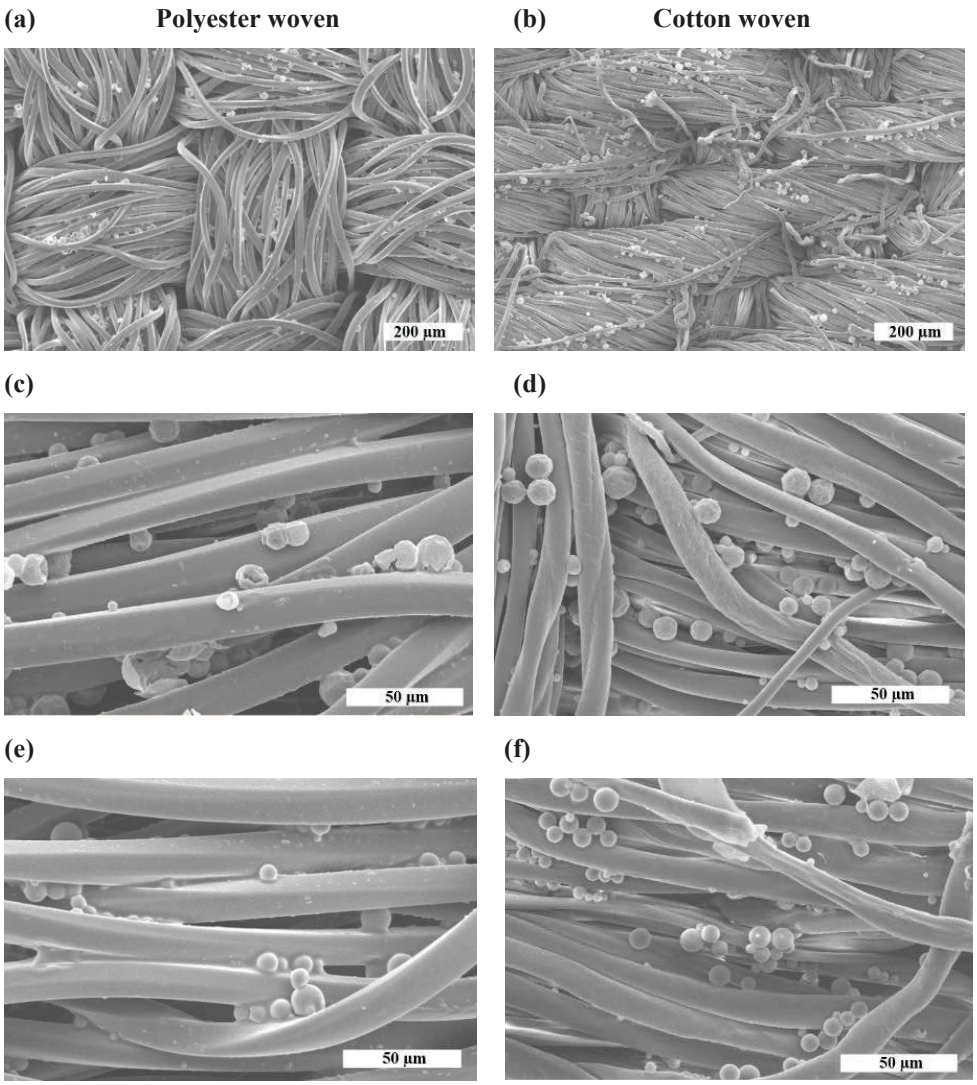

Figure 5.14: SEM micrographs of treated woven: microcapsules PCM-Bp80 on (a) polyester and (b) cotton fibres at lower magnification (magnification x100); and on (c) polyester and (d) cotton fibres at higher magnification (magnification x600) and with microparticles B-Bp80 on (e) polyester and (f) cotton fibres (magnification x600).

The sample B-Bp80 (prepared without octadecane) was also impregnated in these fabrics in order to compare with the microcapsules that contain octadecane. Contrary to the previous microcapsules PCM-Bp80, in this case only undamaged microparticles were observed (see Figure 5.14 (e and f)). This result comes from the absence of octadecane and thus, from the absence of a core/shell structure, which produces a more resistant structure to the pressure applied during the padding process.

Figure 5.15 illustrates SEM micrographs of microcapsules prepared with three different initiators (BPO, AIBN and Trig23) at their corresponding 10 hours half-life decomposition temperatures (sample PCM- Bp70, PCM-Aibn65 and PCM-Trig48). Like in Figure 5.14, spherical microcapsules can be identified. However, especially in sample PCM-Trig48, more broken shells seems to be detected. Additional pictures can be found in Figure C.1, Appendix C (sample PCM-Trig40).

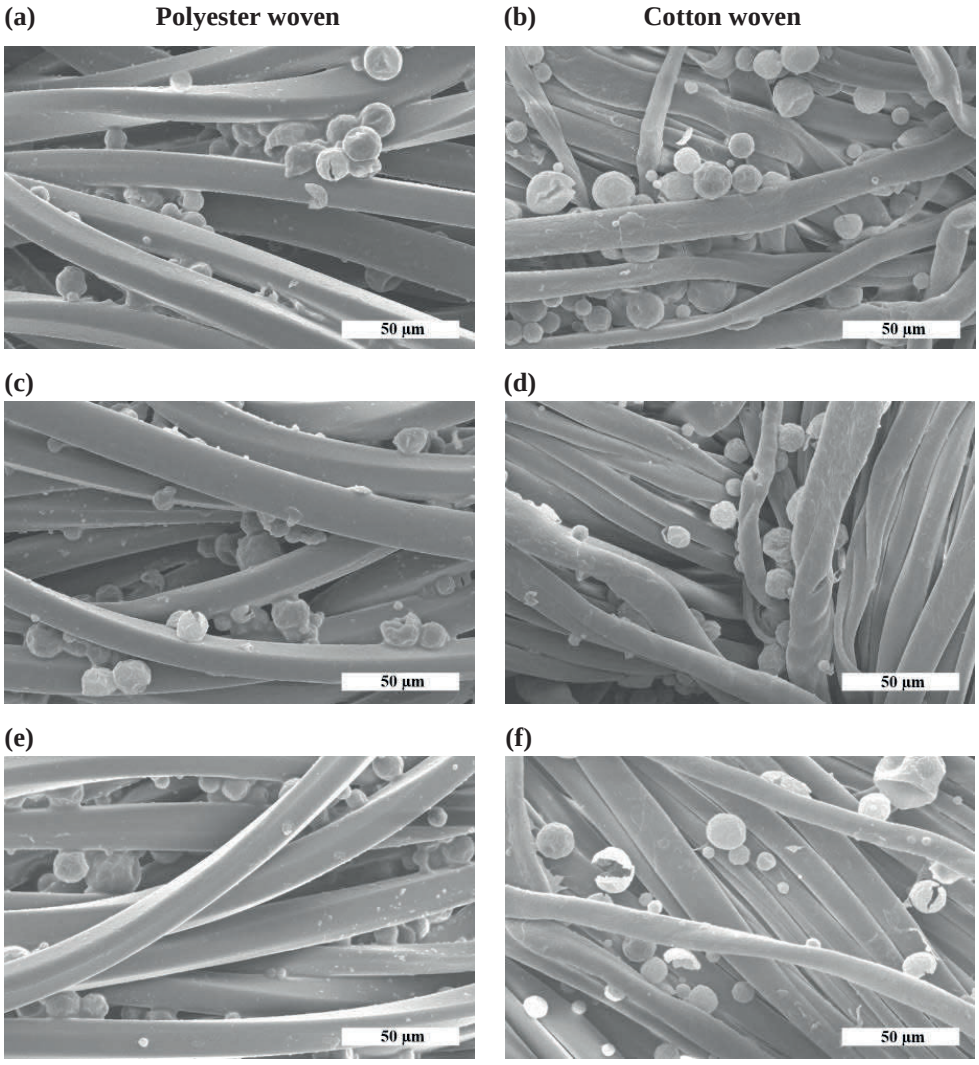

Figure 5.15: SEM micrographs of treated woven: microcapsules PCM-Bp70 on (a) polyester and (b) cotton fibres; microcapsules PCM-Aibn65 on (c) polyester and (d) cotton fibres; and microcapsules PCM-Trig48 on (e) polyester and (f) cotton fibres (magnification x600).

b) Thermo-performance

In Figure 5.16 are represented the DSC thermograms of treated substrates with microcapsules PCM-Bp80 and B-Bp80 (microcapsules prepared with BPO at 80 ºC with and without octadecane, respectively). As expected, due to the absence of octadecane in treated polyester and cotton woven with microparticles B-Bp80, their thermogram do not exhibit any thermal event. This confirms that all the outcomes identified in the remaining samples are originated by the presence this core material.

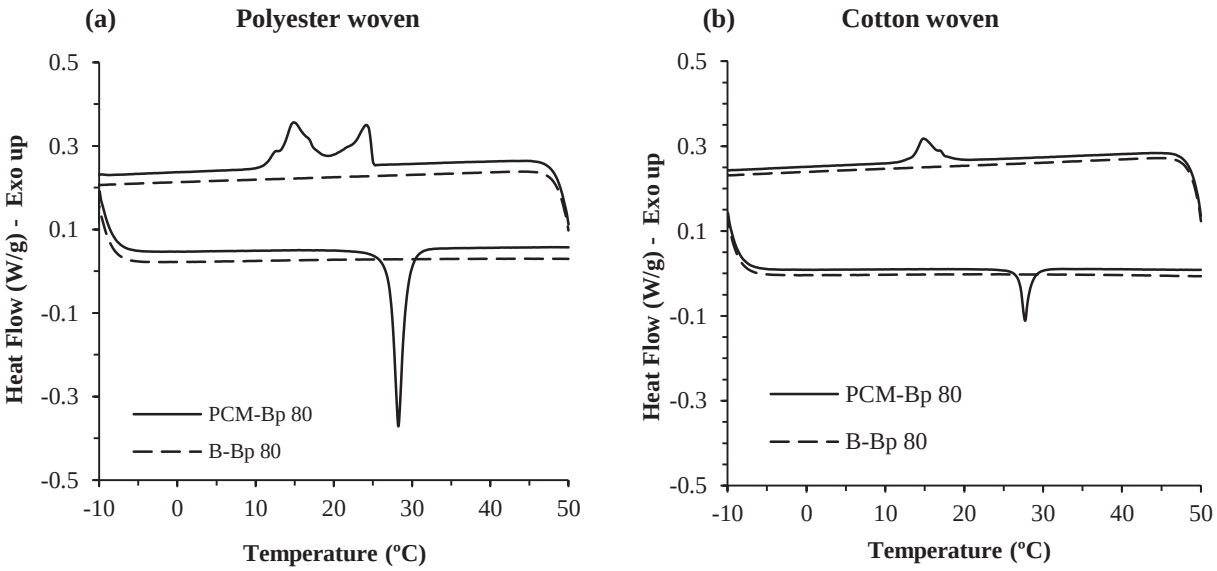

Figure 5.16: DSC curves of (a) polyester and (b) cotton woven with microcapsules prepared using BPO as initiator at 80 ºC (with and without octadecane).

Similarly to treated fabrics with industrial microcapsules, the cotton woven with microcapsules PCM-Bp80 exhibits both endothermic and exothermic peaks with a smaller area than the polyester woven. This profile is originated by the considerably lower WPU percentage of the cotton woven and by the differences between both substrates, being reflected in the low values of ΔH_m for the fabric composed of cotton (see Table 5.3). This behaviour was already described for the industrial microcapsules (section 5.3.1).

Comparing the DSC curves of remaining treated fabrics with the one represented in Figure 5.16 for microcapsules PCM-Bp80, the same profile is identified (see Appendix C, Figure C.2 for the polyester and Figure C.3 for the cotton woven). Table 5.3 summarizes the values of ΔH_m gathered for the several acrylic microcapsules on both fabrics as well as the WPU percentage.

For this series of samples, the WPU values varied between 92 % and 97 % for polyester and between 51 % and 55 % for cotton woven. These values are slightly higher than the WPU obtained for microcapsules Wc-PCM28 and Sl-PCM28 (values of 88 % and 49 % respectively). However, the trend of lower WPU values for the cotton woven, formerly described, has been commonly observed.

Table 5.3: Influence of initiator type and polymerization temperature on the WPU (calculated using equation (5.1)) and on the thermo-performance (values of ΔH_m) of treated polyester and cotton woven.

Microcapsules	**Treated polyester woven**		**Treated cotton woven**	
	WPU (%)	$\Delta \mathbf{H_m}$ (J/g)	**WPU** (%)	$\Delta \mathbf{H_m}$ (J/g)
Wc - PCM28 *	88.7	8.4 ± 1.3	49.5	1.9 ± 0.1
Sl - PCM28 *	88.1	4.5 ± 0.1	48.5	1.3 ± 0.1
B - Bp80	95.4	0	52.2	0
PCM - Bp80	97.2	9.8 ± 1.0	55.7	2.0 ± 0.1
PCM - Bp70	93.1	8.6 ± 0.7	53.0	1.5 ± 0.2
PCM - Aibn65	91.8	9.5 ± 0.7	51.7	1.2 ± 0.1
PCM - Trig48	94.0	7.5 ± 1.3	53.4	1.4 ± 0.2
PCM - Trig40	92.8	8.0 ± 1.8	52.3	1.6 ± 0.1

***** Wc-PCM28 and Sl-PCM28, samples previously presented.

For the polyester woven, the treated fabric with sample PCM-Bp80 exhibits the highest value of ΔH_m (9.8 J/g). This value is most likely due to the highest percentage of WPU of this fabric (97%). Since, in general, the ΔH_m values of these acrylic shell microcapsules are around 175 J/g and their particles size around 12 µm. The only microcapsules that exhibited higher value of ΔH_m (208 J/g) were prepared in experiment PCM-Aibn65. Consequently, without a highest percentage of WPU (in fact, it is the second lowest – 92%), the treated polyester with sample PCM-Aibn65 presents also a great value of ΔH_m (9.5 J/g). In contrast, the lower thermo-performance was determined for the polyester with sample PCM-Trig48, the fabric in which more broken microcapsules were detected by SEM. This probable higher microcapsules fracture could reduce the quantity of octadecane, causing the lower value of ΔH_m.

For the cotton woven, as mentioned before, the values of ΔH_m were significantly lower than that of polyester, values that varied just between 1.2 J/g and 2.0 J/g. Here, the highest thermo-performance was attained for sample PCM-Bp80, which can be the result of slightly higher WPU percentage of this fabric but also coming from the microcapsules properties (like the presence of a more resistant shell that could reduce the shell breakage and the octadecane release).

It should be mentioned that the values of standard deviation calculated for the three measurements of ΔH_m for each fabric are considerably high (reaching 22% of the ΔH_m for polyester with sample PCM-Trig40). These values reveal that the microcapsules distribution throughout the textile substrate is not homogeneous. This problem is most certainly originated by the process of impregnation. Nonetheless, all the results were considered satisfactory, presenting a thermal storage capacities that are generally in the same range than those obtained for the microcapsules Wc-PCM28.

Summing up, the above results show that the acrylic microcapsules were well-incorporated into the polyester and cotton substrates through the process of padding. However, a small fraction seemed to be fractured, mainly in the surface of the fabric. In each type of textile, similar WPU values were obtained and, just like for industrial microcapsules, substantial differences were found for both polyester and cotton woven. As for thermo-performance, ΔH_m values between 7.0 J/g and 9.8 J/g for the polyester woven and 1.2 J/g and 2.0 J/g for cotton woven were achieved, values in the same range that the reference Wc-PCM28. The obtained results suggested that the tested variables (type of initiator and/or reaction temperature) do not greatly affect the microcapsules incorporation.

Characterization of textiles after washing process

a) Scanning electron microscopy observation

As Figure 5.17 shows, for washed polyester and cotton woven with samples PCM-Bp80 and PCM-Aibn65, a significant elimination of microcapsules with the washing process can be noticed. Nevertheless, the presence of spherical microcapsules is still easily detected. These observations were equally found for the washed fabrics with the remaining samples (see micrographs in Figure C.4, Appendix C).

Additionally, for polyester woven with sample PCM-Aibn65, it seems that a significant amount of microcapsules is broken (see Figure 5.17 (c)). It should be reminded that, as described in section 4.3.2, these microcapsules exhibited a higher PCM content, suggesting a low formation of copolymer during the polymerization reaction. This was probably related with a lower formation of shell that could produce a thinner and more fragile shell, partially justifying the larger amount of broken shells after the washing process.

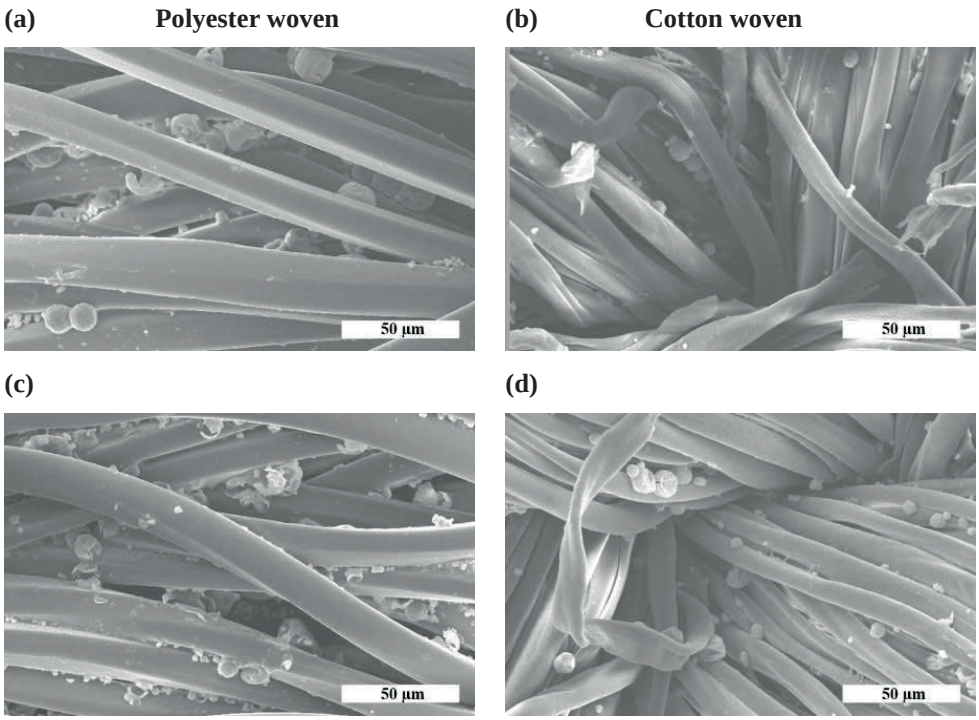

Figure 5.17: SEM micrographs after washing process (5W) of treated woven: microcapsules PCM-Bp80 on (a) polyester and (b) cotton fibres; and microcapsules PCM-Aibn65 on (c) polyester and (d) cotton fibres (magnification x600).

b) Thermo-performance

The results collected by DSC, concerning all these impregnations into polyester woven, are summarized in Figure 5.18. This graph includes the values of ΔH_m determined for the unwashed (previously listed in Table 5.3) and the washed fabrics and the percentage of microcapsules retention.

The DSC curves obtained for the washed polyester show an identical profile to that of unwashed samples (presented in Figure 5.16), but exhibiting peaks with small area (see details in Figure C.5, Appendix C).

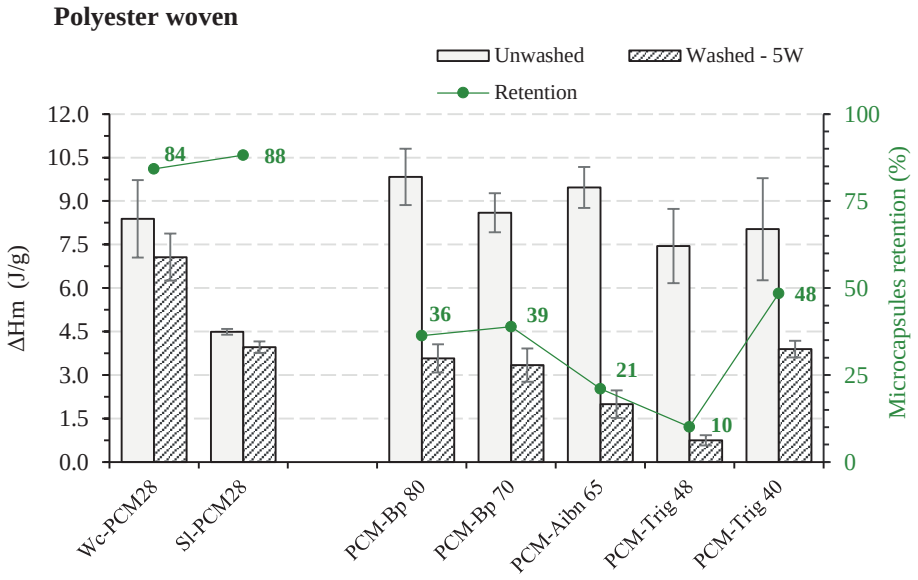

Figure 5.18: Influence of initiator type and polymerization temperature on the thermo-performance (values of ΔH_m) of unwashed and washed (5W) polyester woven and on the corresponding percentage of microcapsules retention (calculated using equation (5.2)). Samples Wc-PCM28 and Sl-PCM28 are represented for comparison.

Figure 5.18 shows much lower ΔH_m values for the washed fabrics (between 0.8 J/g and 3.9 J/g) than for the unwashed, a consequence of the high amount of microcapsules that was removed. This is reflected in the low percentages of retention (between 10 % and 48 %), values that were significantly lower than those observed for the industrial microcapsules (retention of 84 % and 88 %). Including, when compared with sample Wc-PCM28, the industrial sourced sample that presents similar properties (namely the particles size distribution) to the ones obtained for the acrylic shell microcapsules. The small value of retention (10 %) observed for polyester treated with sample PCM-Trig48, was probably due to the high initial breakage extent in their microcapsules. This behaviour has been already suggested from the data obtained for the corresponding unwashed fabric.

As described in section 4.4.3, in general, all the microcapsules prepared in the series of experiments, carried out to study the influence of the thermal initiator and reaction temperature, showed similar properties. Nevertheless, when these microcapsules were impregnated on the polyester fibres, the treated fabrics exhibited different behaviours. This suggests that, despite not earlier identified, small differences between the several samples of microcapsules can exist.

Figure 5.19 illustrates the results of enthalpy obtained for the cotton woven, whereas the DSC curves of these washed substrates are plotted in Figure C.6 in Appendix C. As expected, the values of ΔH_m were even smaller than those of unwashed fabrics, reaching values between 0.3 J/g and 0.6 J/g. Here, percentages of microcapsules retention that varied between 18 % and 39 % were calculated. The cotton woven with sample PCM-Bp80 presents a similar behaviour to sample Wc-PCM28, regarding the values of ΔH_m and the percentage of microcapsules retention.

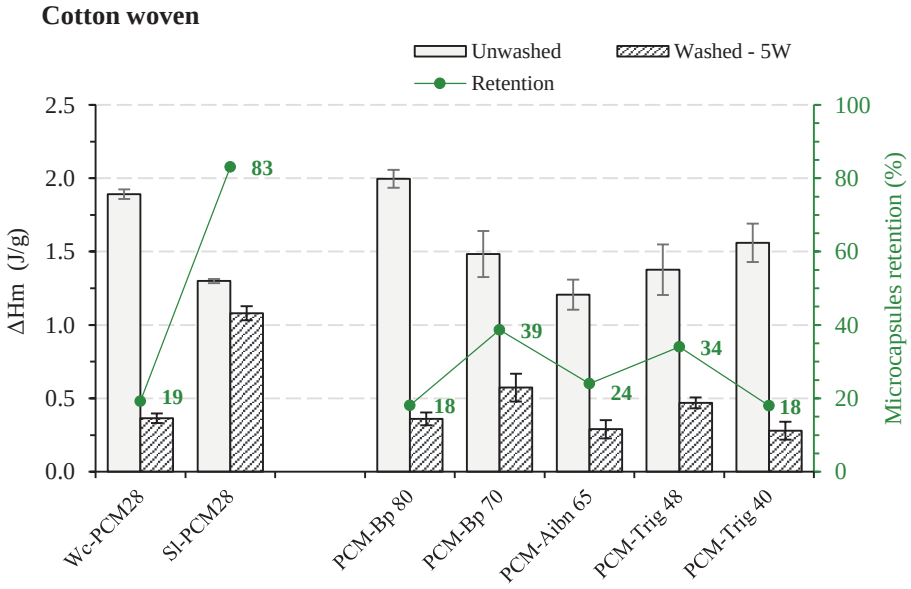

Figure 5.19: Influence of initiator type and polymerization temperature on the thermo-performance (values of ΔH_m) of unwashed and washed (5W) cotton woven and on the corresponding percentage of microcapsules retention (calculated using equation (5.2)). Samples Wc-PCM28 and Sl-PCM28 are represented for comparison

The retention percentages verified for polyester substrates are, in general, larger than those observed for cotton woven substrates. This fact was carefully discussed in Section 5.3.1 for the industrial microcapsules. It was probably associated with the different structure/rearrangement of the fabrics (the cotton woven is composed of the thinner and closer together yarns than the polyester) and with the chemical composition of the fibres (in which the distinct reactive groups of the fibres promote different interactions with the functional groups of the coupling agent).

To study the behaviour of the acrylic microcapsules during the washing process, besides the interaction between the coupling agent and the textile fibres, also the interaction between the coupling agent and the acrylic microcapsules must be studied. The shell of these

microcapsules is composed of a copolymer of MMA, BA and MAA with a proportion of 93/6/1wt. %. From these three monomers, MAA is the one that presents a carboxyl group that can remain available for a potential post-reaction with other functional groups. As only 1 wt.% of MAA was used to prepare the microcapsules, these groups should not have a large impact in the results of microcapsules retention. However, if available, a carboxyl group can react with an epoxide ring, through identical reactions to the ones described for the carboxyl end group of polyester (presented in section 5.1 and in Figure 5.6). Additionally, these carboxyl groups can also form intermolecular forces (hydrogen bond interactions) with the coupling agent or with the textile fibres.

Furthermore, comparing the results obtained for the polyester and cotton fabrics, a pattern between the retention percentage and the conditions used to prepare the microcapsules is not found. Only microcapsules PCM-Bp80 were the ones that showed a better initial thermo-performance in both substrates. Thus, considering the composition of these acrylic shell microcapsules and despite the changes in the reaction conditions used in their preparation, the gathered results suggest that, in this case, the thermo-performance of the treated textiles and the corresponding washing resistance are mainly defined by the chemical nature and structure of the textile substrate.

In order to improve the retention of the microcapsules on the textile fibres, having in mind the shell composition, a new sequence of experiments was planned by modifying the proportions of monomers used in experiment PCM-Bp80. The characterization of these microcapsules was described and discussed in Chapter 4 and, in the following section, the results obtained from their incorporation into the fabrics are presented.

5.3.3 Microcapsules prepared with different monomers proportions

Here, the studies regarding the incorporation of microcapsules containing octadecane with shells consisting of different copolymers of MMA, BA and MAA are reported. Sample PCM-Bp80, which was prepared with 93 wt.% of MMA, 6 wt.% of BA and 1 wt.% of MAA, was taken as reference in the following discussion. This was the sample that stand out from the previous results, due to its behaviour before and after the microcapsules impregnation procedure, and that was the base of the subsequent experiments of suspension polymerization.

Following the nomenclature used during the microcapsules characterization (in section 4.3.3 and that explicits the percentage of the monomers BA and MAA in each experiment), the samples tested here were:

- samples BA14-MAA1 and BA24-MAA1 (based on experiment PCM-Bp80 and prepared by increasing the amount of BA from 6 wt.% to 14 wt.% and 24 wt.%, maintaining MAA and decreasing MMA accordingly). The idea was to decrease the breakage of the microcapsules by increasing the amount of the monomer with low T_g (the BA).

- samples BA6-MAA9 and BA6-MAA19 (prepared by increasing the amount of MAA from 1 wt.% to 9 wt.% and 19 wt.%, maintaining BA and decreasing MMA accordingly). The idea was to increase the quantity of reactive groups (carboxyl groups) in the microcapsules in order to favour the linkages between their shell and the coupling agent.

- sample BA24-MAA19, which was prepared using the highest used percentages of BA and MAA (24 wt.% and 19 wt.%, respectively).

- samples MMA100 and BA100, which were obtained using 100 wt.% of MMA and BA, respectively.

Generally, these microcapsules exhibited ΔH_m values in the range of 175 – 180 J/g, $D_{4,3}$ of around 11 – 12 μm and $T_{5\%}$ between 165 – 220 ºC. The only exception is sample BA100 that presented properties not completely suitable for the incorporation into textiles, namely concerning its thermal stability ($T_{5\%}$ of 135 ºC). Nevertheless, the impregnation of sample BA100 was carried out for comparison purposes.

Characterization of treated textiles

a) Scanning electron microscopy observation

In Figure 5.20 are exemplified the structures obtained for polyester and cotton woven impregnated with microcapsules BA24-MAA1, BA6-MAA19 and BA24-MAA19 (sample PCM-Bp80 presented for comparison). These microcapsules were the ones prepared with higher variation on the monomers proportions of the copolymer. The micrographs of the remaining treated fabrics can be found in Appendix C (Figure C.7).

These pictures denote that, either increasing the amount of BA in the monomers mixture to 24 wt.% (sample BA24-MAA1, Figure 5.20 (c and d)) or increasing the amount of MAA to 19 wt.% (sample BA6-MAA19, Figure 5.20 (e and f)), spherical and well-shaped microcapsules are highly present. The sample BA24-MAA19 (Figure 5.20 (g and h)) showed the same

behaviour when applied into both substrates. During the SEM observation of these new treated fabrics, the identification of broken microcapsules seemed to be lower than in the samples earlier presented (Figure 5.15).

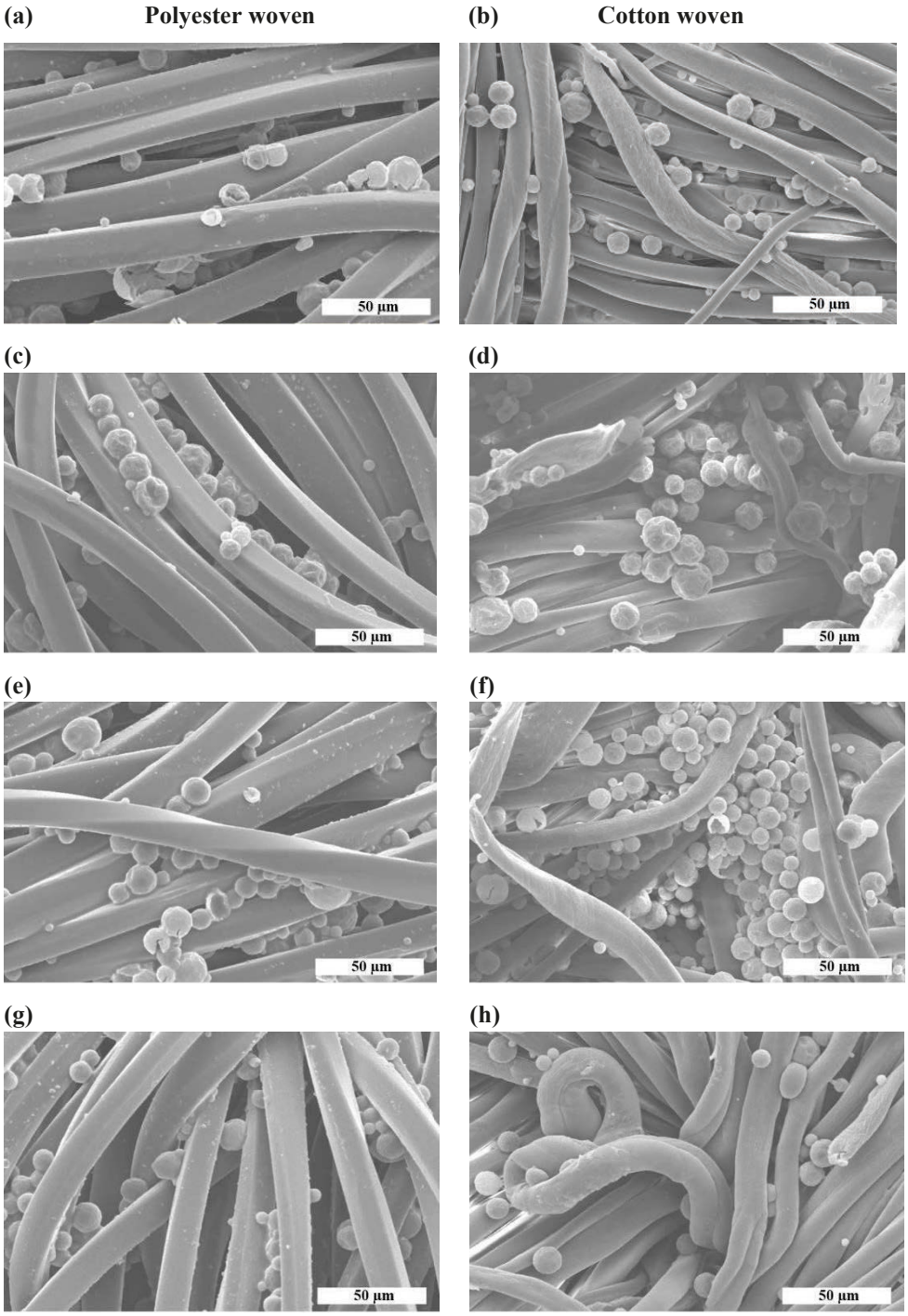

Figure 5.20: SEM micrographs of treated woven: microcapsules PCM-Bp80 (composed of MMA/BA/MAA with 93/6/1 wt.%) on (a) polyester and (b) cotton fibres; microcapsules BA24-MAA1 on (c) polyester and (d) cotton fibres; microcapsules BA6-MAA19 on (e) polyester and (f) cotton fibres; and microcapsules BA24-MAA19 on (g) polyester and (h) cotton fibres (magnification x600).

Figure 5.21 presents the SEM micrographs collected from treated polyester and cotton fibres with samples MMA100 and BA100. The microcapsules MMA100 (Figure 5.21 (a and b)) showed a similar behaviour to sample PCM-Bp80, though in these new micrographs a low number of microcapsules are identified. From the micrographs of sample BA100 before their incorporation in the fabrics (Figure 4.13 (c)), it was noticed that the microcapsules are completely collapsed and thus, the pictures of Figure 5.21 (c and d) were somehow expected. Therefore, no conclusions can be drawn about the effect of the padding process on the microcapsules (namely of the pressure applied in the foulard or the curing temperature).

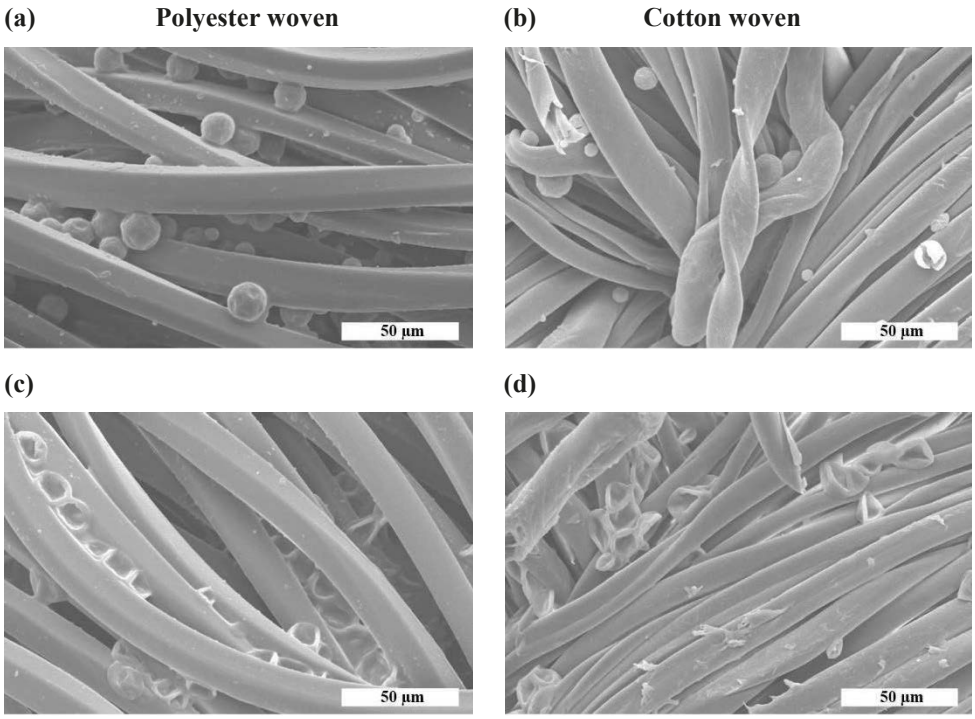

Figure 5.21: SEM micrographs of treated woven: microcapsules MMA100 on (a) polyester and (b) cotton fibres and microcapsules BA100 on (c) polyester and (d) cotton fibres (magnification x600).

b) Thermo-performance

For both substrates, the resulting DSC curves exhibit the same profile than the curves of the former fabrics (see Figure C.8 and C.9 in Appendix C). The respective enthalpy data and the WPU values obtained in the incorporation procedures are listed in Table 5.4.

The WPU percentages are similar to those obtained for the microcapsules prepared with different initiator and polymerization temperature (Table 5.3), varying from about 93 % for the polyester to about 53 % for the cotton woven.

Table 5.4: Influence of monomers proportions on the WPU (calculated using equation (5.1)) and on the thermo-performance (values of ΔH_m) of treated polyester and cotton woven.

Microcapsules	**Polyester woven**		**Cotton woven**	
	WPU (wt.%)	ΔH_m **(**J/g)	**WPU** (wt.%)	ΔH_m **(**J/g)
Wc - PCM28 *	88.7	8.4 ± 1.3	49.5	1.9 ± 0.1
Sl - PCM 28 *	88.1	4.5 ± 0.1	48.5	1.3 ± 0.1
PCM - Bp80 *, **	97.2	9.8 ± 1.0	54.7	2.0 ± 0.1
BA14 - MAA1	92.4	9.2 ± 0.9	54.0	2.1 ± 0.4
BA24 - MAA1	91.3	8.9 ± 2.3	53.2	1.6 ± 0.3
BA6 - MAA9	92.9	8.8 ± 0.2	52.3	1.8 ± 0.4
BA6 - MAA19	93.1	8.8 ± 1.4	53.2	2.2 ± 0.1
BA24 - MAA19	92.7	8.7 ± 0.8	54.0	2.0 ± 0.3
MMA100	93.4	8.7 ± 1.0	53.9	1.8 ± 0.1
BA100	89.0	4.7 ± 0.4	51.2	0

* results of treated fabrics previously presented

** microcapsules PCM-Bp80: prepared with monomers mixture of MMA/BA/MAA with 93/6/1 wt.%

Regarding the values of ΔH_m calculated for the polyester woven, values of about 9 J/g for all the samples were registered, with the exception of BA100 (that showed a ΔH_m of 4.7 J/g). The microcapsules BA100 presented a lower thermal stability ($T_{5\%}$ of 135 ºC versus $T_{5\%}$ between 165 – 220 ºC for the other samples) and as the curing stage reaches temperatures of 140 ºC, these microcapsules certainly undergo degradation with a consequent octadecane removal.

For treated cotton woven, the values of ΔH_m are significantly lower, following the tendency of previous cotton samples. Additionally, in this fabric, the ΔH_m corresponding to the sample BA100 is zero, suggesting a complete removal of the octadecane.

Characterization of textiles after washing process

a) Scanning electron microscopy observation

Figure 5.22 presents the SEM micrographs from cotton and polyester woven with sample BA24-MAA19 after a washing process, these were the substrates that exhibited better results of thermo-performance (as described below). For these washed fabrics, a high quantities of microcapsules are identified, without visible changes compared with the ones unwashed (Figure 5.20 (g and h)). Nevertheless, the quantification of the microcapsules elimination can only be carried out by DSC. The SEM micrographs of other washed substrates are represented in Appendix C (Figure C.10).

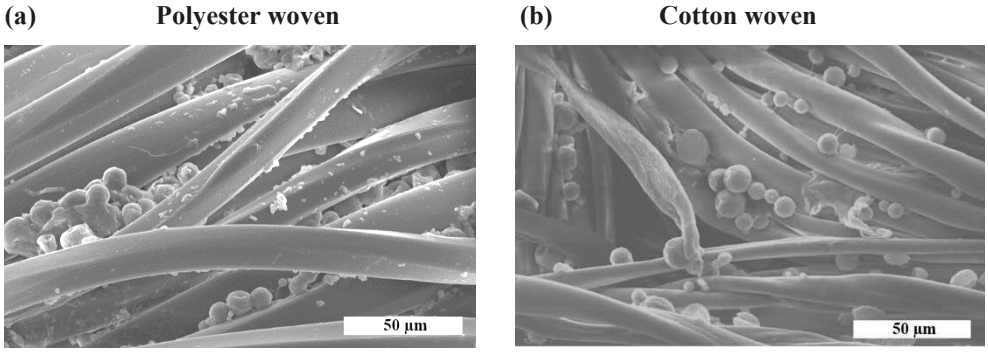

Figure 5.22: SEM micrographs after washing process (5W) of treated (a) polyester and (b) cotton woven with microcapsules BA24-MAA19 (magnification x600).

b) Thermo-performance

Figure 5.23 summarizes the results of DSC and percentage of retention after 5W for polyester woven with the microcapsules prepared with different monomers proportions. Figure 5.24 summarizes similar information regarding the cotton woven. Once more, the data obtained for the industrial samples and for the reference PCM-Bp80 are presented for comparison.

In the series of experiments corresponding to Figure 5.23, the type of fabric (polyester cotton) was maintained while the composition of microcapsules shell was modified (in general, the other properties were identical, including their particles sizes). Thus, the variation of microcapsules retention should be mainly originated by the different interaction between their

shell and the coupling agent. As mentioned before, the composition of shell was modified by changing the proportion of the monomers but not their type, thus the generic reactions between the microcapsules (namely its carboxyl groups) and the functional groups of the coupling agent are the same as the ones discussed for the former acrylic shell microcapsules (section 5.3.2).

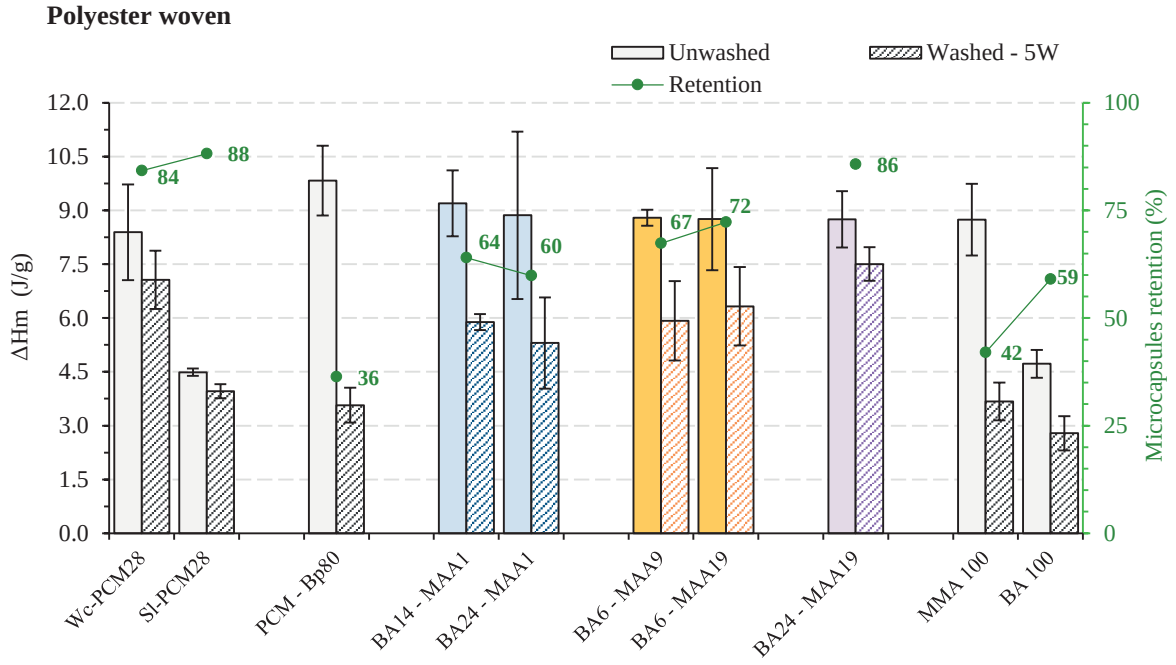

Figure 5.23: Influence of monomers proportions on the thermo-performance (values of ΔH_m) of unwashed and washed (5W) polyester woven and on the corresponding percentage of microcapsules retention (calculated using equation (5.2)). Samples Wc-PCM28, Sl-PCM28 and PCM-Bp80 (MMA/BA/MAA with 93/6/1 wt.%) are represented for comparison.

To simplify the discussion of these results, they are grouped according to the changed monomers:

- For samples BA14-MAA1 and BA24-MAA1, the amount of BA used in suspension polymerization procedure was increased in comparison with PCM-Bp80. As mentioned before, this change aimed to decrease the breakage of the microcapsules during the impregnation and washing processes and, thus, increasing their thermo-performance and washing resistance. For polyester woven this aim seems to be achieved, since the microcapsules retention was improved from 36 % to around 64 % as the percentage of BA was increased from 6 wt.% to 14 wt.%, as Figure 5.23 shows. The further increase of BA does not seem to improve the retention

performance (that slightly decreased to 60%). Nevertheless, this last variation could not to be significant due to its high standard deviation.

- Regarding the tests with samples BA6-MAA9 and BA6-MAA19, the amount of MAA used in the monomer mixture was increased (comparing with PCM-Bp80). In order to increase the presence of carboxyl groups in the microcapsules and, consequently, to intensify the bond between their shell and the coupling agent. For these cases, the microcapsules retention was significantly improved, reaching the percentage of 72 % for polyester woven with sample BA6-MAA19. In fact, the increase of MAA results in microcapsules with a better resistance to the washing cycle, suggesting that among the microcapsules shell and the coupling agent more durable bonds were formed. Probably due to the formation of covalent linkages between carboxyl groups of the microcapsules shell and the epoxide ring of the coupling agent and due to the presence of intermolecular forces (hydrogen bond interaction) between these carboxyl groups and both reactive groups of the coupling agent (as the epoxide ring of coupling agent can also hydrolyse forming hydroxyl groups and the alkoxysilane groups forming silanol groups).

- In experiment BA24-MAA19 the highest percentages of BA (24 wt.%) and of MAA (19 wt.%) were used (reducing the MMA amount). Comparing now the washed polyester with microcapsules BA24-MAA19 with both BA24-MAA1 and BA6-MAA19, it can be concluded that the retention increase even further (to 86%), the maximum of all experiments. This result reinforces the idea that the presence of carboxyl groups favour the fixation of microcapsules onto the polyester fibres.

- The performance of the homopolymers MMA100 and BA100, besides corresponding to the lowest enthalpies also exhibit the lowest retention values. The low ΔH_m values for the washed polyester with BA100 was expected, since their initial value was already low and the presence of collapse microcapsules was revealed by the SEM observation.

Comparing the results obtained for polyester woven with the acrylic microcapsules, namely with sample BA24-MAA19, with the one observed for the industrial sample Wc-PCM28 a similar behaviour is detected (values of ΔH_m and of microcapsules retention).

Regarding the incorporation of this series of acrylic shell microcapsules into the cotton woven, a different behaviour was observed, as discussed next (see Figure 5.24):

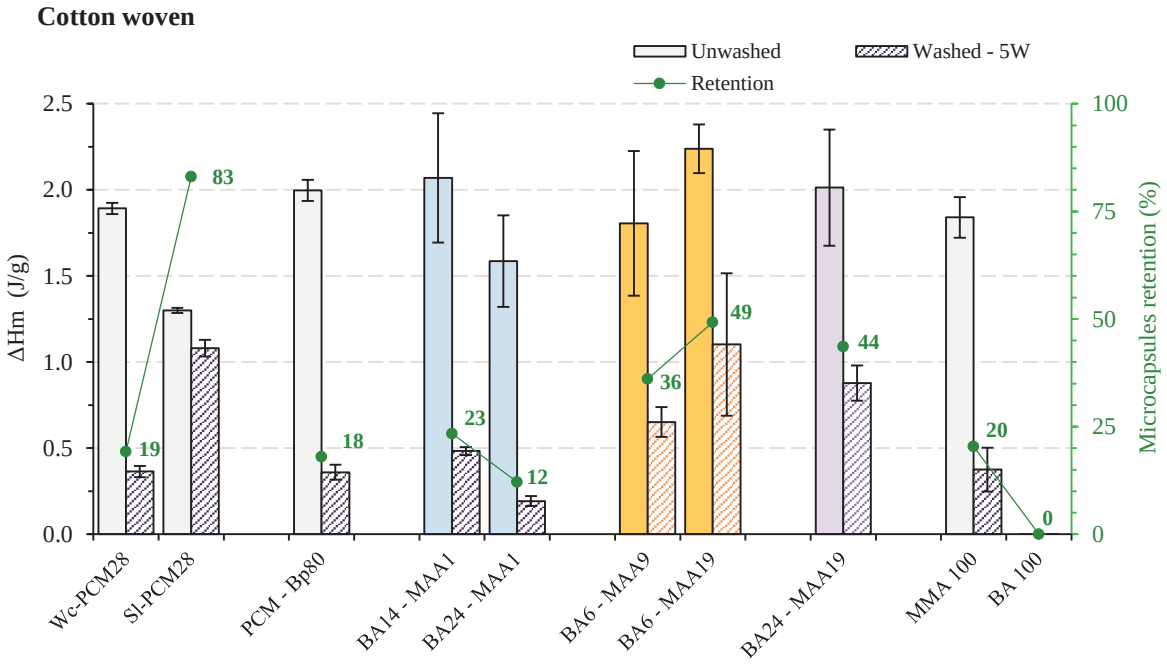

Figure 5.24: Influence of monomers proportions on the thermo-performance (values of ΔH_m) of unwashed and washed (5W) cotton woven and on the corresponding percentage of microcapsules retention (calculated using equation (5.2)). Samples Wc-PCM28, Sl-PCM28 and PCM-Bp80 (MMA/BA/MAA with 93/6/1 wt.%) are represented for comparison.

- For the experiments of which the amount of BA was increased (BA14-MAA1 and BA24-MAA1) compared with PCM-Bp80, the percentage of microcapsules retention for sample BA14-MAA1 was slightly improved (from 18% to 23%), while for sample BA24-MAA1 these percentages were reduced (to 12%). It seems that a higher addition of BA in the monomers mixture and lower of MMA, did not favour the affinity between the microcapsules and the cellulose fibres.

- In contrast, increasing the MAA proportion improves the washing resistance of microcapsules in the cotton woven. The value of retention increases progressively from 18% for sample PCM-Bp80, to 36% for BA6-MAA9 and, finally, to 49 % for BA6-MAA19. This behaviour should reflect the higher presence of carboxyl groups in the microcapsules shell, which were introduced in their composition by the monomer MAA. As previously described for the polyester woven, this reactive group seems to favour the microcapsules fixation onto the

textile fibres, due to their reaction with the coupling agent. In addition, despite the existence of hydrogen bonds between and within the cellulose fibres, a possible presence of these intermolecular forces between them and the acrylic shell could also improve the microcapsules fixation.

- The microcapsules retention for the cotton with sample BA24-MAA19 (44 %) was slightly lower than for sample BA6-MAA19 (49 %, which considering its high standard deviation could not be significant), but it was greatly higher than BA24-MAA1 (12 %). This result demonstrates, once more, the effect of the carboxyl groups in the microcapsules shell composition and it emphasises the importance of the MAA in the monomers mixture.

- Finally, it is also possible to observe that the microcapsules MMA100 show a similar behaviour to sample PCM-Bp80. This result was the already expected since microcapsules PCM-Bp80 contains of 93 wt.% of MMA.

For cotton woven fabric, the samples BA6-MAA19 and BA24-MAA19 showed better results of microcapsules retention than the industrial sample Wc-PCM28, presenting a higher value of ΔH_m after the 5W.

The study of the influence of the monomers proportions on microcapsules shell revealed that, for the polyester woven, the composition with the highest tested percentages of BA and MAA (sample BA24-MAA19) corresponds to best performance in terms of thermo-performance and washing retention. Whereas for the cotton woven is also the composition with the highest percentage of MAA but with low amount of BA (sample BA6-MAA19). Nevertheless, due to their values standard deviation, this sample does not seems to have a significant difference from sample BA24-MAA19. Therefore, for both substrates, the addition of the MAA to the monomers mixture favoured the microcapsules fixation onto the textile fibres, most likely due to the presence of carboxyl groups in the microcapsules shell and their reaction with the functional groups of the coupling agent.

In summary, the microcapsules BA24-MAA19 (was prepared with 57 wt.% of MMA, 24wt.% of BA and 19 wt.% of MAA) show great potential to be impregnated in different textile substrates. These microcapsules will be further studied, comparing their performance with new acrylic microcapsules functionalized with different reactive groups (Chapter 6).

5.4 CONCLUSIONS

This chapter describes the incorporation in textiles of different microcapsules specimens: two types of industrial samples (described in section 3.3.3); and acrylic shell microcapsules prepared using different experimental conditions (described in section 4.3.2 and 4.3.3). This procedure was carried out by padding into two types of fabrics (polyester and cotton woven) using a finishing formulation supplied by Devan-Micropolis and established according to the company's technology [5]. Thus, following to this methodology, in order to increase the microcapsules fixation onto the surface of the fabrics, a di-functional coupling agent was used to react with the textile fibres and with the microcapsules shell.

For treated fabrics with industrial samples, it was observed that the values of ΔH_m for the polyester woven were higher than for the cotton. This outcome results from their WPU values (as the WPU was around 90 % for polyester and 50 % for cotton) and from their different fibres rearrangement and fabric structure (in the fabric of cotton the yarns are thinner and closer together than in the polyester woven). Additionally, for the sample Wc-PCM28 the values of ΔH_m were higher than for the Sl-PCM28. A consequence of the ΔH_m values of these microcapsules (sample Wc-PCM28 presents a ΔH_m of 195 J/g while Sl-PCM28 presents a value of 160 J/g), but also of the small particle size of sample Sl-PCM28 (that exhibited a mean diameter of around 3 µm while sample Wc-PCM28 showed a value of 15 µm).

Afterwards, with the washing tests, it was determined that the microcapsules with smaller size (sample Sl-PCM28) present higher washing resistance in both textile substrates. Therefore, the particles size was shown to be an important factor in this process. Since microcapsules with smaller size present a lower ΔH_m but, on the other hand, they present a better washing resistance. Concerning the microcapsules Wc-PCM28, for the polyester woven a higher washing resistance than in the cotton was observed (84 % versus 19 %). This difference between both substrates could be probably explained by the different structure of the fabrics and by the distinct chemical composition of the fibres. First, it seems that the structure of polyester woven favours the fixation of microcapsules more than the one of the cotton (structure described above). In addition, regarding the composition of the fibres, the lower microcapsules washing resistance of the fabric of cotton can be influenced by the presence of hydrogen bonds within and between the hydroxyl groups of cellulose molecules. These bonds could probably reduce the formation of new linkages between the OH groups and the bi-functional coupling agent used in the finishing formulation. In contrast, considering that the polyester is composed mainly for non-reactive groups, the fixation of microcapsules could be favoured by a possible reaction

between the polyester end groups (carboxyl and hydroxyl groups) and the coupling agent. This different behaviour of polyester and cotton woven, concerning their thermo-performance and washing resistance, was also observed when using acrylic shell microcapsules.

Regarding the samples prepared with different initiators and reaction temperatures, for polyester woven a ΔH_m between 7.5 J/g and 9.8 J/g was obtained, whereas for cotton the values were between 1.2 J/g and 2.0 J/g. Nevertheless, in both substrates, spherical and well-defined microcapsules with only a few of them broken at the fabric' surface were observed. In addition, it was determined that a significant amount of microcapsules was removed and/or broken during the washing process, decreasing significantly the ΔH_m of treated fabrics. Based on the thermo-performance results, sample PCM-Bp80 was the one that revealed the best behaviour. However, comparing with industrial sample Wc-PCM28, for the polyester woven with sample PCM-Bp80 a lower percentage of retention was found (only 36 % compared with 84 %), while for the cotton woven a similar behaviour was observed (values of 19 %).

In order to improve the microcapsules retention and having in mind the shell composition, a new sequence of experiments was planned by modifying the proportions of monomers used in the batch PCM-Bp80. Through the impregnation of the obtained microcapsules and for each type of fabric, treated textiles with similar thermo-performance were obtained (with the exception of sample BA100). Moreover, through SEM observation seemed that, in most of the cases, the number of broken microcapsules was reduced. With the washing tests, it was verified that the microcapsules washing resistance is influenced by the composition of their shell. The best results were: sample BA24-MMA19 for polyester woven, reaching the retention of 86 %; and sample BA6-MMA19 for cotton woven, presenting the value of 49%. In both cases, the microcapsules were prepared with the higher proportion of monomer MAA, suggesting that the carboxyl groups of their shell react with the di-functional coupling agent and, consequently, increasing the microcapsules fixation level onto the surface of the fibres. Once more, comparing these outcomes with industrial sample Wc-PCM28, for cotton woven a slightly better performance was shown with the acrylic microcapsules, whereas for polyester a similar performance was revealed.

Herein, it was demonstrated that acrylic shell microcapsules containing octadecane present suitable properties to produce thermo-regulating textiles, especially the ones prepared with 57 wt.% of MMA, 24 wt.% of BA and 19 wt.% of MAA. These tests reveal the importance of the shell composition to enhance the microcapsules washing resistance, namely the importance of carboxyl groups. These acrylic shell microcapsules can be an alternative to the ones composed of melamine-formaldehyde.

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CHAPTER 6

FUNCTIONALIZATION OF ACRYLIC MICROCAPSULES WITH DIFFERENT REACTIVE GROUPS

ABSTRACT

The aim of this study was the production of new acrylic microcapsules containing reactive groups in their shell. These microcapsules must be compatible with the Devan Chemicals´ technology, in which microcapsules with reactive groups are incorporated into textile substrates creating durable bond with a coupling agent and presenting a high washing resistance. The procedure of suspension polymerization was based on the monomers mixture methyl methacrylate, butyl acrylate and methacrylic acid (MMA/BA/MAA) of 57/24/19 wt.% (described in section 4.3.3). Here, the MAA was replaced by other monomers: hydroxyethyl methacrylate (HEMA), 3-(trimethoxysilyl) propyl methacrylate (TMSMA) and glycidyl methacrylate (GMA). While the MAA presents a carboxyl group, these monomers present either a hydroxyl group, or alkoxysilane groups or an epoxide group, respectively. As indicated in the previous chapter, the obtained microcapsules were impregnated by padding in polyester and cotton woven and their thermo-performance and washing resistance were evaluated.

Minor differences on microcapsules properties were detected, while the washing resistance tests demonstrated that microcapsules prepared with TMSMA and with MAA as dual reactive monomer show better washing resistance, respectively, on polyester and on cotton fibres.

6.1 INTRODUCTION

In chapter 3, a standard procedure of microencapsulation, based on suspension polymerization technique, was established. By changing some reaction parameters the microcapsules properties were modified and their performance when incorporated in the fabrics was enhanced. However, some improvements can still be searched, namely trying to modify the microcapsules shell composition in order to increase, as much as possible, their washing resistance.

As previously indicated, in order to differentiate its product range, Devan Chemicals developed expertise on the preparation of microcapsules and on their incorporation into textiles. One of the focus of the company was the enhancement of microcapsules resistance and durability when applied into textiles, by using microcapsules with shells containing reactive

groups compatible with bi-functional coupling agents and with textile fibres [1,2]. In line with this methodology, the final goal of the present work was to modify the composition of microcapsules previously prepared by adding new reactive groups in their shell. With these products, it was aimed to enlarge the range of functionalities of the microcapsules shell and to increase their fixation on different types of fibres.

The results obtained with the washing resistance tests, presented in the previous chapter, suggested that the carboxyl groups of the microcapsules shell (introduced in the copolymer by the MAA) can react with the coupling agent increasing the microcapsules washing resistance. From all the acrylic shell microcapsules that were impregnated into the textile substrates (in chapter 5), sample BA24-MAA19 (that was prepared with the monomers mixture of 57 wt.% of MMA, 24 wt.% of BA and 19 wt.% of MAA) presents the better results of washing resistance. Here, based on this experiment, new modifications in the microcapsules shell were performed, replacing the MAA by new reactive monomers capable to covalently react with the coupling agent. So, as the finishing formulation includes a coupling agent with one epoxide group and three methoxy groups (described in section 5.1), monomers containing either hydroxyl groups, alkoxysilane groups or epoxide groups were applied (see Figure 6.1):

- hydroxyethyl methacrylate (HEMA);
- 3-(trimethoxysilyl) propyl methacrylate (TMSMA);
- glycidyl methacrylate (GMA).

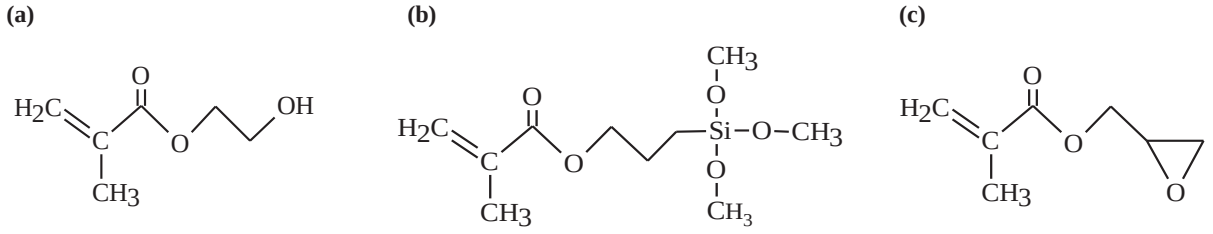

Figure 6.1: Chemical structure of (a) hydroxyethyl methacrylate (HEMA), (b) 3-(trimethoxysilyl) propyl methacrylate (TMSMA) and (c) glycidyl methacrylate (GMA).

HEMA is an acrylic monomer that could introduce hydroxyl groups in the microcapsules shell (see Figure 6.1). In order to increase the fixation of microcapsules on the textile fibres, these groups should post-react with the coupling agent during the incorporation process. Their reactions can be identical to the ones previously described for the OH groups of cellulose (see Figure 5.3 and 5.5) [3,4]. In addition, based on the mechanisms of these figures, a representation

of the reaction between the hydroxyl group of a functionalized microcapsule and the silanol groups of CoupA01 (formed by their methoxy groups hydrolysis) is presented in Figure 6.2 (a) [3]. Whereas, its reaction with the epoxide group of CoupA01 (exemplifying only one route of reaction) is presented in Figure 6.2 (b) [5].

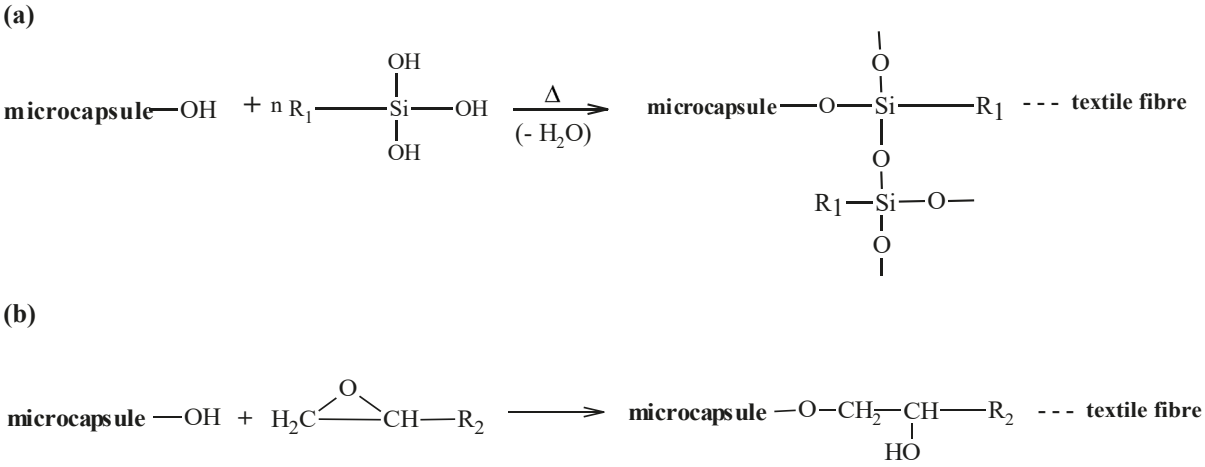

Figure 6.2: Mechanism of reaction between the hydroxyl group of a functionalized microcapsule and (a) the silanol groups of CoupA01 (formed by the hydrolysis of their methoxy groups) and (b) the epoxide group of CoupA01.

As the TMSMA is an organosilane compound (see Figure 6.1 (b)) with three methoxy groups (alkoxysilane groups), it was aimed to prepare microcapsules maintaining these groups available to post-react with the coupling agent. As both, TMSMA and CoupA01, present methoxy groups, they can form silanol groups (Si-OH), through the reaction of hydrolysis (by a mechanism identical to the one represented in Figure 5.3). Then, these groups can condensate to create siloxane bonds (Si-O-Si) [3].

However, as the alkoxysilane groups of TMSMA can hydrolyse in contact with water (forming silanol groups), side reactions during the microcapsules formation can occur [6–8]. The mechanism of TMSMA hydrolysis with water is represented in Figure 6.3 [6–8]. The silanol groups resulting from the hydrolysis can, subsequently, condensate to form siloxane bonds. In order to functionalize the acrylic microcapsules, the hydrolysis reaction of TMSMA in the polymerization process is not a key constrain, since the silanol groups can still react with the coupling agent. In contrast, the subsequent condensation reaction has to be avoided because, after the formation of siloxane bonds, the chemical reaction with the coupling agent is no longer possible [6]. One of the solutions discussed in the literature to reduce these premature hydrolysis and condensation reactions is the control of pH values. For most systems, the hydrolysis of

alkoxysilane is catalysed by both acidic and basic conditions, being the minimum hydrolysis rate at pH of about 7 [6,8]. Therefore, to minimize this premature condensation, the experiment using TMSMA as monomer was carried out at neutral pH.

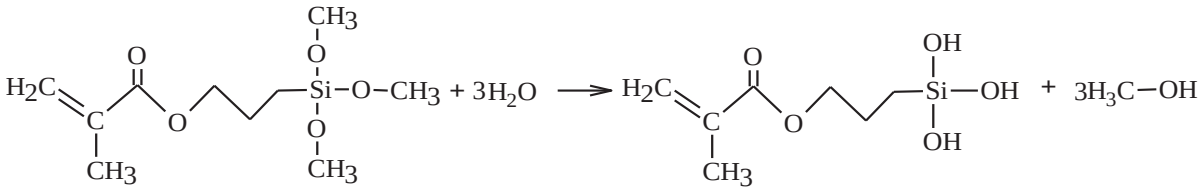

Figure 6.3: Mechanism of hydrolysis reaction of TMSMA in the presence of water, forming the silanol groups [6].

Finally, the GMA was also used due to its reactive groups: the methacrylate and the epoxide (Figure 6.1 (c)). The polymers produce from GMA are widely used due to presence of the epoxide groups and their capacity to enter into a large number of chemical reactions, namely allowing their post-reaction [9,10]. These reactions should form a similar arrangement to the one represented for the microcapsules functionalized with hydroxyl groups (Figure 6.2), since, like HEMA and in contrast with TMSMA, the GMA only has one reactive group (beside the double bond C=C). As it is well known, GMA undergoes radical polymerization. However, it is also possible that the OH groups formed by hydrolysis of its epoxide groups react with the new unreacted groups of the other chains.

In sum, the production of new microcapsules with different types of reactive groups in their shell was proposed. This work completes the studies previously described, namely the one in which microcapsules with a shell functionalized with higher amount of carboxyl groups were prepared. Here, alternative functionalities were selected: the hydroxyl group (from HEMA), the alkoxysilane group (from TMSMA) and the epoxide group (from GMA). After the microencapsulation procedure, these groups should remain available for post-reaction with the coupling agent during the procedure of microcapsules incorporation into the textiles.

6.2 EXPERIMENTAL

6.2.1 Materials

All monomers, methyl methacrylate (MMA), *n*-butyl acrylate (BA), hydroxyethyl methacrylate (HEMA), 3-(trimethoxysilyl) propyl methacrylate (TMSMA), glycidyl methacrylate (GMA), and all crosslinkers, ethylene glycol dimethacrylate (EGDMA) and pentaerythritol tetraacrylate (PETRA) were purchased from Sigma-Aldrich. The octadecane (purity of 97 wt. % and melting onset temperature of about 27 ºC) was received from Devan Chemicals (Belgium). The benzoyl peroxide (75%, contains 25% water, BPO) was supplied by ACROS and poly(vinyl alcohol) (Mw = 31000 – 50000 g/mol and degree of hydrolysis = 87-89 %, PVA) was purchased from Sigma-Aldrich. All the reagents were used as received.

6.2.2 Microencapsulation procedure using several dual reactive monomers

The new experiments were carried out following the standard procedure of suspension polymerization developed in previous studies, which is described in Chapter 4 (section 4.2.2). This series of experiments was based on the experiment BA24-MAA19 (24 wt.% of BA, 19wt.% of MAA and the remaining 57 wt.% of MMA), maintaining its procedure and only replacing the MAA by either HEMA, TMSMA or GMA (as presented in Table 6.1). Besides these monomers, EGDMA and PETRA were used as crosslinker (5 wt.% of each related to monomers), BPO as initiator (1.2 wt.% related to monomers) and PVA as stabilizer (1 wt.% related to water). Finally, a PCM/monomers mass ratio of 2 was used.

Table 6.1: Recipe for the preparation of acrylic microcapsules using different dual reactive monomers.

Experiment	**Monomer (wt. %)**		
			Dual reactive monomer
BA24 - MAA19 *	MMA 57	BA 24	MAA 19
MMA - BA - HEMA	MMA 57	BA 24	**HEMA** 19
MMA - BA - TMSMA	MMA 57	BA 24	**TMSMA** 19
MMA - BA - GMA	MMA 57	BA 24	**GMA** 19

* BA24-MAA19: experiment previously presented

6.2.3 Incorporation of microcapsules into textile substrates and washing process

The incorporation of microcapsules into the textile substrates was carried out following the procedure presented in section 5.2.2, without any modification. Summarizing, this process was performed by the technique of padding using a foulard with the nip roll pressure of 4 bar and applying a drying and curing step (140 ºC during 4 minutes). The composition of finishing formulation and the microcapsules concentration (40 g/L) was maintained as well as the added coupling agent (CoupA01).

After the microcapsules incorporation a segment of each textile substrate was washed according to the procedure described in section 5.2.3, which is equivalent to 5 cycles of normal washing (5W). For the treated textiles in which the best results of microcapsules washing resistance were obtained, the washing process was extended to 25 cycles of normal washing (25W). Between each washing procedure the textiles were dried at room temperature.

6.2.4 Characterization techniques

Microcapsules characterization

The microcapsules characterization was accomplished by using the techniques described in Chapter 3, section 3.2.3. Their chemical characterization was done by FT-IR spectroscopy, the morphological characterization by SEM and laser diffraction and the thermal characterization by DSC and TGA.

Textiles characterization

The characterization of treated textiles was performed according to the techniques described in Chapter 5, section 5.2.4. The textile substrates were evaluated before and after the washing process by SEM observation and by DSC analyses. For the washed substrates, the DSC analyses were carried out after 5W, 15W and 25W.

6.3 RESULTS AND DISCUSSION

6.3.1 Characterization of functionalized microcapsules

For this series of experiments, the main microcapsules properties were investigated, focusing on the identification of their chemical structure and determining their morphological and thermal properties. In this evaluation the sample BA24-MAA19 was taken as reference.

a) Chemical characterization

As mentioned before, with these new experiments, to obtain acrylic microcapsules presenting a shell with different functional groups was intended. FT-IR spectroscopy was used to confirm the presence of these functionalities. Though, it was difficult to prove the existence of these monomers in the microcapsules, due to its low concentration compared to the high concentration of octadecane. In Figure 6.4 are shown the FT-IR spectra of all three new samples (MMA-BA-HEMA, MMA-BA-TMSMA and MMA-BA-GMA) together with the corresponding monomers and the octadecane.

The FT-IR spectra of all used monomers (including HEMA TMSMA and GMA) are characterized by a strong peak at around 1720 cm^{-1} from the C=O stretching vibration and other at around 1160 cm^{-1} assigned to the C-O-C stretching vibration of the ester group. In addition, these spectra also present one peak at 1637 cm^{-1}, attributed to the stretching vibration of the double bond (C=C) (see Figure 6.4). As represented in this figure and as described in the previous FT-IR analyses, the spectrum of octadecane is characterized by: two strong peaks at 2913 cm^{-1} and 2847 cm^{-1} (assigned to asymmetric and symmetric C-H stretching vibration of CH_2); one at 1470 cm^{-1} (assigned to the bending vibration of CH_2); and another at 716 cm^{-1} (from its alkane long chain) [11]. In the spectra of the diverse microcapsules, the peaks previously attributed to the monomers and to the octadecane are detected. As expected, the only exception is the one attributed to the double bond C=C, since during the formation of the copolymer this linkage disappears to form a new simple bond.

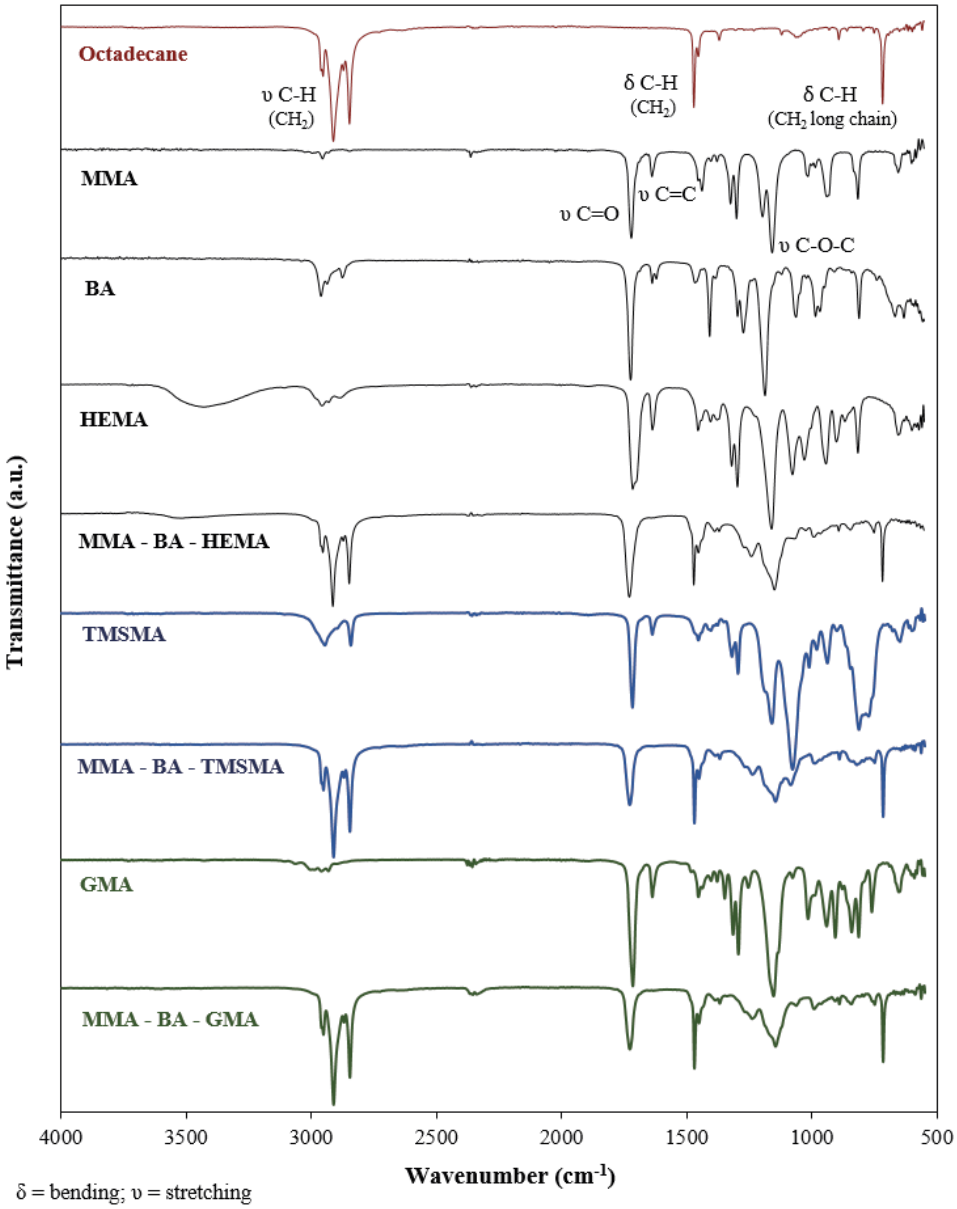

Figure 6.4: FT-IR spectra of octadecane, of used monomers and of samples MMA-BA-HEMA, MMA-BA-TMSMA and MMA-BA-GMA.

HEMA is the monomer that can be differentiated from the MMA and BA by the presence of a hydroxyl group. The peak ascribed to the O-H stretching vibration of this group was identified in its spectrum by a broad band at 3430 cm^{-1}. For the spectra of sample MMA-BA-HEMA a small band in the range of 3500 – 3400 cm^{-1} seems to be distinguished (see Figure 6.4 and enlargement in Figure 6.5). Comparing with the spectra of octadecane and monomers but

mostly with one of HEMA, this peak could indicate that the hydroxyl groups, initially identified in HEMA spectrum, are present in these new microcapsules.

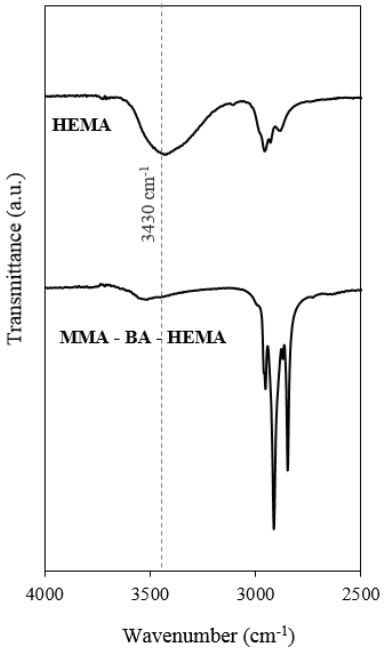

Figure 6.5: Enlargement of spectra of HEMA and sample MMA-BA-HEMA in the wavenumber range of 4000 - 2500 cm^{-1}.

Concerning the sample MMA-BA-TMSMA, the same preparation conditions of experiment MMA-BA-HEMA were employed, but instead of HEMA, TMSMA was used. This monomer is a silane compound characterized by the presence of $Si\text{-}OCH_3$ groups. So, it can be distinguished from the remaining monomers by the Si-O vibration of $Si\text{-}OCH_3$ group, which normally appears through one strong peak at around 1100 cm^{-1} and other at around 850 - 800 cm^{-1} [11]. In TMSMA spectrum, corresponding to these vibrations, one strong peak at 1078 cm^{-1} and one large and strong band between about 810 and 775 cm^{-1} were identified. In the spectrum of sample MMA-BA-TMSMA, the first signal seems to be present at 1084 cm^{-1} (despite their low intensity), while in the wavenumber of the second one a small band with several peaks with low intensity is detected (see Figure 6.6). These observations, mainly the identification of the peak at 1078 cm^{-1}, seem to indicate the existence of $Si\text{-}OCH_3$ groups in new microcapsules.

Nevertheless, as mentioned in section 6.1, the $Si\text{-}OCH_3$ groups can undergo hydrolysis forming silanol groups (Si-OH) or undergo hydrolysis and condensation forming siloxane linkages (Si-O-Si) during the polymerization reaction. In the FT-IR spectra:

- the silanol group can be identified by the appearing of a band between around 3700 and 3200 cm^{-1}, assigned to Si-OH stretching vibrations [11]. In the spectrum of sample MMA-BA-TMSMA, it was not possible to detect this peak. Thus, if present, the concentration of the silanol group should be low.

- for the siloxane linkages, its symmetric stretching vibration normally appears at around 1100 - 1000 cm^{-1} [11]. Some doubt about the presence of these groups could arise, because its characteristic wavenumber includes the peak at 1084 cm^{-1} identified in the microcapsules spectrum and attributed to the $Si\text{-}OCH_3$ group. However, due to the similarity between this peak (1084 cm^{-1}) and the one at 1078 cm^{-1} present in spectrum of the monomer TMSMA ascribed to the $Si\text{-}OCH_3$ group, and due to the similarity with other references [12], it was considered that some $Si\text{-}OCH_3$ groups remained unreacted in microcapsules MMA-BA-TMSMA.

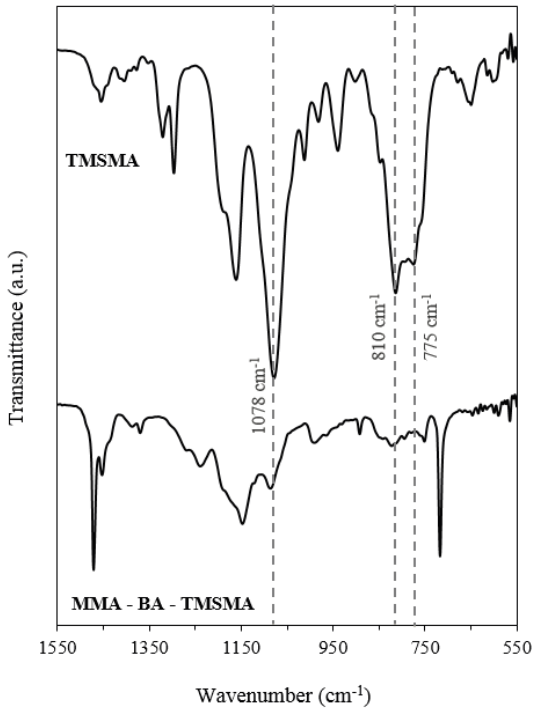

Figure 6.6: Enlargement of spectra of TMSMA and sample MMA-BA-TMSMA in the wavenumber range of 1550 - 550 cm^{-1}.

Finally, the spectra of GMA and corresponding microcapsules are also represented in Figure 6.4. In its spectrum, it is possible to identify two strong peaks from this epoxide group: one ascribed to the asymmetric ring deformation that normally appears between 950 and 815 cm^{-1} and that here was identified at 907 cm^{-1}; and a second one attributed to symmetric ring

deformation that normally appears at 835 cm^{-1} and that was identified at 841 cm^{-1} (see spectra enlargement in Figure 6.7) [11] . For the spectrum of sample MMA-BA-GMA, these signals were also identified (at 908 cm^{-1} and 843 cm^{-1} respectively), despite its low intensity, suggesting the presence of epoxide ring in the microcapsules shell.

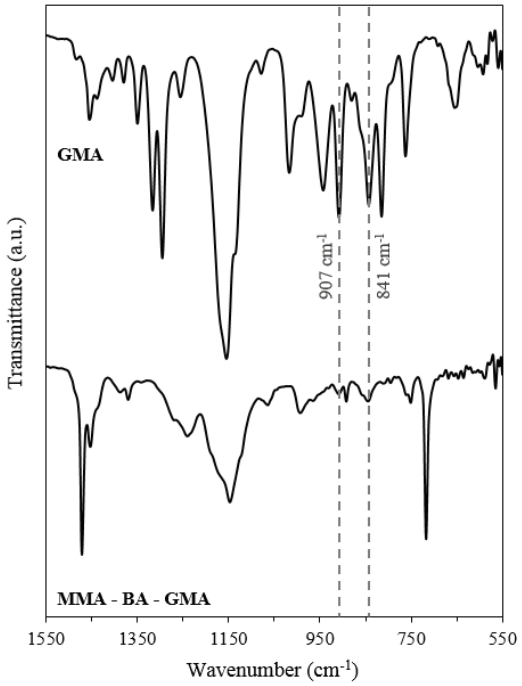

Figure 6.7: Enlargement of spectra of GMA and sample MMA-BA-GMA in the wavenumber range of 1550 - 550cm^{-1}.

b) Morphological characterization

In all the new samples, the SEM analyses confirmed the presence of individual and spherical microcapsules with a rough shell surface (see Figure 6.8). Furthermore, as in sample BA24-MAA19 (Figure 6.8 (a)), the existence of microcapsules with distinct particles sizes was identified.

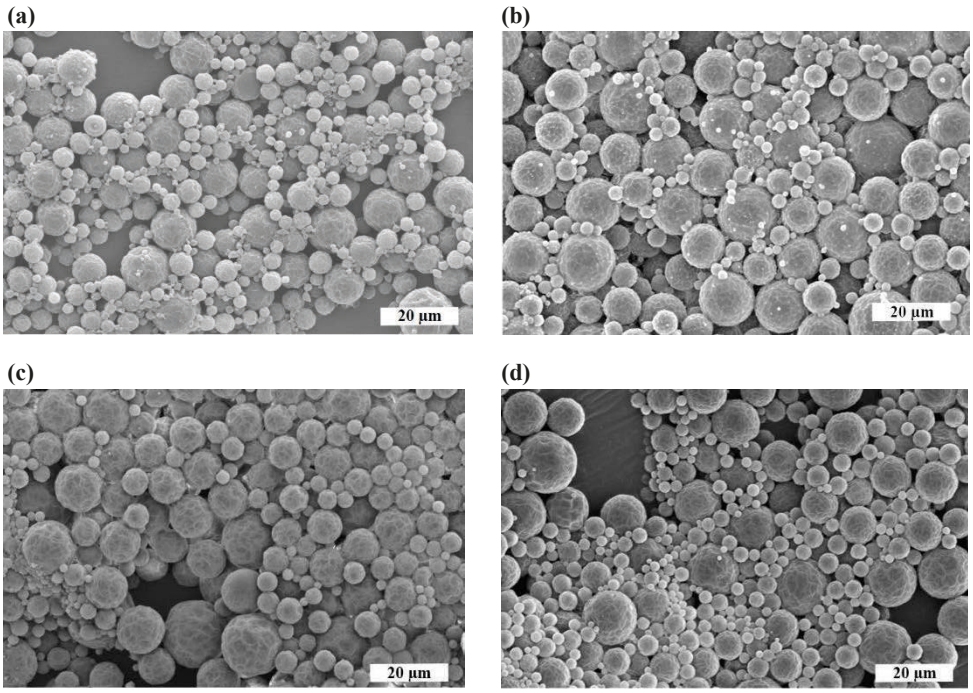

Figure 6.8: SEM micrographs of microcapsules prepared with different dual reactive monomers: (a) sample BA24-MAA19; (b) sample MMA-BA-HEMA; (c) sample MMA-BA-TMSMA; and (d) sample MMA-BA-GMA (magnification x1000).

In this series of experiments, the particle size analysis was also carried out. As the former samples and in agreement with the results observed by SEM, here the particle size distribution curves exhibit a bimodal profile (see Figure D.1 in Appendix D). The statistical diameters gathered from these curves are listed in Table 6.2. This table shows that the size distribution of the several types of microcapsules is only slightly different, presenting a D_{10} and D_{90} that spread from about 2 to about 23 µm.

Table 6.2: Statistical diameters of microcapsules size distributions, samples prepared using different dual reactive monomers (values of mean diameter ($D_{4,3}$), D_{10}, D_{50} and D_{90}).

Sample	Mean diameter, $D_{4,3}$ (µm)	D_{10} (µm)	D_{50} (µm)	D_{90} (µm)
BA24 - MAA19 *	10.7	2.3	10.4	19.2
MMA-BA-HEMA	11.6	2.5	11.3	20.2
MMA-BA-TMSMA	13.0	2.4	12.8	22.8
MMA-BA-GMA	11.8	2.3	11.6	21.0

* BA24 - MAA19: sample presented in section 4.3.3.

c) Thermal characterization

In the same way as in chapter 4, in this section only the most relevant results obtained from DSC and TGA are presented, being the remaining information in Appendix D (in Tables D.1 and D.2). Concerning the DSC curves, the same curve profile of the former acrylic microcapsules was obtained: an endothermic peak (downwards) for the heating process and an exothermic peak (upwards) for the cooling process (see Figure D.2 in Appendix D). The corresponding values ΔH_m and PCM content are summarized in Table 6.3, where similar values among all types of microcapsules are observed, including sample BA24 - MAA19. Regardless, the nature of the dual reactive monomer used to prepare these samples, their ΔH_m was around 180 J/g and the PCM content around 71%.

Table 6.3: Thermal properties of microcapsules prepared using different dual reactive monomers, determined by DSC (ΔH_m: melting enthalpy (average ± standard deviation) and PCM content) and by TGA ($T_{5\%}$: temperature corresponding to 5% of weight loss; T_{on1} and T_{on2}: extrapolated onset temperature; and weight loss (%)).

Sample	ΔH_m (J/g)	PCM content (wt.%)	$T_{5\%}$ (ºC)	1st stage		2nd stage
				T_{on1} (ºC)	Weight Loss (%)	T_{on2} (ºC)
BA24 - MAA19 *	176.5 ± 1.0	70.7	197.0	214.5	68.4	377.7
MMA-BA-HEMA	177.6 ± 2.3	71.1	165.2	188.6	68.1	359.5
MMA-BA-TMSMA	179.6 ± 3.8	71.8	148.6	162.3	68.0	354.9
MMA-BA-GMA	182.2 ± 3.7	72.8	150.7	169.9	68.4	353.8

***** BA24 - MAA19: sample presented in section 4.3.3.

Concerning the values of $T_{5\%}$, the sample BA24-MAA19 exhibits the higher value ($T_{5\%}$ of 197 ºC) followed by sample MMA-BA-HEMA ($T_{5\%}$ of about 165 ºC) and, finally, by samples MMA-BA-GMA and MMA-BA-TMSMA that present lower and similar values ($T_{5\%}$ of about 150 ºC). As initially described in section 3.3.1, the TG curve of pure octadecane shows that its weight loss occurs in one stage (see Figure 6.9), due to its evaporation before the flash point and boiling point ($T_{5\%}$ of 118 ºC). For the microcapsules that contain octadecane, the first degradation stage is originated by the weight loss of this core that diffuses out through the shell and evaporates. Therefore, these TG results demonstrated that the type of monomers influences the thermal stability of the obtained microcapsules and it is responsible by the formation of a shell with different levels of resistance and protection to the octadecane release.

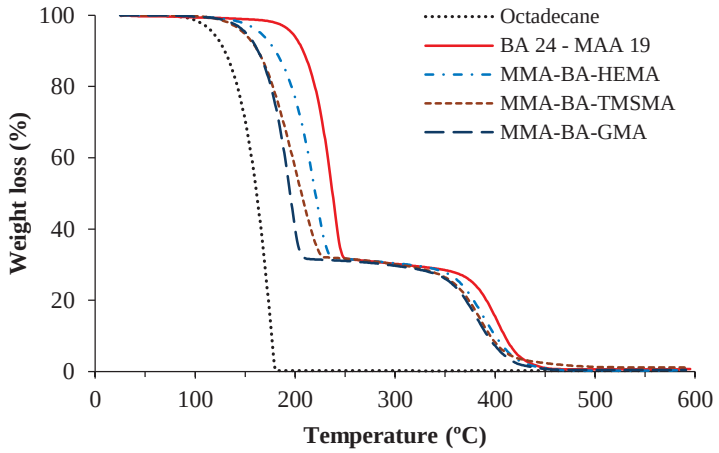

Figure 6.9: TG curves of microcapsules MMA-BA-HEMA, MMA-BA-TMSMA and MMA-BA-GMA. Sample BA24-MAA19 and pure octadecane are plotted for comparison.

In chapter 4, with the study of the monomers proportions of mixture MMA/BA/MAA, it was verified that the microcapsules prepared with a higher amount of MAA exhibited greater thermal stability (sample BA6-MAA19 and BA24-MAA19 showed a $T_{5\%}$ of 223 ºC and 197ºC, respectively). While the microcapsules with higher amount of BA exhibited lower stability (sample BA24-MAA1 showed $T_{5\%}$ of 165 ºC). As discussed before, this increase of BA can induce a reduction in the stiffness of the copolymer, producing microcapsules shells that allow an easier octadecane release. This inferior thermal stability seems to be created by the lower T_g of BA compared with MAA.

In this series of experiments, the lower $T_{5\%}$ values of the new samples compared with microcapsules BA24-MAA19 can also be related with phenomenon described above. Since all new monomers have a T_g lower than MAA. Despite the decrease of the microcapsules stability, their values should not be a constraint for the later incorporation into the textile substrates, since they are still above the 140 ºC implemented in the curing stage.

Similarly to the former acrylic shell microcapsules, these new samples present values of ΔH_m and, mainly, values of mean diameter in the same range that the ones identified for the commercial sample Wc-PCM-29 (ΔH_m of about 195 J/g and a $D_{4,3}$ of 15 µm) and different from the ones of sample Sl-PCM28 (ΔH_m of 160 J/g and $D_{4,3}$ of 3 µm).

It can then be concluded that the changes on the monomers mixture, more specifically the addition of 19 wt.% of HEMA, TMSMA or GMA instead of MAA, did not alter significantly the microcapsules morphology, the structure of their shell surface or even their mean diameter. This was the expected result, since the procedure of microencapsulation was not extensively

modified and the process of microcapsules formation remained the same. The major change was carried out in the microcapsules shell composition and, consequently, their thermal stability and the chemical structure identified by FT-IR were distinct.

The experiments carried out by changing the monomers mixture composition led to the production of microcapsules suitable to encapsulate octadecane. To complete the microcapsules characterization and to try to evaluate if these functional groups react with the coupling agent, these samples were impregnated into the fabrics woven and washing tests were carried out.

6.3.2 Characterization of treated textile substrates

Herein, as in chapter 5, the obtained microcapsules were incorporated into polyester and cotton woven and the treated textiles were evaluated. As the main focus of the present study is on the microcapsules washing resistance, the washing tests were extended until 25W for the polyester and 15W for the cotton woven. Targets that were defined according to the results of microcapsules washing resistance obtained after 5W. It was also considered that 25W is the standard specification for the apparel (which includes this type of woven) and it is the specification normally required by the company's customers. Additionally, these tests were also carried out using treated fabrics with microcapsules BA24-MAA19 (taken as reference) and with industrial microcapsules described in section 5.3.1 (samples Wc-PCM28 and Sl-PCM28).

Characterization of treated textiles

a) Scanning electron microscopy observation

Figure 6.10 shows the SEM micrographs collected for the polyester and cotton woven with microcapsules MMA-BA-HEMA, MMA-BA-TMSMA and MMA-BA-GMA. As for the fabrics impregnated with sample BA24-MAA19, in all these new treated fabrics mostly spherical microcapsules with only slight visible deformations were observed.

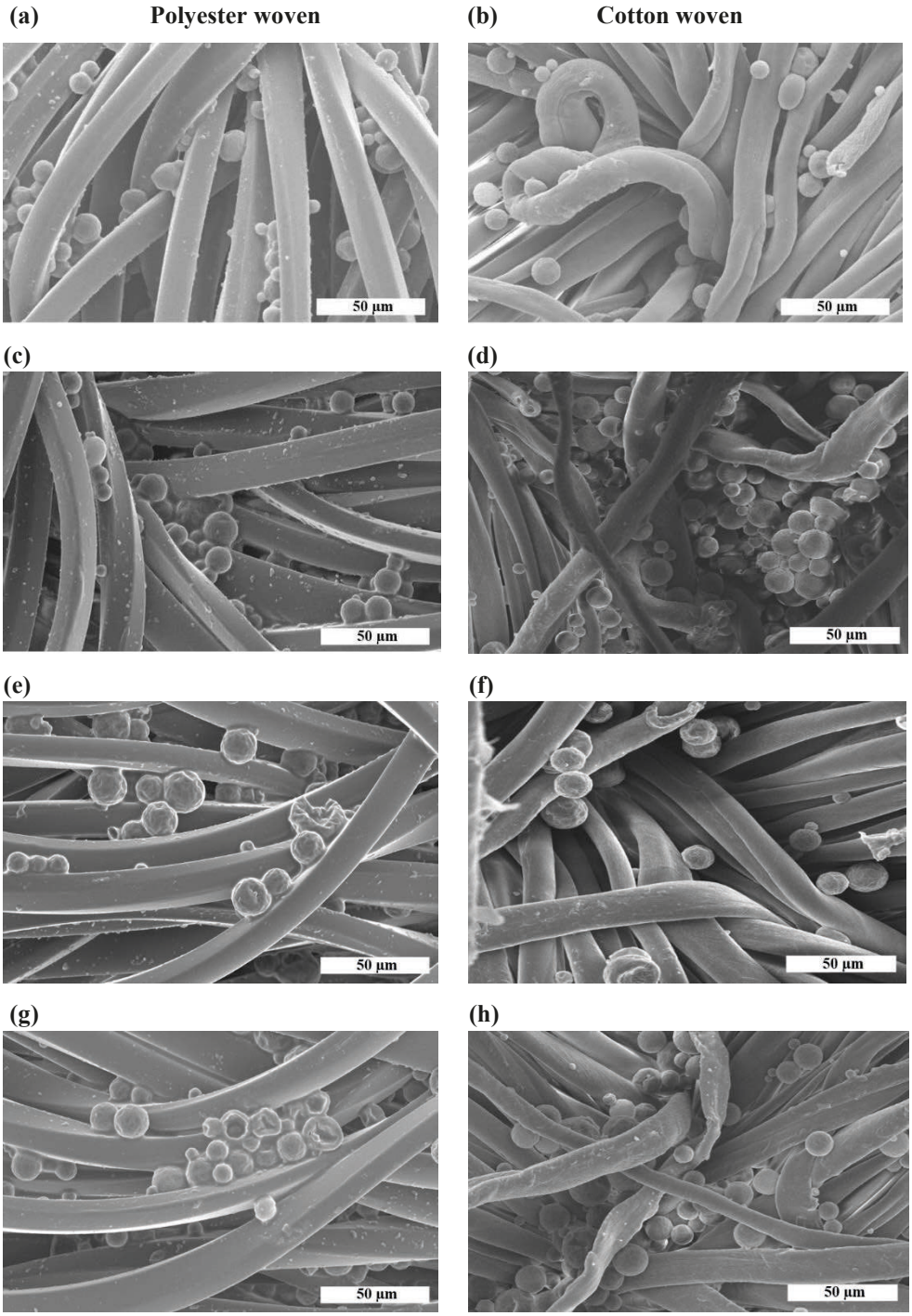

Figure 6.10: SEM micrographs of treated woven: microcapsules BA24-MAA19 on (a) polyester and (b) cotton fibres; microcapsules MMA-BA-HEMA on (c) polyester and (d) cotton fibres; microcapsules MMA-BA-TMSMA on (e) polyester and (f) cotton fibres; and microcapsules MMA-BA-GMA on (g) polyester and (h) cotton fibres (magnification x600).

b) Thermo-performance

The WPU obtained during the incorporation of the several samples in both substrates and their final ΔH_m are listed in Table 6.4 (see corresponding DSC curves in Figure D.3, Appendix D). In the same way that the previous treated textiles, the polyester woven with the new microcapsules show a considerably higher WPU than the cotton woven. As described in section 5.3.1 (for treated fabrics with industrial samples), this difference is mostly originated by the distinct structure of both fabrics. Where the thinner and closer together yarns of the cotton woven (see Figure 5.9) seem to retain a small quantity of finishing formulation. As a consequence of these differences, the ΔH_m values of polyester and cotton woven are quite distinct (see Table 6.4).

Additionally, for each type of fabrics values of ΔH_m in the same range were obtained. This similarity was created by the identical values of ΔH_m of all microcapsules (varying from around 177 J/g to 182 J/g, see Table 6.3). For the polyester woven, values of around 8.6 J/g were determined, while for cotton woven, the values were around 1.8 J/g. This thermo-performance is identical to one obtained with sample Wc-PCM28, the industrial sample that showed characteristics analogous to these acrylic microcapsules.

Table 6.4: Influence of the type of dual reactive monomer on the WPU (calculated using equation 5.1)) and on the thermo-performance (values of ΔH_m) of treated polyester and cotton woven.

Microcapsules	**Polyester woven**		**Cotton woven**	
	WPU (wt.%)	$\Delta \mathbf{H_m}$ (J/g)	**WPU** (wt.%)	$\Delta \mathbf{H_m}$ (J/g)
Wc - PCM28 *	88.7	8.4 ± 1.3	49.5	1.9 ± 0.1
Sl - PCM 28 *	88.1	4.5 ± 0.1	48.5	1.3 ± 0.1
BA24 - MAA19 *	92.7	8.7 ± 0.8	54.0	2.0 ± 0.3
MMA-BA-HEMA	93.6	8.6 ± 0.3	53.1	1.7 ± 0.1
MMA-BA-TMSMA	93.4	8.2 ± 0.5	53.5	1.9 ± 0.1
MMA-BA-GMA	92.9	7.8 ± 0.7	54.3	1.9 ± 0.2

* samples previously presented in chapter 5.

Neither from the SEM observations nor from thermo-performance analysis of treated substrates, it was possible to select the shell composition with better performance. In fact, all of them present well-shaped microcapsules and reach similar values of ΔH_m. This was somehow the expected, since the initial properties of the microcapsules also seems to be quite similar

(except their composition). The treated substrates characterization was then completed performing the washing tests.

Characterization of textiles after washing process

a) Scanning electron microscopy observation

Figure 6.11 exemplifies the micrographs of polyester and cotton woven impregnated with microcapsules MMA-BA-TMSMA after 5W, showing also the fabrics with microcapsules BA24-MAA19 for comparison. For the remaining microcapsules, a similar structure was observed (see Figure D.6 in Appendix D). The results suggested that, with the washing cycle, a few microcapsules were removed from both substrates, being the observation of microcapsules easier in the washed polyester than in the cotton woven.

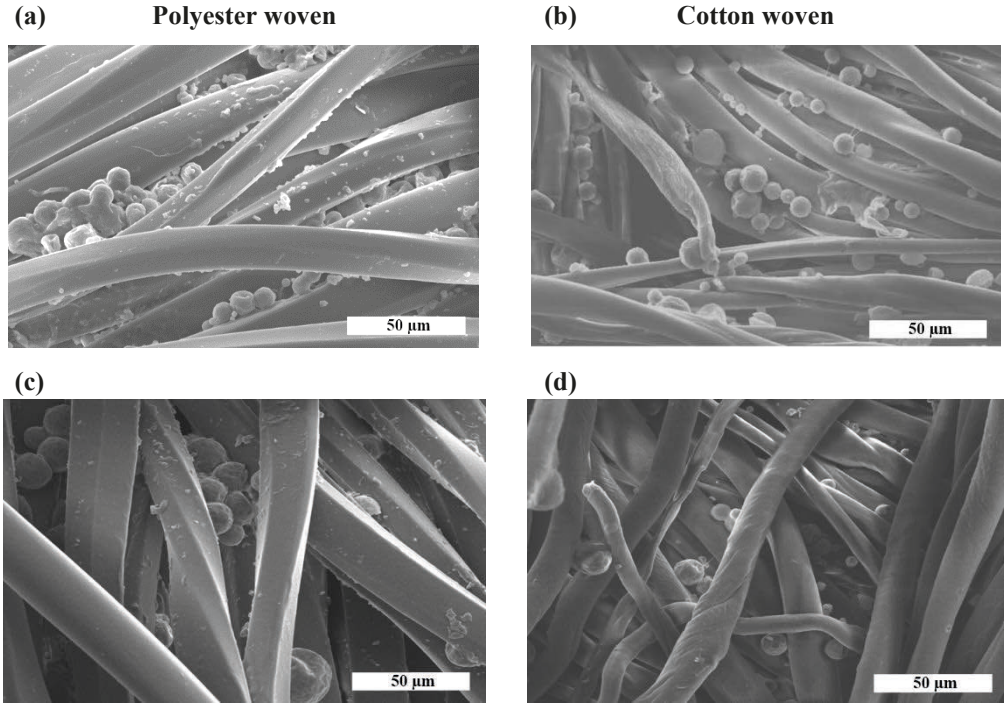

Figure 6.11: SEM micrographs after washing process (5W) of treated woven: microcapsules MMA-BA-MAA (a) polyester and (b) cotton fibres and microcapsules MMA-BA-TMSMA (c) polyester and (c) cotton fibres and (magnification x600).

As previously mentioned, for these new samples the number of washing cycles was increased. Thus, Figure 6.12 shows the micrographs of polyester woven after 25W and cotton woven after 15W for the microcapsules prepared with the several dual reactive monomers.

In general, for the all the specimens of polyester woven, the presence of well-shaped microcapsules are still identified after 25W. However, it was also observed fragments of broken microcapsules as well as a large quantity the laundry detergent. For the cotton woven, a very low quantity of microcapsules was identified.

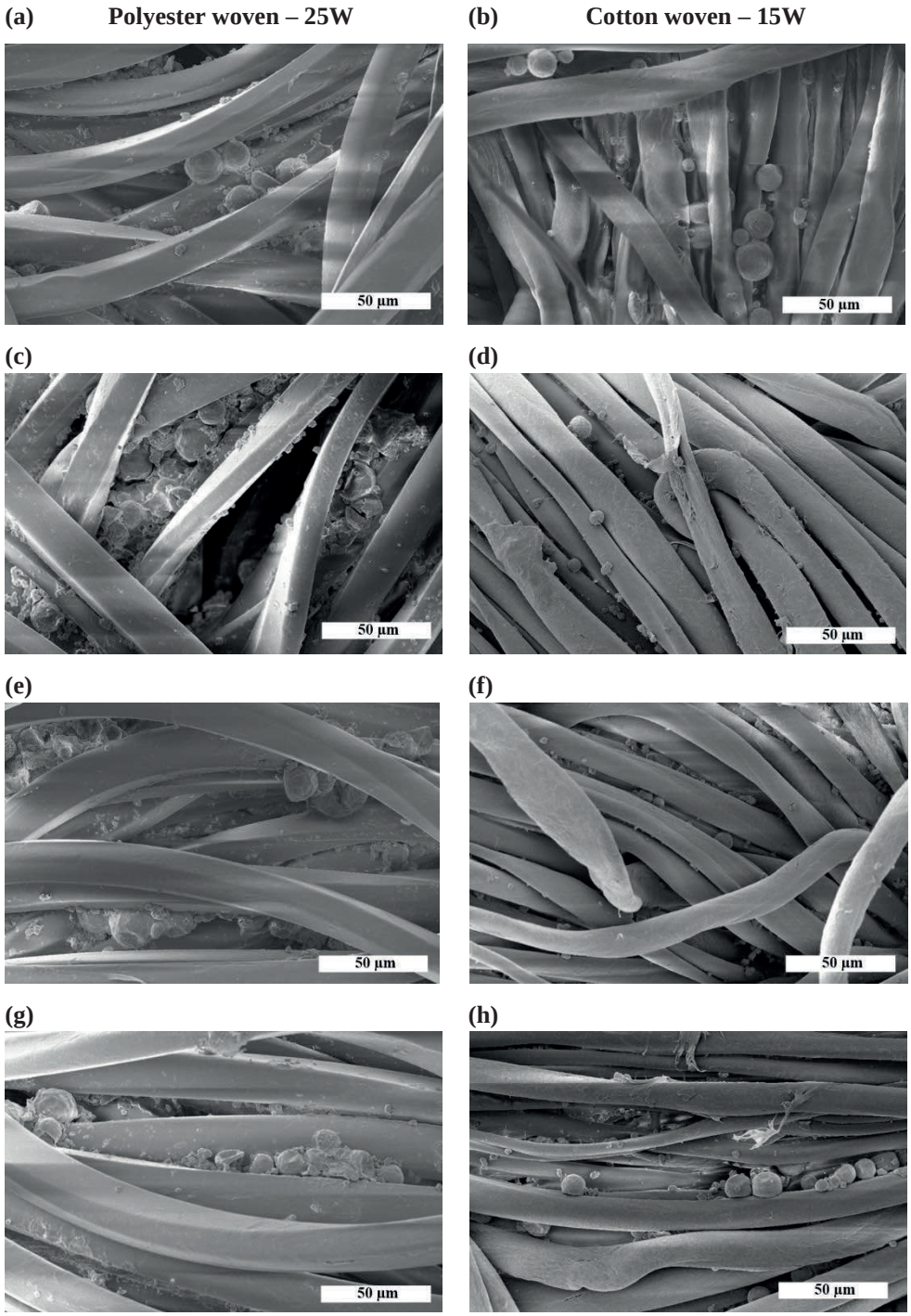

Figure 6.12: SEM micrographs after washing process (25W for the polyester and 15W for the cotton woven) of treated woven: microcapsules BA24-MAA19 on (a) polyester and (b) cotton fibres; microcapsules MMA-BA-HEMA on (c) polyester and (d) cotton fibres; microcapsules MMA-BA-TMSMA on (e) polyester and (f) cotton fibres; and microcapsules MMA-BA-GMA on (g) polyester and (h) cotton fibres (magnification x600).

b) Thermo-performance

Figure 6.13 summarizes the ΔH_m values determined for unwashed polyester woven (previously listed in Table 6.4) together with the new values for washed substrates and percentage of microcapsules retention after the washing process. Here, the washing procedure was repeated until 25W. So, their thermo-performance was evaluated after 5 cycles (5W) (like in Chapter 5), but also after 15W and 25W. The resultant DSC curves are summarized in Appendix D (Figure D.4 and D.5). In addition, corresponding results obtained for treated polyester with microcapsules BA24-MAA19 as well as with industrial microcapsules (samples Wc-PCM28 and Sl-PCM28) were also represented in Figure 6.13.

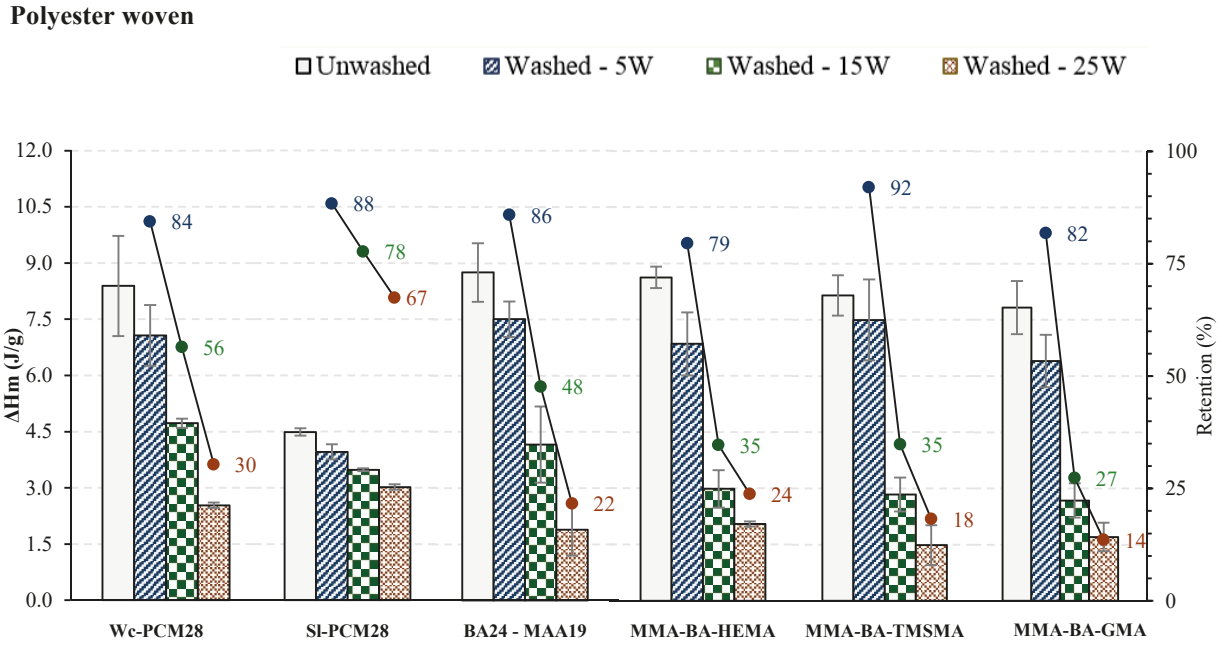

Figure 6.13: Thermo-performance (values of ΔH_m) of unwashed and washed (5W, 15W and 25W) polyester woven with industrial microcapsules and with acrylic microcapsules prepared using different dual reactive monomers, and the corresponding percentage of microcapsules retention (calculated using equation (5.2)).

The results of retention after 5W are highly influenced by the particles size distribution of microcapsules. For the industrial samples, it was verified that microcapsules with smaller size (Sl-PCM28) presents higher washing resistance in the polyester and cotton woven (section 5.3.1). However, the washing resistance results of the several acrylic shell microcapsules, should not be influenced by this factor, since their particles sizes are very similar (with values of $D_{4,3}$ that varied from around 11 µm to 13 µm, see Table 6.2).

Comparing the percentage of microcapsules retention of the new samples of polyester woven after 5W with the one of sample BA24-MAA19 (84 %), it is observed that the retention of samples MMA-BA-HEMA and MMA-BA-GMA is slightly lower (79 % and 82 %, respectively), whereas the one of sample MMA-BA-TMSMA is higher (92 %). The results obtained for these new samples are quite similar to the values obtained with the industrial microcapsules Wc-PCM28 and Sl-PCM28 (that showed percentages of 84 % and 88 %, respectively). Being the comparison with sample Wc-PCM28 the most important due to the similarity of their particles sizes.

The results presented in the previous chapter, section 5.3.3, suggested that by increasing the amount of MAA of the monomers mixture used in the suspension polymerization, the microcapsules washing resistance is enhanced (experiment BA24-MAA19). Most likely, due to the formation of covalent bonds between the carboxyl groups of the microcapsules shell and the reactive groups of the coupling agent. Moreover, this more durable immobilization of microcapsules on the textile fibres can also be helped by the presence of intermolecular forces (through hydrogen bond interaction) between their shell and the coupling agent.

Concerning the microcapsules MMA-BA-HEMA, the possible interactions between their hydroxyl groups and the methoxy or the epoxide groups of the coupling agent (CoupA01) are analogous to the ones described for the hydroxyl groups of cellulose (section 5.1) and they were represented in section 6.1 (Figure 6.2). The mentioned slightly low washing resistance obtained for this sample compared with microcapsules BA24-MAA19 can be probably explained by the different reactivity of carboxyl and hydroxyl groups or by the presence of weak intermolecular forces created by the hydroxyl groups (due to their low polarity).

Microcapsules MMA-BA-TMSMA showed the highest value of retention after 5W, suggesting that their shells have reactive groups capable of reacting with the coupling agent (CoupA01). These reactive groups can be free Si-OCH_3 groups (as the chemical identification done by FT-IR analysis for the microcapsules suggested) or they can be silanol groups (originated by the hydrolysis of the Si-OCH_3 group). These functional groups could react with the identical three methoxy groups of the CoupA01. In the same way that for the microcapsules MMA-BA-HEMA, the presence of weak intermolecular forces can also be present here, mainly because of the silanol groups (Si-OH) that could be formed either in the microcapsule shell or in the coupling agent. In contrast to the remaining dual reactive monomers, the TMSMA present three reactive methoxy groups (besides the double bond C=C), which could be responsible for this higher microcapsules retention.

In the same way, the results obtained with microcapsules MMA-BA-GMA point to the presence of reactive groups in their shell, since percentages of microcapsules retention in the same range were obtained. This reactivity can be originated by unreacted epoxide groups from the GMA or by the hydroxyl groups formed through their ring opening. In general, these groups should be able to react with epoxide groups, like the ones existent in the coupling agent.

It must be mentioned that, despite of using the same proportion of monomers to prepare the different microcapsules, the final amount of functional groups for each sample should be different. As discussed in section 6.1, the functional groups of the monomer TMSMA from microcapsules MMA/BA/TMSMA and of GMA from microcapsules MMA/BA/GMA can suffer premature reaction during the polymerization. These reactions can decrease the quantity of reactive groups in the polymeric shell and, consequently, reduce their ability to post-react.

Due to the good performance of the treated polyester with these acrylic microcapsules after 5W, the washing tests were extended until 25W, determining their profile of microcapsules retention (as represented in Figure 6.13).

For the polyester woven with industrial microcapsules, the microcapsules retention of sample Wc-PCM28 decreased from 79 % after 5W, to around 56 % after 15W and to 30 % after 25W (see Figure 6.13). Concerning sample Sl-PCM28, the percentages of retention were higher than in samples Wc-PCM28, presenting a value of 67 % after 25W. The higher microcapsules retention of sample Sl-PCM28 after 5W (described in chapter 5) is also detected in the following washing cycles, supporting the idea that the lower particle size of sample Sl-PCM28 decreases the impact of the washing process. Nevertheless, despite the different values of microcapsules retention after 25W, the value of ΔH_m of polyester woven with sample Sl-PCM28 was only slightly higher than sample Wc-PCM28 (3.0 J/g versus 2.5 J/g, respectively).

For the acrylic microcapsules, the higher reduction on the thermo-performance occurred between 5W and 15W, being the polyester woven with microcapsules BA24-MAA19 the one that shows higher values of ΔH_m and microcapsules retention after 15W (with values of 4.2 J/g and 48 %, respectively). The best results of microcapsules retention after 5W for sample MMA-BA-TMSMA was not observed after 15W. Probably because, besides the influence of the reactive groups in their shell and of the microcapsules fixation on the fibres, the results can be influenced by other factors. Such as, the microcapsules fracture, which after 5W could not have a significant impact but, here, after 15W could already determine the microcapsules behaviour. In the SEM micrographs, the presence of microcapsules fragments was not identified after 5W, however, after 25W they were detected (see Figure 6.12).

After these 25W, the washed substrates presented a ΔH_m of around 1.5 – 2.0 J/g, corresponding to 15 – 20 % of the initial amount of microcapsules. These final values of microcapsules retention were only slightly lower than that of sample Wc-PCM28 (retention of 30%), the sample that present microcapsules with initial properties identical to these acrylic shell microcapsules.

Figure 6.14 shows the corresponding results for the cotton woven. In line with the low values of microcapsules retention of this fabric, the washing cycles were only extended to 15W.

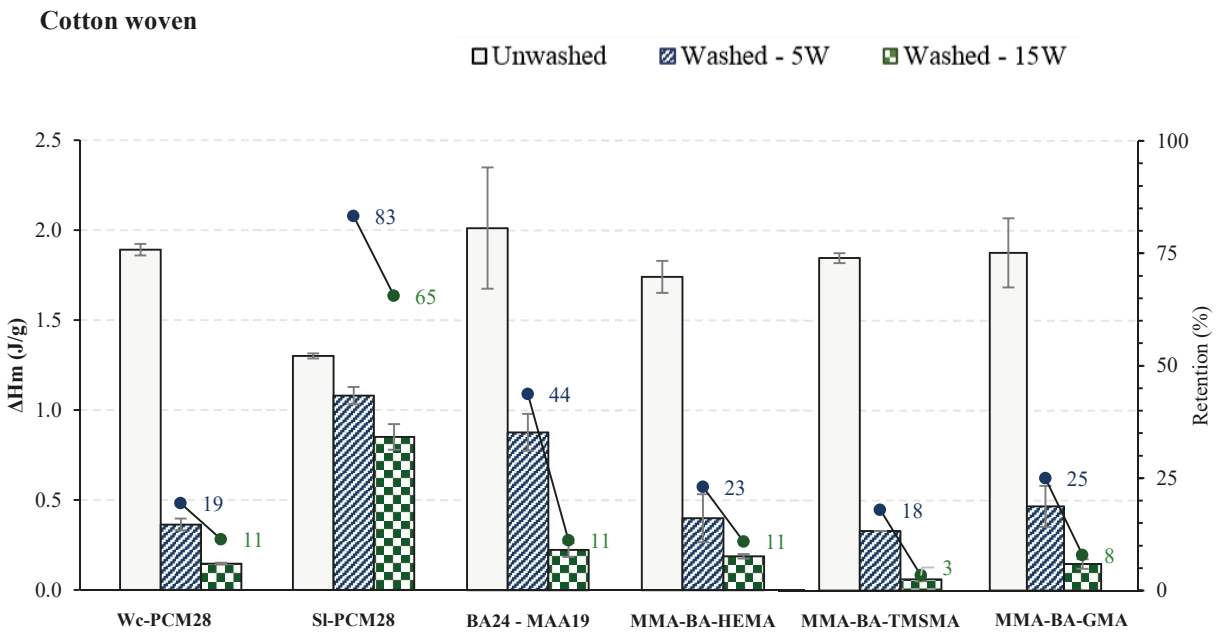

Figure 6.14: Thermo-performance (values of ΔH_m) of unwashed and washed (5W and 15W) cotton woven with industrial microcapsules and with acrylic microcapsules prepared using different dual reactive monomers and the corresponding percentage of microcapsules retention (calculated using equation (5.2)).

In chapter 5, after the incorporation of microcapsules into the polyester and cotton woven, the latter showed lower values of microcapsules retention after 5W. Most likely, due to the different structure of the fabrics as well as of the different chemical composition of the fibres. Regarding the composition of the cotton fibres, as already discussed, the strong hydrogen bond interactions between the OH groups of cellulose [13] could reduce the formation of covalent bonds or even intermolecular forces with the coupling agent, reducing the fixation of microcapsules onto these fibres. Here, as the data summarized in Figure 6.14 show, the same tendency was observed, reinforcing the previous results. With this low capacity of cellulose to react with the

coupling agent, it is difficult to study the influence of several reactive groups on the washing resistance.

Unlike to the outcomes obtained in polyester woven, all the new samples present a lower performance than microcapsules BA24-MAA19, since their values of microcapsules retention were inferior in all of them. These results suggest that the presence of carboxylic groups favours the microcapsules fixation level on the textile fibres more than the hydroxyl and epoxide groups or even alkoxysilane groups.

As the microcapsules impregnated on the polyester and on the cotton fibres were the same, the different microcapsules behaviour on both fabrics (i.e. better washing resistance of microcapsules MMA-BA-TMSMA on polyester and microcapsules BA24-MAA19 on cotton woven) could be originated by the different chemical nature of the textile fibres. On cotton fibres, the best performance of the microcapsules functionalized with carboxyl groups should not result only from their ability to form covalent bonds and intermolecular forces (hydrogen bond interactions) with the coupling agent. In addition, it could also be result of their interaction with this substrate, like formation of intermolecular forces with the cellulose molecules of cotton fibres.

Despite the significant removal of microcapsules after 5W, at the end of 15W a few microcapsules seem to remain in the textiles. Since their percentages of retention are around 10%, except for microcapsules MMA-BA-TMSMA where a value of 3% was obtained (see Figure 6.14). The same behaviour was observed by using the industrial microcapsules Wc-PCM28. Though, the cotton with microcapsules Sl-PCM28 exhibited a retention of 65 %, due to the small sizer of their microcapsules.

During the microcapsules characterization (section 6.3.1), the main doubt about the presence of reactive groups in the microcapsules shells was related with the experiments carried out with TMSMA and GMA, due to the possible premature reaction of their alkoxysilane and epoxy groups. However, the results obtained during these characterization together with the washing tests outcomes suggest that these reactive groups are indeed present.

Therefore, with the technique of suspension polymerization and using acrylic monomers, the preparation of microcapsules containing octadecane with different reactive groups in their shell is possible. The washing tests revealed that the microcapsules prepared with TMSMA as dual reactive monomer (besides the monomers MMA and BA) show the best washing resistance when incorporated in polyester woven, whereas the ones with MAA show the best results in cotton woven.

6.4 CONCLUSIONS

Herein, the functionalization of acrylic microcapsules, by using MMA and BA with different dual reactive monomers, was investigated. The final challenge of this work was the improvement of the microcapsules washing resistance, by introducing new reactive groups in the microcapsules shell and so increase their affinity with the coupling agent and the textile fibers.

In order to incorporate hydroxyl, alkoxysilane and epoxide groups in the polymeric shells, HEMA, TMSMA and GMA were used, respectively. The new batches were based on the experiment BA24-MAA19 replacing the monomer MAA by the other reactive monomers. The encapsulation of octadecane was successfully achieved and samples with similar structure to the ones of microcapsules BA24-MAA19 were obtained. The chemical identification, carried out by FT-IR spectroscopy, suggests the existence of these reactive groups in the new samples. Additionally, the microcapsules MMA/BA/TMSMA and MMA/BA/GMA revealed a lower thermal stability than that of microcapsules BA24-MAA19 (with a $T_{5\%}$ of around 150 ºC instead of 197 ºC). Despite the differences, the PCM content of these samples was similar, presenting values of about 72 %.

As indicated in Chapter 5, the functionalized microcapsules were incorporated in polyester and in cotton woven by the technique of padding and using the same finishing formulation. In all treated textiles, mostly well-shaped microcapsules were observed on the textile fibres. Moreover, a thermo-performance identical to that previously determined for sample BA24-MAA19 was also obtained (around 8.6 J/g for the polyester and 1.8 J/g for the cotton woven).

For the polyester woven, the improvement of the microcapsules washing resistance was accomplished with microcapsules MMA/BA/TMSMA, in which a retention of 92% was reached. Additionally, treated polyester with microcapsules MMA/BA/HEMA and MMA/BA/GMA presented slightly lower percentages (with values of 79 % and 82 %, respectively). Nevertheless, all these values are considered high and, consequently, the fabrics washing was repeated until 25W. After these 25 cycles, the polyester woven remained with around 15-20 % of the initial amount of acrylic microcapsules. These tests suggested that, like in the case of sample BA24-MAA19, the new microcapsules are able to create strong interactions with the coupling agent in order to resist to the washing process. Here, covalent

bonds and intermolecular forces (namely hydrogen bonding) between the several reactive groups of the microcapsules shell and the coupling agent could be formed.

As observed with the results presented in Chapter 5, also here the cotton woven showed a lower thermo-performance compared with the polyester, presenting a small retention of microcapsules after 5W. From all the sample of washed cotton woven, BA24-MAA19 was the one with the high ΔH_m, greater the industrial microcapsules Wc-PCM28. After 15 cycles, the cotton woven with this sample BA24-MAA19 showed a retention of around 10 %. The carboxyl groups seem to be the reactive groups more favourable to increase the fixation of the microcapsules in this fabric of cotton, since for the samples with the new shell compositions, low resistance to the washing cycles was observed.

Nonetheless, the results presented in this chapter showed that, by using the technique of suspension polymerization, is possible to produce acrylic microcapsules with different shell compositions, namely with different reactive groups suitable to form durable bonds with the functional groups of a coupling agent. These microcapsules fit well in the product range of Devan Chemicals, due to the presence of these reactive groups and their ability of being impregnated on polyester and cotton fibres without using binders. They also present a similar behaviour to the industrial sample Wc-PCM28 (thermo-performance and washing resistance). Therefore, the new microcapsules presented here show a high potential to be an alternative to microcapsules composed of melamine-formaldehyde, but with the added value of being a formaldehyde-free product.

6.5 REFERENCES

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CHAPTER 7

FINAL REMARKS

7.1 CONCLUSIONS

The present work aimed to contribute for the development of a new type of microcapsules for Devan Chemicals' product portfolio. Their main goal was to prepare formaldehyde-free microcapsules with encapsulated PCM in order to produce textile substrates with thermo-regulating properties.

For this purpose and in order to encapsulate the selected PCM (octadecane) into acrylic shells, a new procedure using the suspension polymerization technique was developed. In a first approach, a mixture of three monomers (MMA, BA and MAA) and two crosslinkers (EGDMA and PETRA) was applied. The preliminary tests led to the conclusion that the PVA was the most adequate stabilizer to prepare individualized microcapsules. Thus, with these compounds and using a PCM/monomer mass ratio of 1, microcapsules with a mean diameter (volume based - $D_{4,3}$) of around 7 µm, a ΔH_m value of 160 J/g , a PCM content of 65 % and a $T_{5\%}$ of 175 ºC were obtained.

Once established this microencapsulation procedure and in order to maximize the amount of encapsulated octadecane, a series of experiments was subsequently performed. These trials were carried out increasing the PCM/monomers mass ratio until 2.5. This study demonstrated that, using the same procedure, this ratio could be increased up to 2, enhancing the PCM content to 77 % and the ΔH_m value to 194 J/g (for $D_{4,3}$ of 10 µm).

The study of the new microcapsules performance was always carried out with reference to two specimens of microcapsules industrially produced and currently commercialized by Devan Chemicals (Wc-PCM28 and Sl-PCM28). So, comparing the former microcapsules with these references, it could be observed that they show similar characteristics to the industrial sample Wc-PCM28, which presents a ΔH_m value of 195 J/g and $D_{4,3}$ of 15 µm. These results confirm that the acrylic microcapsules containing octadecane exhibited properties appropriate for thermal energy storage.

In the second part of the work, the experiments to encapsulate octadecane were performed in a new experimental setup available at Devan-Micropolis. Using this setup, which contains a larger reactor equipped with an improved heating system, and adjusting to it the initial formulation, microcapsules containing octadecane were successfully prepared. However, it was confirmed that the microcapsules obtained in the new reactor had a larger diameter ($D_{4,3}$ of around 13 µm) and a lower value of ΔH_m (175J/g).

Subsequently the influence of different reaction parameters on the developed microencapsulation procedure and on the microcapsules properties was investigated:

1) Influence of the type of initiator and polymerization temperature: in order to study the effect of these parameters, BPO, AIBN and Trig23 were used as thermal free radical initiators and the reaction polymerization was carried out at different temperatures. This study showed that, using these three initiators at corresponding 10 hours half-life decomposition temperature (at 70 ºC, 65 ºC and 48 ºC, respectively), the monomer conversion rate of the suspension polymerization has an identical behaviour. Additionally, it was verified that, as expected, with the increasing of the reaction temperature, the polymerization rate increased. In all these experiments a final monomer conversion higher than 90% was reached. The microcapsules characterization revealed only small differences between them. In general, these microcapsules exhibited a ΔH_m of around 175 J/g, a PCM content of 70 % and $T_{5\%}$ of 170 ºC, being the mean particle diameter of about 12 µm. Moreover, this study confirmed that performing the suspension polymerization technique using Trig23 as initiator, it is possible to encapsulated octadecane at temperatures as low as 40 ºC. This result suggests that this procedure can be adapted to encapsulate core materials that degrade at moderate temperature (like probiotics currently used in textile materials).

2) Influence of the monomers proportions: this parameter was studied by preparing microcapsules with MMA, BA and MAA, using several monomers proportions. In order to improve the microcapsules performance, either by decreasing the microcapsules shell breakage (by using a higher amount of BA in the monomers mixture of MMA, BA and MAA) or by increasing the presence of reactive groups in their shell (using a higher amounts of MAA). The major difference obtained between the properties of the microcapsules prepared in this series of experiments was detected by thermal stability analysis. Microcapsules prepared with higher amounts of BA showed low thermal stability ($T_{5\%}$ of 136 ºC), whereas the shells with higher amounts of MAA presented greater stability (reaching $T_{5\%}$ of 223 ºC).

3) Influence of the core material: in order to study this variable, the developed encapsulation procedure was applied using core materials with different chemical nature. It was concluded that this procedure can be followed to encapsulate other compounds. However, the success of encapsulation, namely the production of microcapsules with a core/shell structure is limited by the properties of these compounds. It was shown that their polarity highly affects the microcapsules structure

and only core materials with lower polarity (log $P_{o/w}$ higher than about 4.6) resulted in microcapsules with a well-defined core/shell structure. These tests proved that the developed microencapsulation process is not restricted to the use of octadecane. Thus, this procedure can be applied to prepare microcapsules for applications other than production of textile material with thermo-regulating properties.

From these several studies a wide range of microcapsules containing octadecane was prepared, apparently with suitable characteristics to produce textile substrates with thermo-regulating properties. Thus, in order to observe the performance these microcapsules during and after the incorporation process, they were incorporated in polyester and cotton woven fabrics. The incorporation process was carried out by the technique of padding and using a finishing formulation supplied by Devan-Micropolis. Here, the industrial samples (that were taken as reference) and the acrylic shell microcapsules prepared using different experimental conditions (different initiators and polymerization temperature and different monomers proportions) were tested. The main results obtained can be summarized as follows:

1) For treated fabrics with industrial microcapsules (Wc-PCM28 and Sl-PCM28), it was verified that, for both types of microcapsules, the values of ΔH_m are higher for the polyester woven than for the cotton (ΔH_m of 8.4 J/g and 4.5 J/g for polyester woven and 1.9 J/g and 1.3 J/g for cotton woven). This behaviour results from different WPU values for both fabrics (around 90 % for polyester and 50% for cotton) and from the different structure/rearrangement of the fabrics. These experiments also showed that the differences detected in the thermo-performance of both samples is a consequence of their distinct microcapsules ΔH_m values and of their particle size. As expected, for the same type of substrate, microcapsules with higher values of ΔH_m and larger particles sizes (sample Wc-PCM28) correspond to treated fabrics with better thermo-performance.

   However, the washing tests carried out with the fabrics treated with these samples (5 cycles of normal washing) demonstrated that the microcapsules with smaller size (sample Sl-PCM28) present higher washing resistance in both polyester and cotton substrates. This suggests that, in general, the mechanical action of the washing process on the smaller microcapsules is lower than on the larger ones. Comparing the behaviour of the same type of microcapsules, it was observed that the treated polyester woven is characterized by a higher washing resistance than the cotton woven (a retention of 84% and 19 %, respectively, for samples Wc-PCM28). This difference could be probably

explained, as described above, by the different structure of the fabrics and/or by the distinct chemical composition of the fibres.

2) For fabrics treated with the microcapsules prepared using different initiators and reaction temperatures, spherical and well-defined microcapsules with only a few of them broken at the fabric' surface were observed by SEM. These microcapsules reached values of thermo-performance identical to those of microcapsules Wc-PCM28 (for polyester woven values of ΔH_m varied between 7.5 J/g and 9.8 J/g and for cotton between 1.2 J/g and 2.0 J/g).

   Regarding the washing tests, the acrylic microcapsules prepared in this series of experiments did not reach the performance of the industrial microcapsules. Even the sample that showed the best performed, sample PCM-Bp80 that exhibited a microcapsules retention of 36 % for the polyester and 18 % for the cotton woven (versus 84 % and 19 % of sample Wc-PCM28). In addition, it was verified that the different initiators and reaction temperatures tested did not have a major influence on the microcapsules thermo-performance nor on washing resistance. This was somehow the expected since, for these experiments, the initial monomers mixture was the same.

3) The microcapsules prepared with different monomers proportions were prepared in order to improve the former results of microcapsules washing resistance. After the incorporation of these series of microcapsules in both fabrics, the SEM observations seem to indicate that the microcapsules breakage was really reduced. Moreover, the DSC analyses reveal that these treated fabrics exhibited a thermo-performance identical to the last samples (prepared using different initiators and reaction temperatures).

   From the washing tests, it was confirmed that the target established for these new microcapsules was accomplished. Besides some improvements in microcapsules retention for the samples prepared by increasing the amount of BA, the greater improvement was obtained for samples prepared with the high amount of MAA. In fact, the best results of washing resistance were obtained for the microcapsules prepared using the mixture of MMA/BA/MAA with the proportion of 57/24/19 wt.%. These microcapsules reached a retention of 86 % on polyester woven and 44 % on cotton woven after 5W. These results suggest that the carboxyl groups present in the microcapsules shell can react with the di-functional coupling agent, increasing their fixation onto the surface of the textile fibres. In contrast to the last series of acrylic microcapsules, here a slightly better washing resistance was observed compared with the industrial sample Wc-PCM28 for cotton woven and polyester.

In the latter part of the work, the encapsulation procedure was also applied to produce new acrylic microcapsules using the monomers MMA and BA but adding different dual reactive monomers instead of MAA. MAA was replaced by HEMA, TMSMA and GMA in order to change the former carboxyl groups of the microcapsules shell by new hydroxyl groups: alkoxysilane groups or epoxide group. In these experiments, microcapsules with distinct compositions were successful prepared. The characterization results as well as the ones obtained in the washing tests suggested that the new reactive groups are indeed present in the microcapsules shell. Additionally, the washing tests revealed that the microcapsules prepared with TMSMA as dual reactive monomer showed the best washing resistance when incorporated in the polyester woven (reaching a value of 92 % after 5W). Nonetheless, for the cotton woven the best results were still the ones obtained with microcapsules prepared with MAA (presenting a retention of 44 %). In this series of experiments, the washing tests were extended until 25W for the polyester and 15W for the cotton woven. For the polyester woven after 25W, a ΔH_m values of around 1.5 – 2.0 J/g was attained, corresponding to 15 – 20 % of the initial amount of microcapsules. For the cotton woven, after 15W, 10 % of microcapsules retention was found.

Summing up, the suspension polymerization procedure developed in the present work seems to be a robust process with great potential to be applied to industrial production. Its novelty consisted on the preparation of microcapsules via suspension polymerization technique along with their incorporation into textile substrates using a di-functional coupling agent. A suspension polymerization based on the combination of the monomers MMA and BA with different dual reactive monomers (such as MAA, HEMA, TMSMA and GMA) and with the crosslinkers EGDMA and PETRA. This process proved also versatility to be used with different monomer proportions of MMA, BA and MAA and/or different types of monomers, being also appropriate for encapsulating different core materials.

Finally, it is expected that the produced acrylic microcapsules can, in the near future, be included in the Devan Chemical product portfolio.

7.2 FUTURE WORK

The work developed throughout these years and the results that were obtained suggest some further studies in order to finalize the microcapsules improvement and allow their production at industrial environment. Therefore, the recommended research lines for future work are:

- To continue the optimization of the suspension polymerization conditions, namely: encapsulating the octadecane with a nucleating agent in order to reduce the supercooling effect observed in the prepared microcapsules; producing microcapsules with smaller particle size distribution and studying the relationship between their thermo-performance and washing resistance.

- To explore the use of new coupling agents (with different reactive groups) in the finishing formulation will be of great importance, trying to increase the fixation of microcapsules on different textile fibres in order to prolong their resistance to a higher number of washing cycles.

- To incorporate the obtained microcapsules in other types of substrates, such as mattress ticking or substrates of foam, and to test also different incorporation procedures, like the technique of coating or spray. Furthermore, to incorporate these microcapsules in substrates with different composition, such as polyamide or blends of polyester and cotton, will be also of interest. Evaluating in all these cases the microcapsules performance.

- To perform the scaling-up studies, evaluating the viability to produce the microcapsules at pilot-scale and defining the optimum conditions of manufacture. Additionally, it will be important to study the economic viability of developed microencapsulation process for large-scale production (including, among others, equipment investment, materials cost and operating costs);

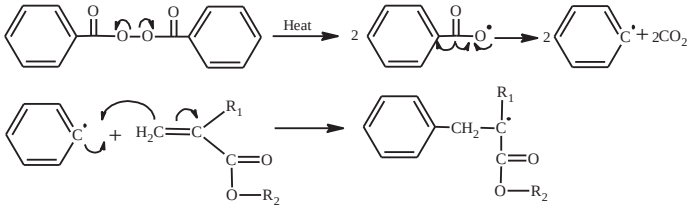
- To define the target market and carry out the studies of economic viability for the developed product (microcapsules formaldehyde-free with PCM encapsulated).

APPENDICES

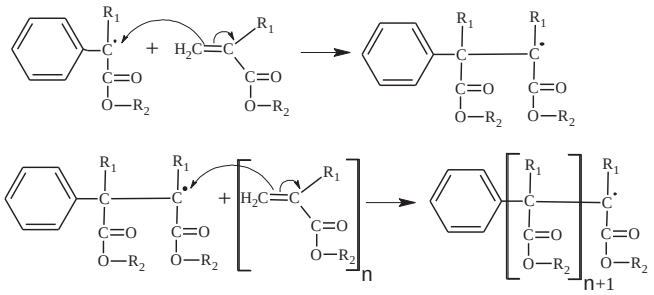
Appendix A

Supporting information for Chapter 3: Microencapsulation procedure via suspension polymerization

(a) Initiation



(b) Propagation



MMA: R_1= CH_3 and R_2= CH_3

BA: R_1= H and R_2= C_4H_9

MAA: R_1= CH_3 and R_2= H

Figure A.1: General mechanism for the free radical polymerization of selected monomers initiated by BPO, until the macroradical formation. The groups R_1 and R_2 differ according to the chemical structure of the monomers.

Appendix B

Supporting information for Chapter 4: Influence of different reaction parameters

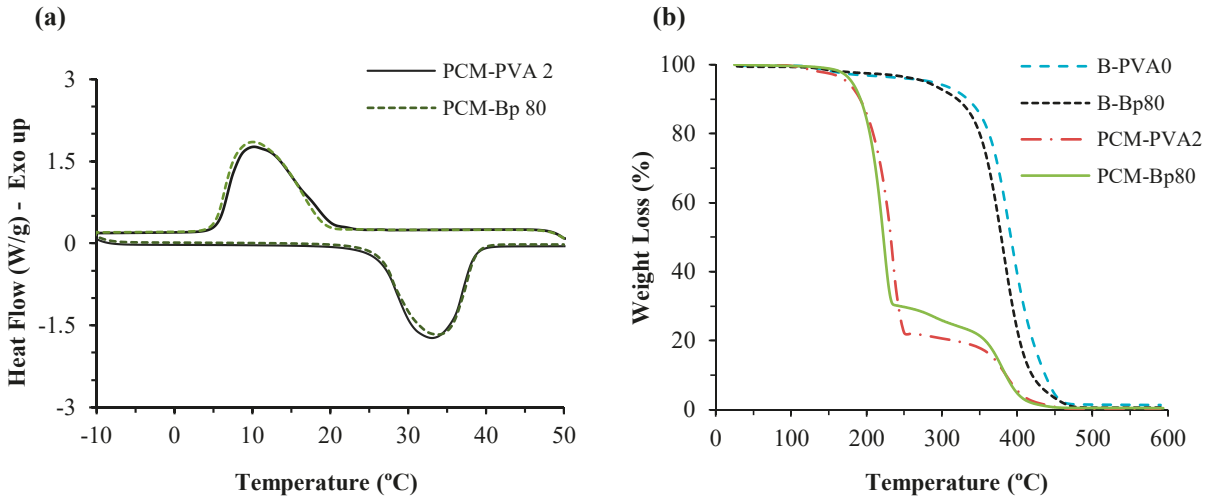


Figure B.1: Comparison of the thermal properties obtained for the two pairs of experiments: (a) DSC curves of samples PCM-PVA2 and PCM-Bp80; and (b) TG curves of samples B-PVA0, B-Bp80, PCM-PVA2 and PCM-Bp80.

Table B.1: Comparison of the thermal performance (average ± standard deviation) for the two pairs of experiments (ΔH_m and ΔH_c: melting and crystallization enthalpies; T_{om} and T_{oc}: melting and crystallization onset temperatures; PCM content was calculated using equation (3.1)).

Sample	T_{om} (ºC)	ΔH_m (J/g)	T_{oc} (ºC)	ΔH_c (J/g)	PCM content (wt.%)
PCM-PVA2	26.5±0.3	193.9±3.3	21.5±0.1	196.1±2.3	77.3
PCM-Bp80	26.4±0.1	174.4±0.9	19.0±0.2	175.5±1.8	69.3

Table B.2: Comparison of the thermal stability (average ± standard deviation) for the two pairs of experiments ($T_{5\%}$ and $T_{10\%}$: temperatures corresponding to 5% and 10% of weight loss; T_{on1} and T_{on2}: extrapolated onset temperatures of the first and second degradation stage; Weight loss: weight loss (%) in each degradation stage).

Sample	$T_{5\%}$ (ºC)	$T_{10\%}$ (ºC)	1st stage		2nd stage	
			T_{on1} (ºC)	Weight Loss (%)	T_{on2} (ºC)	Weight Loss (%)
B-PVA0	285.9	334.5	118.5	3.1	357.4	95.0
B-Bp80	278.3	320.6	126.7	1.9	345.5	96.8
PCM-PVA2	173.7	191.5	209.8	77.9	357.8	21.8
PCM-Bp80	181.2	192.2	199.7	70.2	351.6	29.3

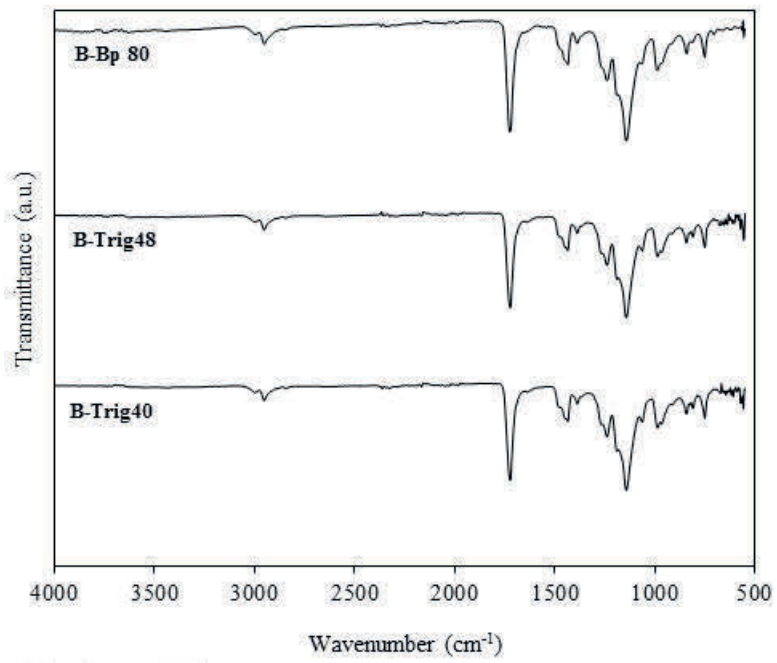


Figure B.2: FT-IR spectra of samples prepared without octadecane: samples B-Bp80, B-Trig48 and B-Trig40.

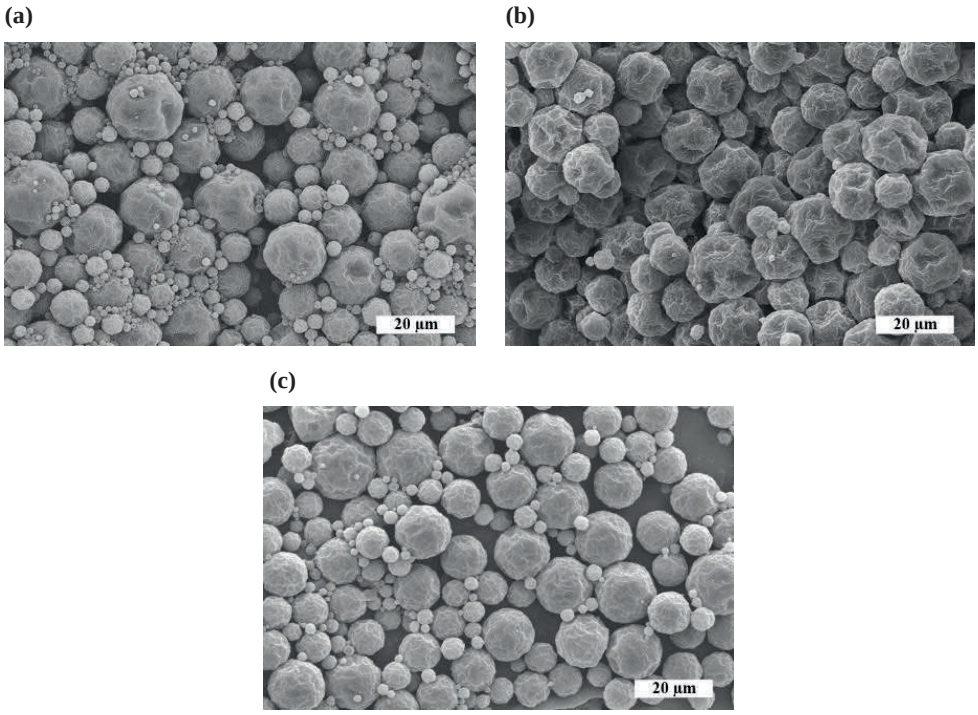


Figure B.3: SEM micrographs of microcapsules (a) PCM-Bp70, (b) PCM-Aibn65 and (c) PCM-Trig48 (magnification x1000).

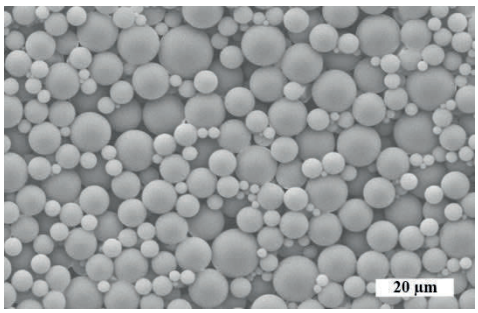


Figure B.4: SEM micrographs of sample B-Trig48 (magnification x1000).

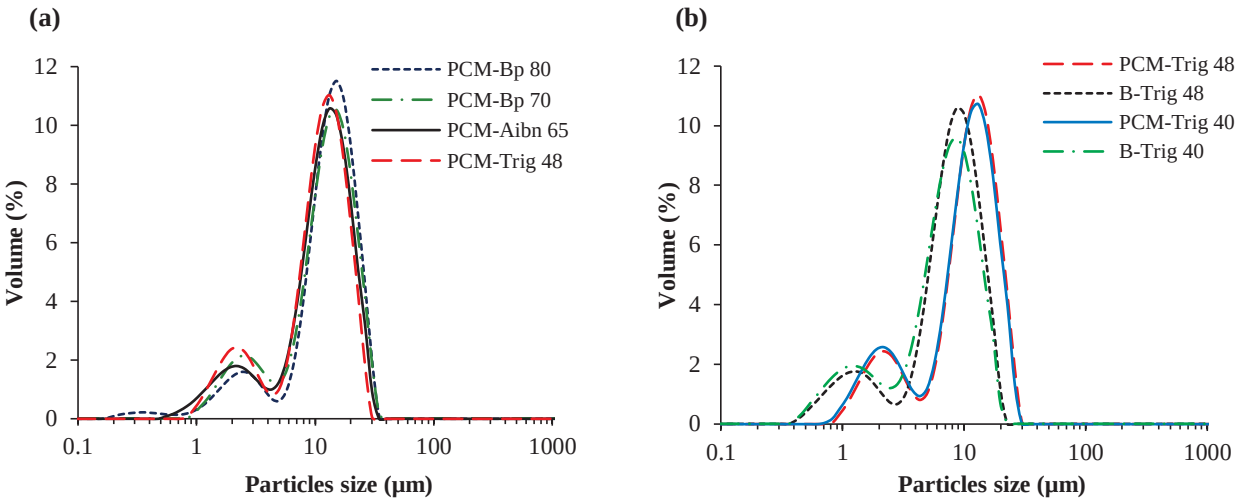


Figure B.5: Particle size distribution curves of microcapsules prepared (a) with BPO, AIBN and Trig23 at respective 10 hour half-life temperature (b) with Trig23 at 48 ºC and at 40ºC in the presence and absence of octadecane (PCM-Bp80 is represented for comparison).

Table B.3: Influence of initiator type and polymerization temperature on the values of mean diameter ($D_{4,3}$), D_{10}, D_{50} and D_{90}.

Sample	**Mean diameter, $D_{4,3}$** (µm)	**D_{10}** (µm)	**D_{50}** (µm)	**D_{90}** (µm)
PCM-Bp80	12.6	2.6	12.5	21.3
PCM-Bp70	12.0	2.5	11.7	20.9
PCM-Aibn65	11.2	2.2	11.0	19.7
PCM-Trig48	12.2	2.4	12.1	21.1
PCM-Trig40	11.7	2.2	11.6	20.5
B-Bp80	7.3	1.4	7.2	12.8
B-Trig48	8.7	1.5	8.5	15.2
B-Trig40	8.0	1.4	7.7	14.5

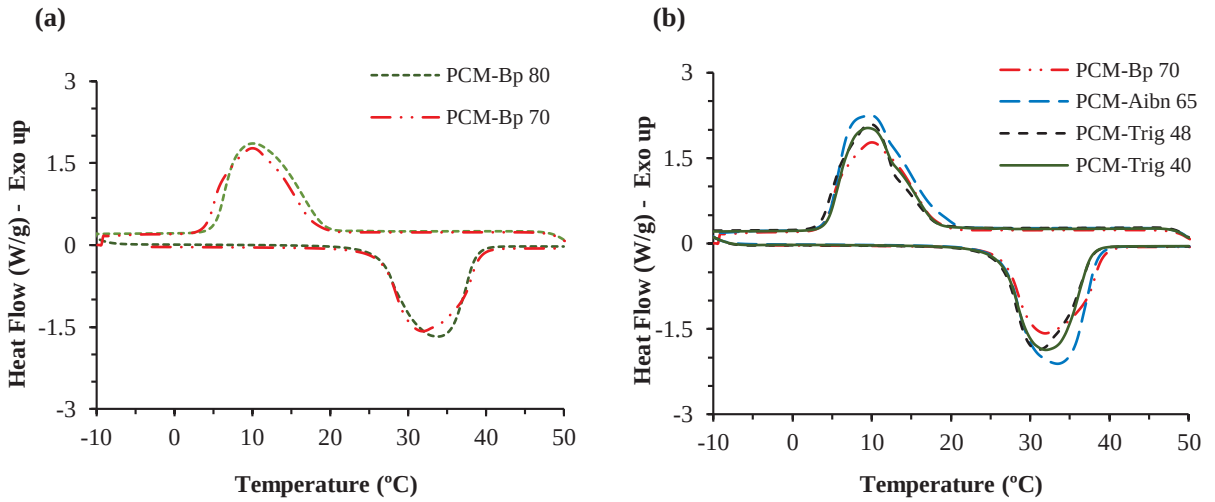


Figure B.6: Influence of initiator type and polymerization temperature on thermal performance. DSC curves of microcapsules prepared: (a) with BPO at 80 ºC and 70 ºC and (b) with BPO at 70 ºC, AIBN at 65 ºC and Trig23 at 48 ºC and 40 ºC.

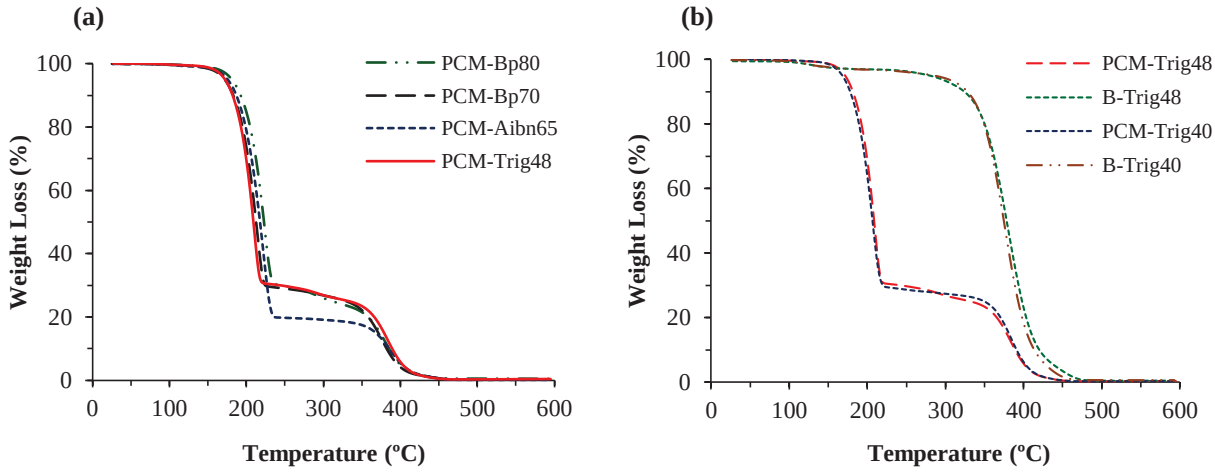


Figure B.7: Influence of initiator type and polymerization temperature on thermal stability. TG curves of microcapsules prepared (a) with BPO at 70 ºC and at 80 ºC, AIBN at 65 ºC and Trig23 at 48 ºC; and (b) with Trig23 at 48 ºC and 40 ºC (with and without octadecane).

Table B.4: Influence of initiator type and polymerization temperature on thermal performance (average ± standard deviation) (ΔH_m and ΔH_c: melting and crystallization enthalpies; T_{om} and T_{oc}: melting and crystallization onset temperatures; PCM content was calculated using equation (3.1)).

Sample	T_{om} (ºC)	ΔH_m (J/g)	T_{oc} (ºC)	ΔH_c (J/g)	PCM content (wt.%)
PCM-Bp80	26.4±0.1	174.4±0.9	19.0±0.2	175.5±1.8	69.3
PCM-Bp70	26.5±0.0	178.1±8.8	18.4±0.1	180.6±9.3	71.1
PCM-Aibn65	26.4±0.1	207.8±7.6	18.7±0.3	209.0±8.4	82.6
PCM-Trig48	26.3±0.0	181.1±5.3	15.2±0.1	183.2±4.7	72.2
PCM-Trig40	26.3±0.1	183.5±4.6	15.8±0.1	185.4±5.5	73.1

Table B.5: Influence of initiator type and polymerization temperature on thermal stability ($T_{5\%}$ and $T_{10\%}$: temperatures corresponding to 5% and 10% of weight loss; T_{on1} and T_{on2}: extrapolated onset temperatures of the first and second degradation stage; Weight loss: weight loss (%) in each degradation stage).

Sample	$T_{5\%}$ (ºC)	$T_{10\%}$ (ºC)	1st stage		2nd stage	
			T_{on1} (ºC)	Weight Loss (%)	T_{on2} (ºC)	Weight Loss (%)
PCM-Bp80	181.2	192.2	199.7	70.2	351.6	29.3
PCM-Bp70	172.4	183.0	190.1	70.8	347.7	29.0
PCM-Aibn65	175.5	187.0	195.2	80.2	361.8	19.6
PCM-Trig48	172.2	181.8	188.4	69.7	354.4	30.0
PCM-Trig40	168.5	178.2	184.4	71.4	361.3	28.4
B-Bp80	278.3	320.6	126.7	1.9	345.5	96.8
B-Trig48	280.2	324.9	103.9	2.3	344.0	96.6
B-Trig40	284.0	327.7	99.4	2.7	344.2	96.4

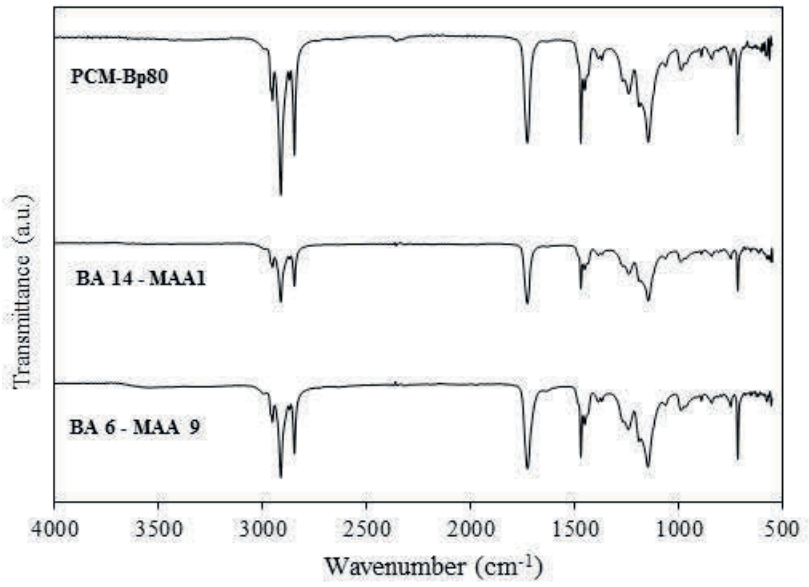


Figure B.8: FT-IR spectra of samples BA14-MAA1 and BA6-MAA9 (PCM-Bp80 was represented for comparison).

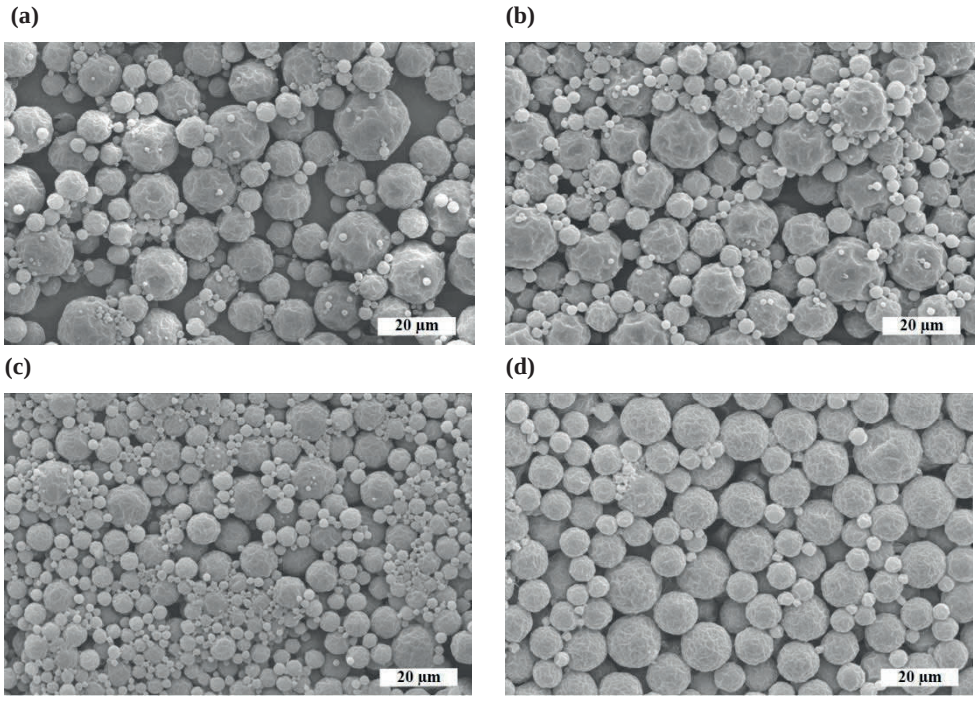


Figure B.9: SEM micrographs of microcapsules prepared with different monomers proportions, sample (a) BA14-MAA1, (b) BA24-MAA1, (c) BA6-MAA9 and (d) BA6-MAA19 (magnification x1000).

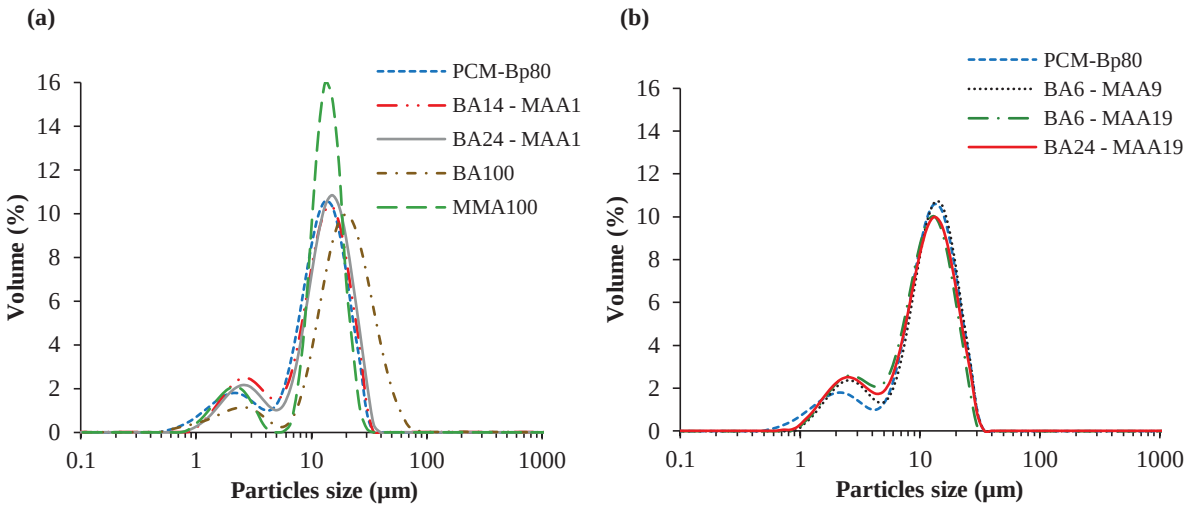


Figure B.10: Particle size distribution curves of microcapsules prepared with different monomers proportions: (a) progressively increasing the amount of BA and microcapsules MMA100; and (b) progressively increasing the amount of MAA. Samples PCM-Bp80 (monomer mixture of MMA/BA/MAA with 93/6/1 wt.%) is plotted for comparison.

Table B.6: Influence of the monomers proportions on the values of mean diameter ($D_{4,3}$), D_{10}, D_{50} and D_{90}.

Sample	**Mean diameter, $D_{4,3}$** (µm)	**D_{10}** (µm)	**D_{50}** (µm)	**D_{90}** (µm)
PCM -Bp80 *	12.6	2.2	11.0	19.7
BA14 - MAA1	11.4	2.4	11.4	20.4
BA24 - MAA1	12.4	2.6	12.2	21.6
BA6 - MAA9	11.4	2.5	11.2	19.8
BA6 - MAA19	10.2	2.4	9.9	18.2
BA24 - MMA19	10.7	2.3	10.4	19.2
MMA100	11.7	2.3	12.1	18.0
BA100	19.6	4.1	17.6	34.5

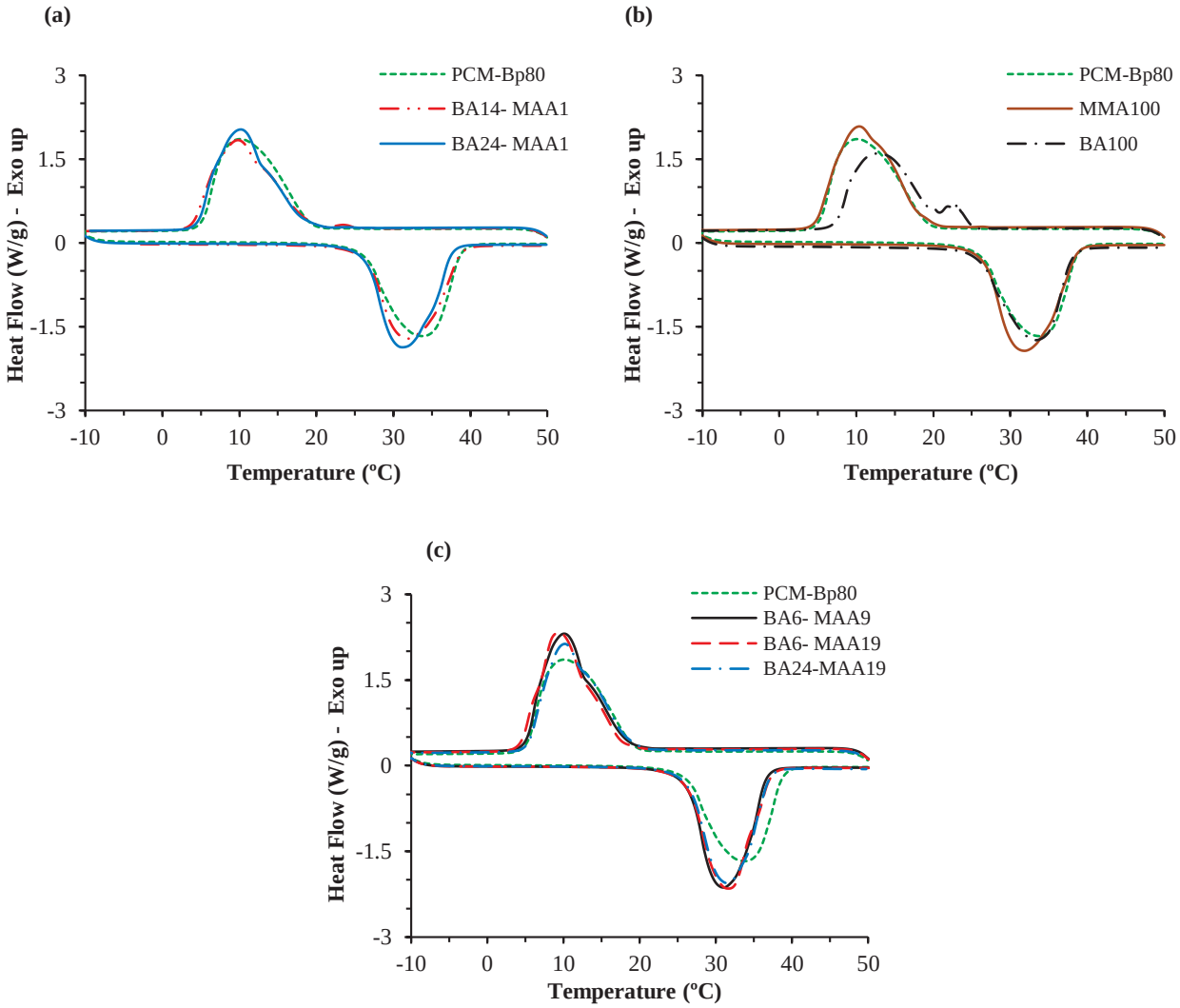


Figure B.11: Influence of monomers proportions on thermal performance. DSC curves of (a) microcapsules prepared increasing the amount of BA; and (b) microcapsules BA100 and MMA100 and (c) microcapsules prepared increasing the amount of MAA. Samples PCM-Bp80 (monomer mixture of MMA/BA/MAA with 93/6/1 wt.%) is plotted for comparison.

Table B.7: Influence of monomers proportions on thermal performance (average ± standard deviation) (ΔH_m and ΔH_c: melting and crystallization enthalpies; T_{om} and T_{oc}: melting and crystallization onset temperatures; PCM content was calculated using equation (3.1)).

Sample	T_{om} (ºC)	ΔH_m (J/g)	T_{oc} (ºC)	ΔH_c (J/g)	PCM content (wt.%)
PCM-Bp80	26.4 ± 0.1	174.4 ± 0.9	19.0 ± 0.2	175.5 ± 1.8	69.3
BA14 - MAA1	26.5 ± 0.1	173.7 ± 3.3	16.9 ± 0.4	176.1 ± 3.6	69.4
BA24 - MAA1	26.4 ± 0.0	176.3 ± 6.6	15.7 ± 0.2	178.7 ± 6.9	70.4
BA6 - MAA9	26.4 ± 0.0	180.5 ± 3.1	15.2 ± 0.0	183.9 ± 3.4	72.2
BA6 - MAA19	26.3 ± 0.1	180.0 ± 2.8	15.3 ± 0.3	183.0 ± 3.6	72.0
BA24 - MMA19	26.4 ± 0.1	176.5 ± 1.0	18.1 ± 1.5	180.0 ± 1.3	70.7
MMA100	26.6 ± 0.1	184.8 ± 5.6	21.0 ± 0.1	187.8 ± 5.6	73.9
BA100	25.8 ± 0.3	168.1 ± 9.1	20.7 ± 0.1	173.6 ± 1.3	67.8

Table B.8: Influence of monomers proportions on thermal stability ($T_{5\%}$ and $T_{10\%}$: temperatures corresponding to 5% and 10% of weight loss; T_{on1} and T_{on2}: extrapolated onset temperatures of the first and second degradation stage; Weight loss: weight loss (%) in each degradation stage).

Sample	$T_{5\%}$ (ºC)	$T_{10\%}$ (ºC)	1st stage		2nd stage	
			T_{on1} (ºC)	Weight Loss (%)	T_{on2} (ºC)	Weight Loss (%)
PCM -Bp80 *	181.2	192.2	199.7	70.2	351.6	29.3
BA14 - MAA1	165.9	178.5	185.8	68.0	362.9	31.6
BA24 - MAA1	164.5	176.5	183.6	69.3	366.0	30.4
BA6 - MAA9	204.4	215.6	222.8	70.4	379.3	28.9
BA6 - MAA19	222.5	232.6	240.4	69.9	384.2	28.9
BA24 - MMA19	197.0	208.0	214.5	68.4	377.7	30.6
MMA100	175.5	186.6	193.8	73.3	355.9	26.5
BA100	136.4	153.5	134.6	65.7	371.1	33.0

Appendix C

Supporting information for Chapter 5: Incorporation of microcapsules into textile substrates

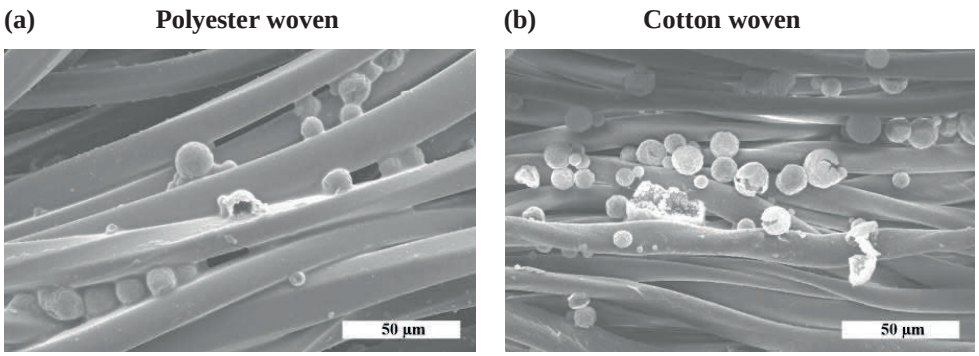


Figure C.1: SEM micrographs of treated woven with microcapsules PCM-Trig40 (a) polyester and (b) cotton fibres (magnification x600).

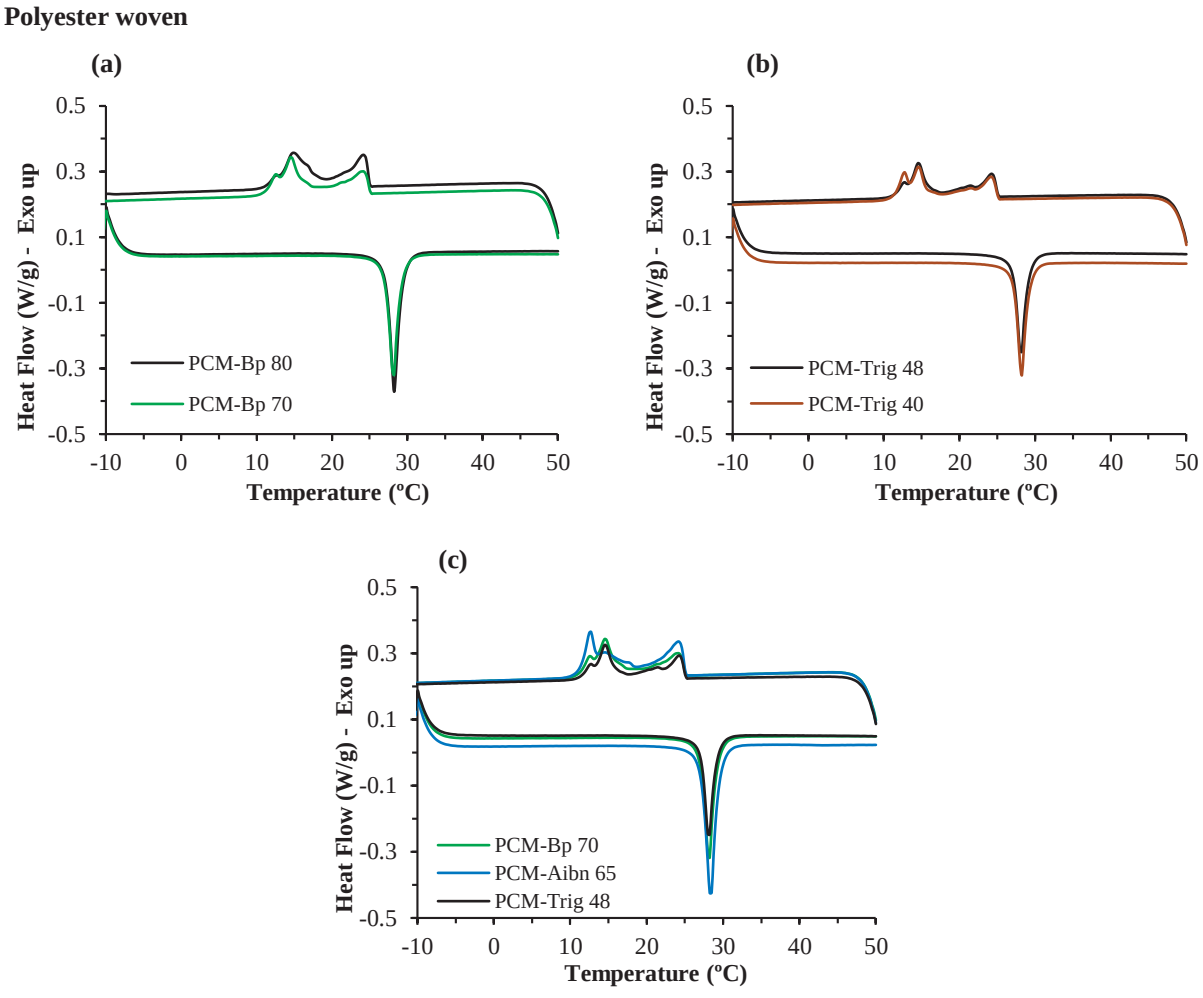


Figure C.2: DSC curves of treated polyester woven with microcapsules prepared (a) using BPO at 80 ºC and 70 ºC; (b) using Trig23 at 48 ºC and at 40 ºC; and (c) using BPO at 70 ºC, AIBN at 65 ºC and Trig23 at 48 ºC.

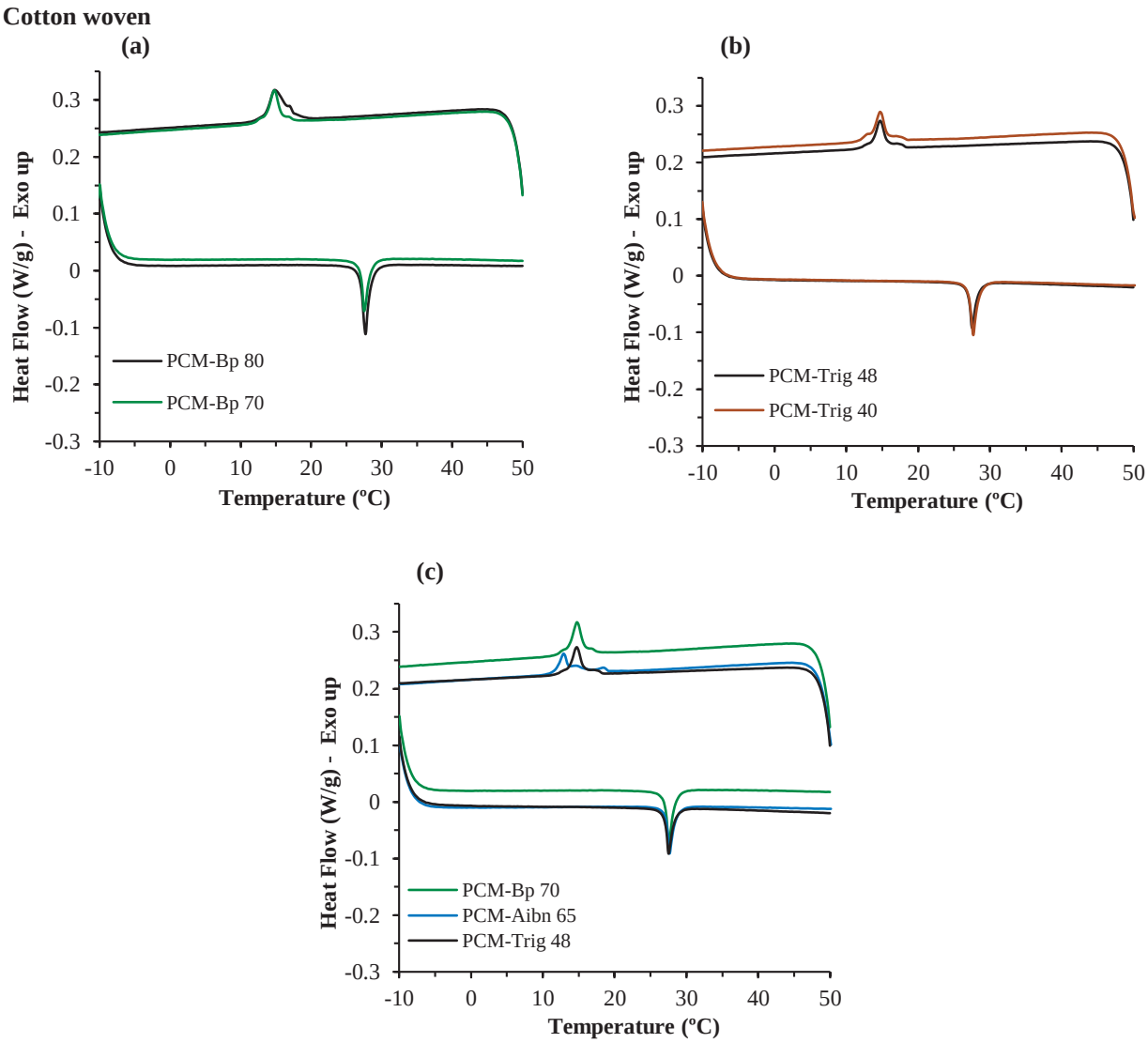


Figure C.3: DSC curves of treated cotton woven with microcapsules prepared (a) using BPO at 80 ºC and 70 ºC; (b) using Trig23 at 48 ºC and at 40 ºC; and (c) using BPO at 70 ºC, AIBN at 65 ºC and Trig23 at 48 ºC.

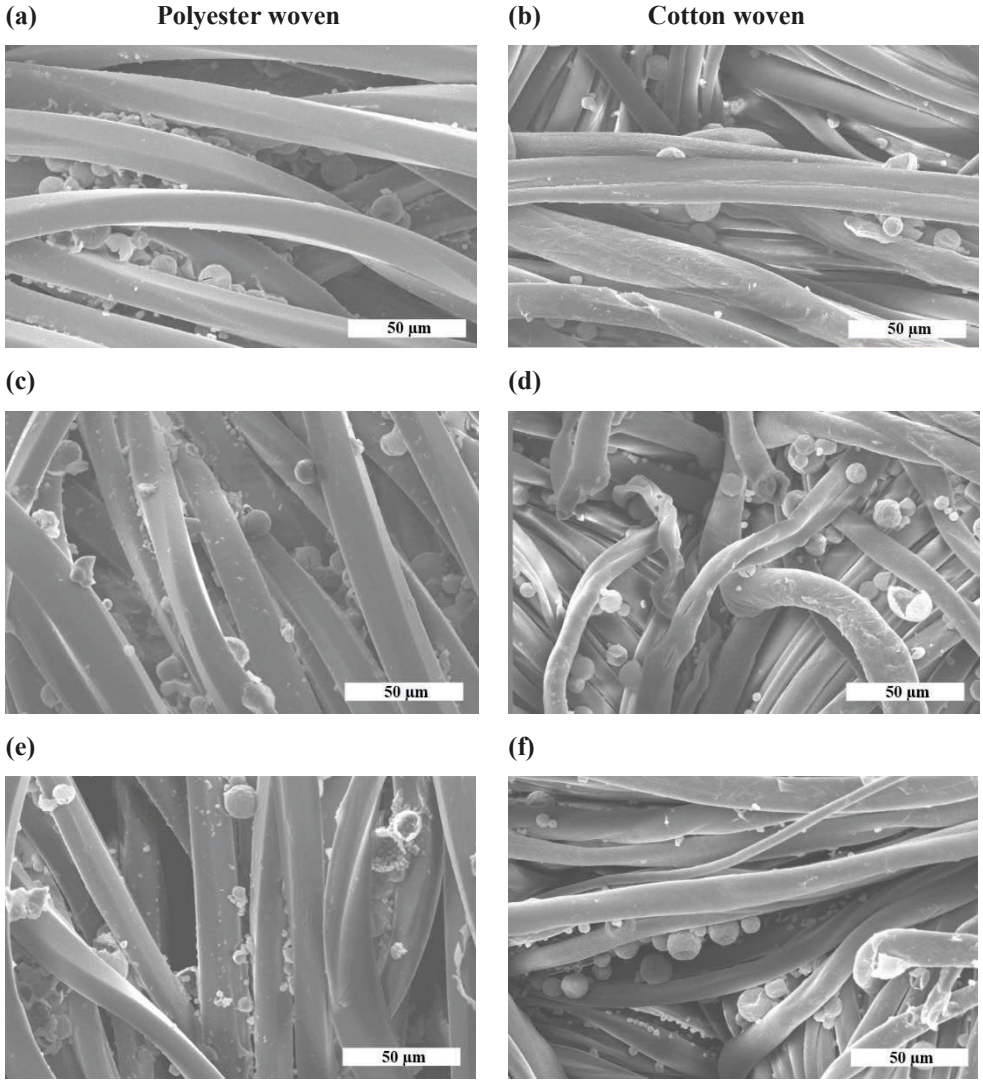


Figure C.4: SEM micrographs after washing process (5W) of treated woven: microcapsules PCM-Bp70 on (a) polyester and (b) cotton fibres; microcapsules PCM-Trig48 on (c) polyester and (d) cotton fibres; and microcapsules PCM-Trig40 on (e) polyester and (f) cotton fibres (magnification x600).

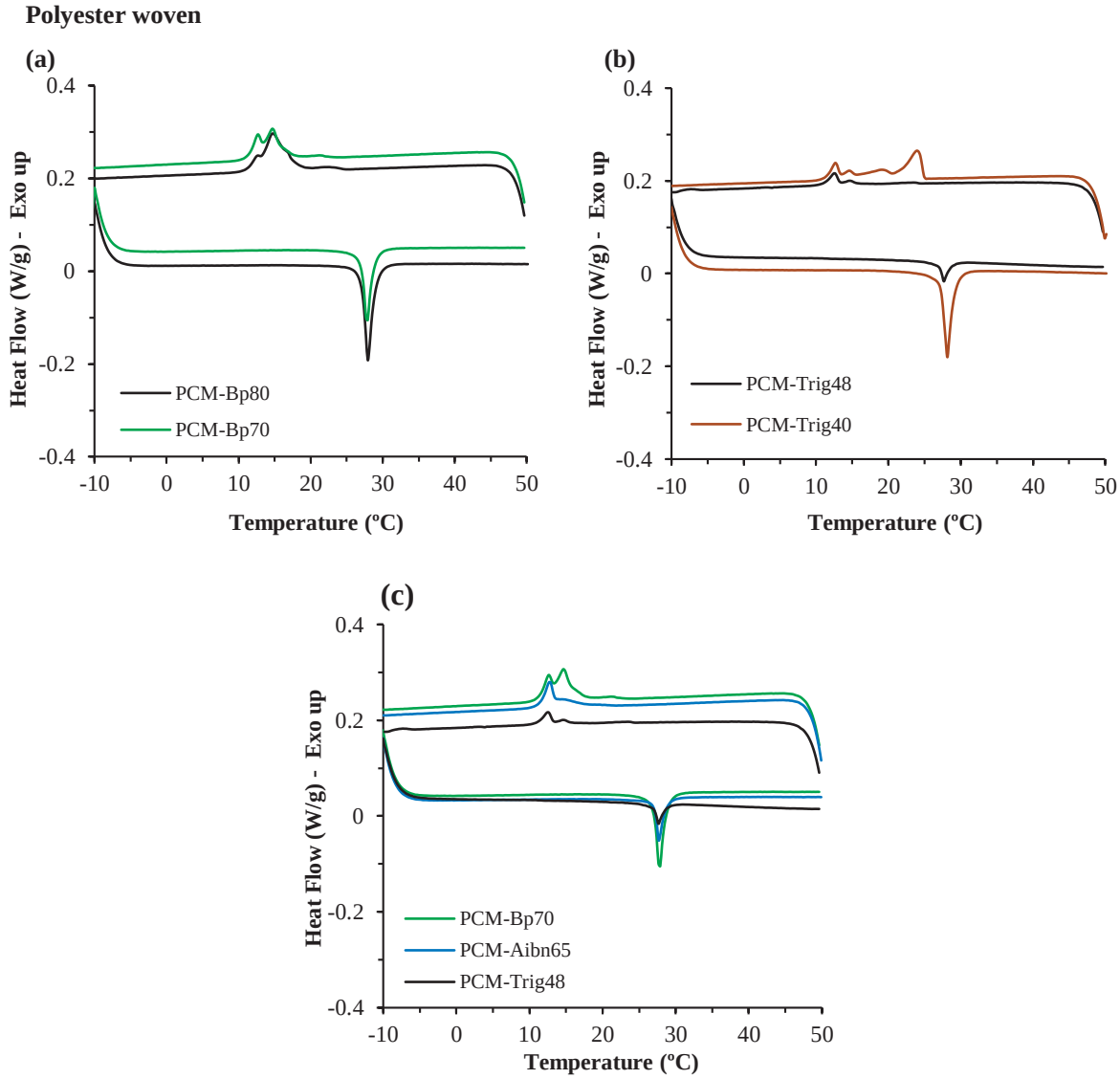


Figure C.5: DSC curves of washed polyester woven (5W) with microcapsules prepared (a) using BPO at 80 ºC and 70ºC; (b) using Trig23 at 48 ºC and at 40 ºC; and (c) using BPO at 70 ºC, AIBN at 65 ºC and Trig23 at 48 ºC.

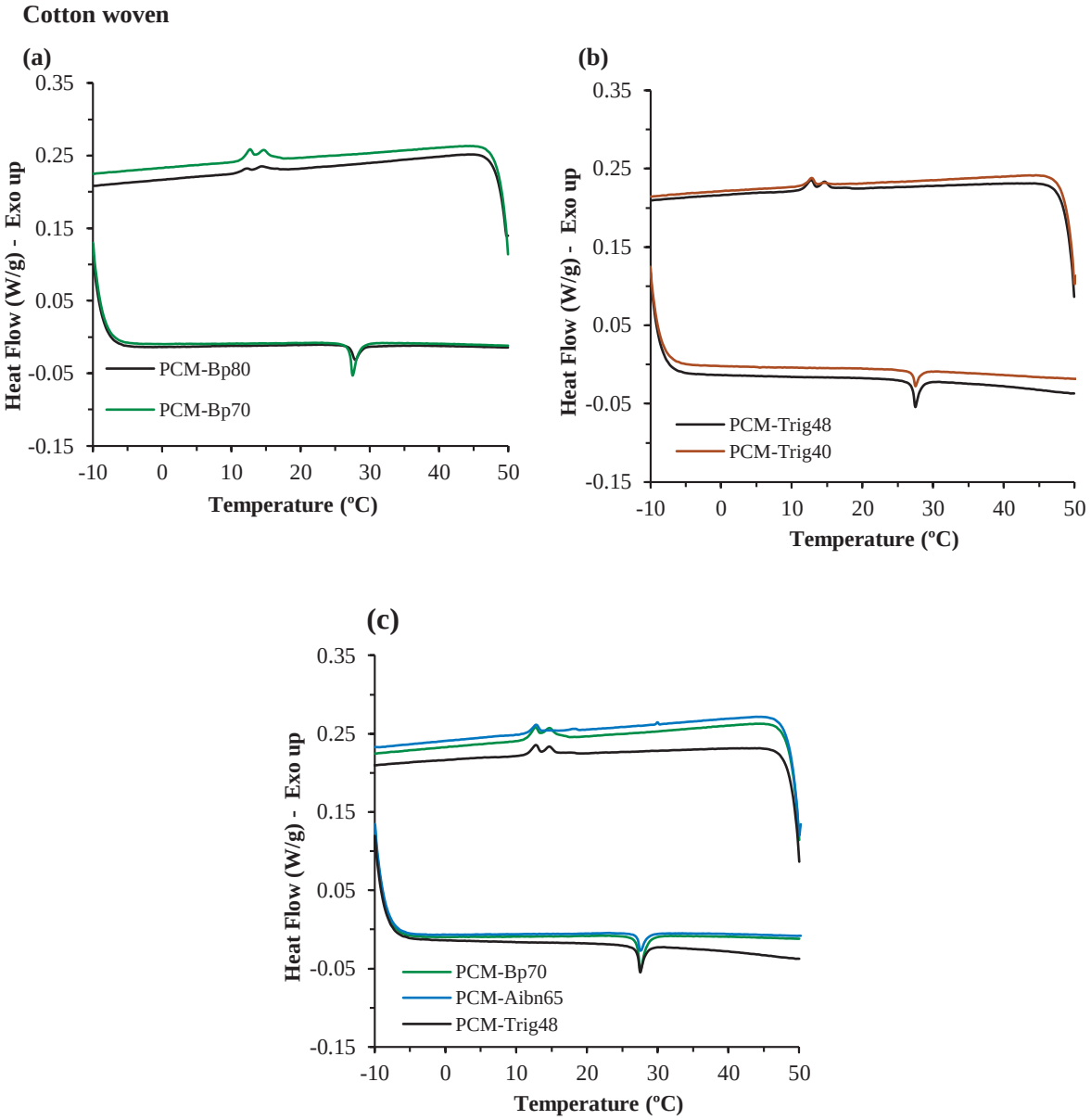


Figure C.6: DSC curves of washed cotton woven (5W) with microcapsules prepared (a) using BPO at 80 ºC and 70ºC; (b) using Trig23 at 48 ºC and at 40 ºC; and (c) using BPO at 70 ºC, AIBN at 65 ºC and Trig23 at 48 ºC.

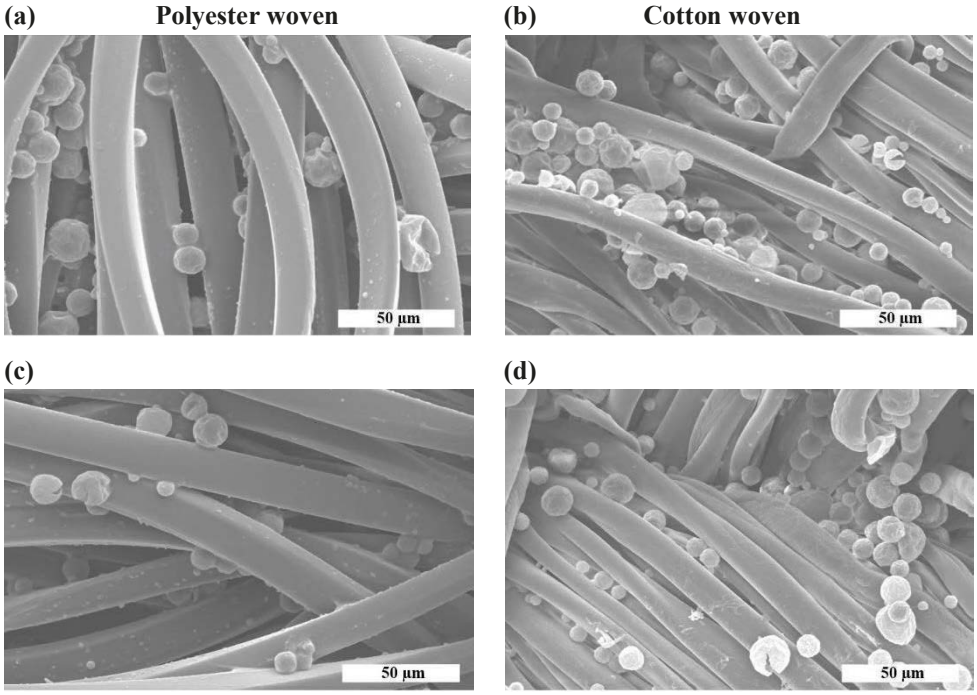


Figure C.7: SEM micrographs of treated woven: microcapsules BA14-MAA1 on (a) polyester and (b) cotton fibres; microcapsules BA6-MAA9 on (c) polyester and (d) cotton fibres (magnification x600).

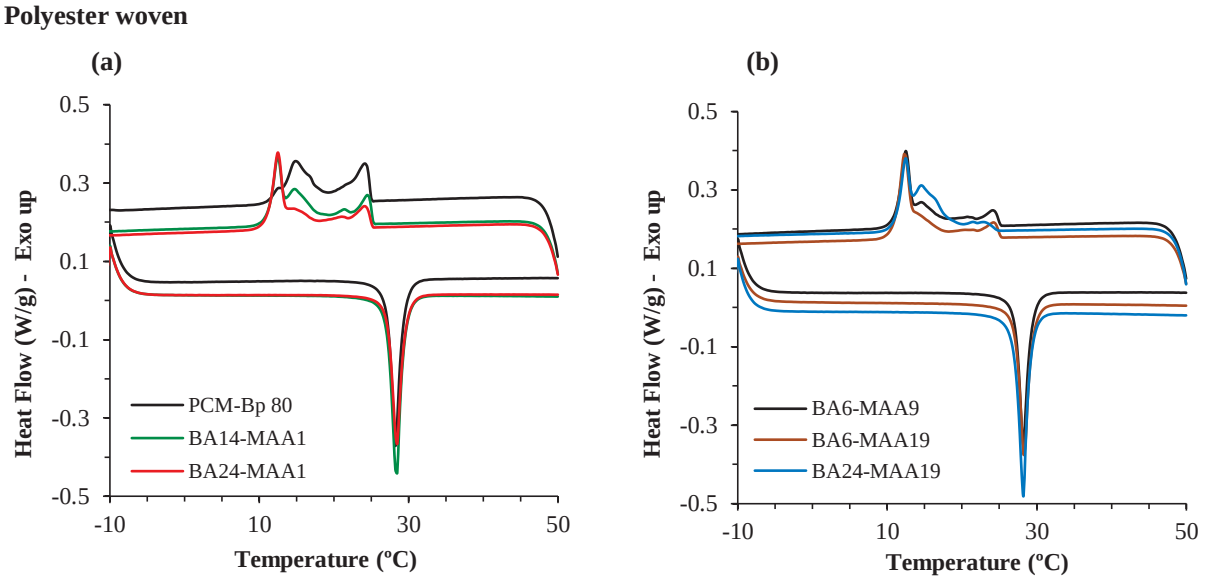


Figure C.8: DSC curves of treated polyester woven with microcapsules prepared with different monomers proportions: (a) progressively increasing the amount of BA; and (b) progressively increasing the amount of MAA.

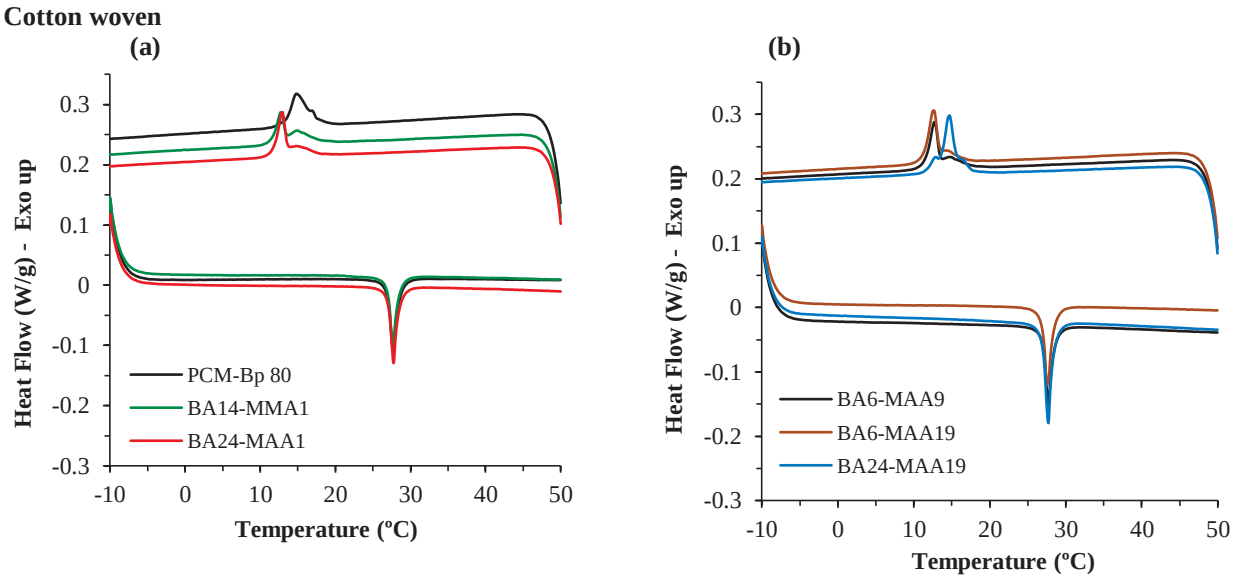


Figure C.9: DSC curves of treated cotton woven with microcapsules prepared with different monomers proportions: (a) progressively increasing the amount of BA; and (b) progressively increasing the amount of MAA.

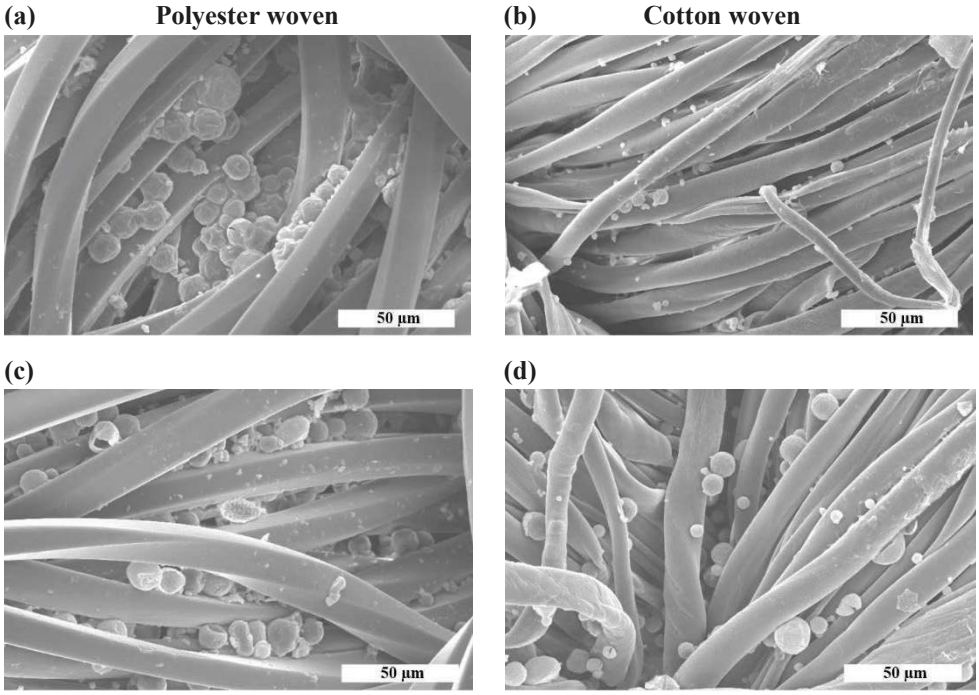


Figure C.10: SEM micrographs after washing process (5W) of treated woven: microcapsules BA24-MAA1 on (a) polyester and (b) cotton fibres; microcapsules BA6-MAA19 on (c) polyester and (d) cotton fibres (magnification x600).

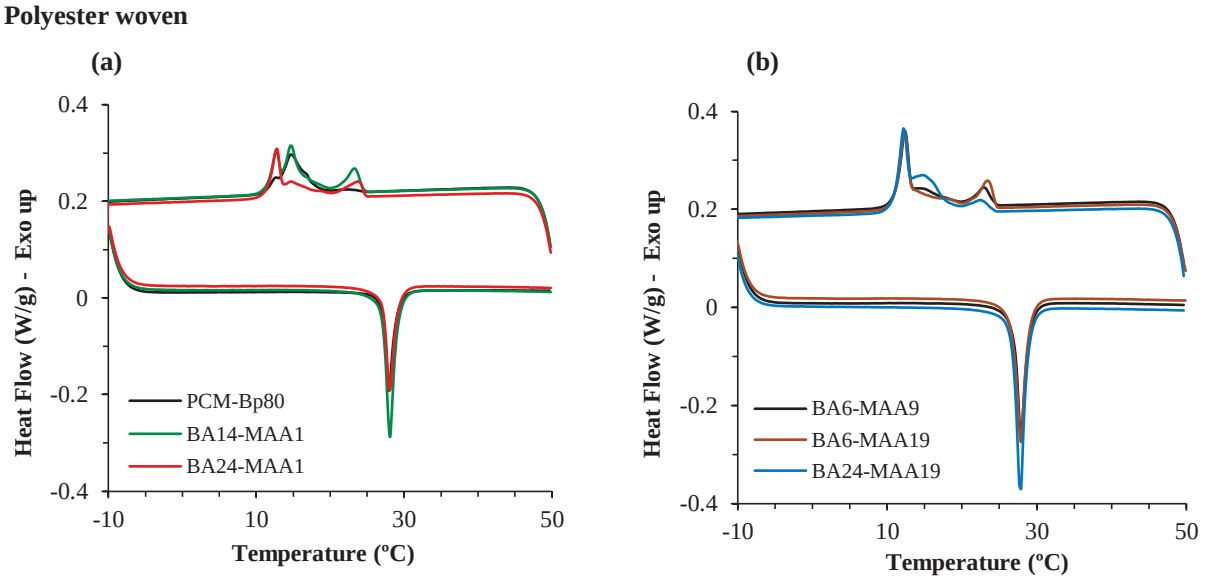


Figure C.11: DSC curves of washed polyester woven (5W) with microcapsules prepared with different monomers proportions: (a) progressively increasing the amount of BA; and (b) progressively increasing the amount of MAA.

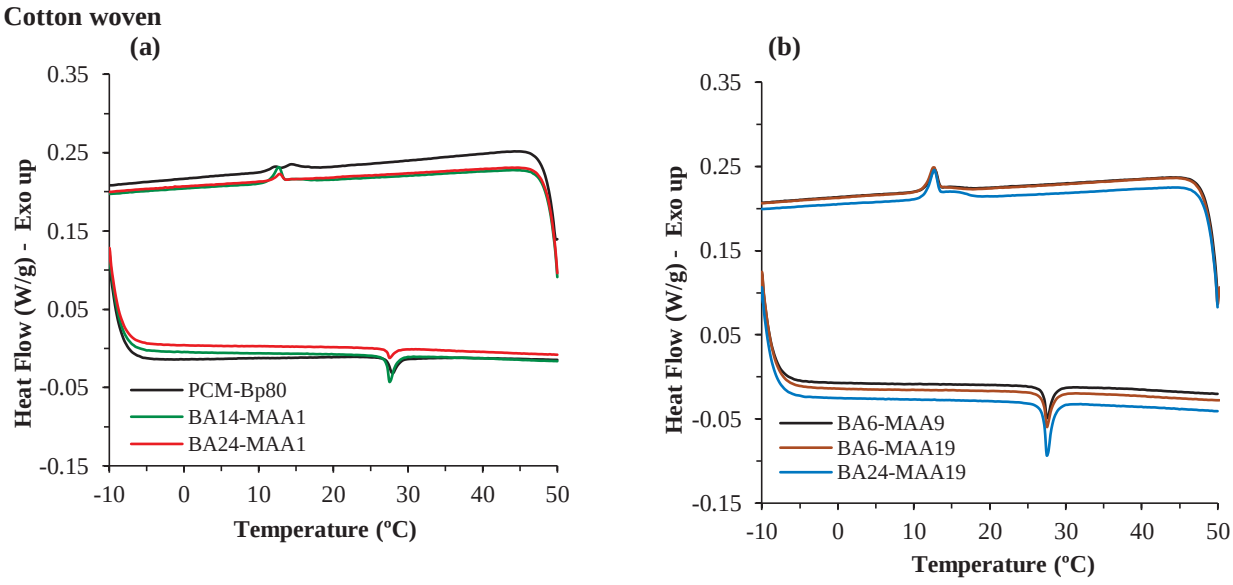


Figure C.12: DSC curves of washed cotton woven (5W) with microcapsules prepared with different monomers proportions: (a) progressively increasing the amount of BA; and (b) progressively increasing the amount of MAA.

Appendix D

Supporting information for Chapter 6: Functionalization of acrylic microcapsules with different reactive groups

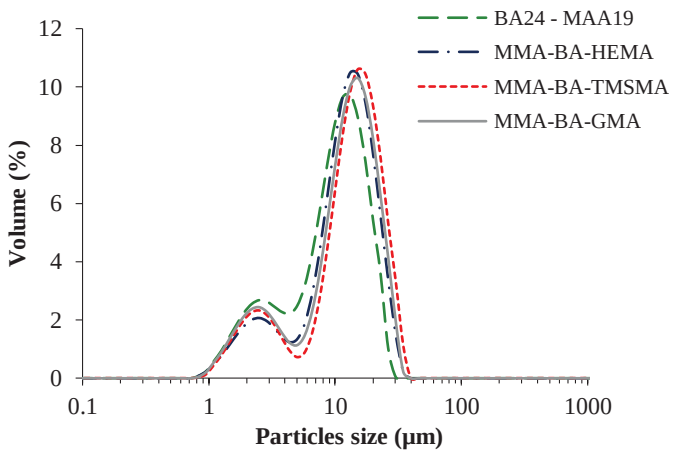


Figure D.1: Particle size distribution of microcapsules prepared with different dual reactive monomers. Sample BA24-MAA19 is represented for comparison.

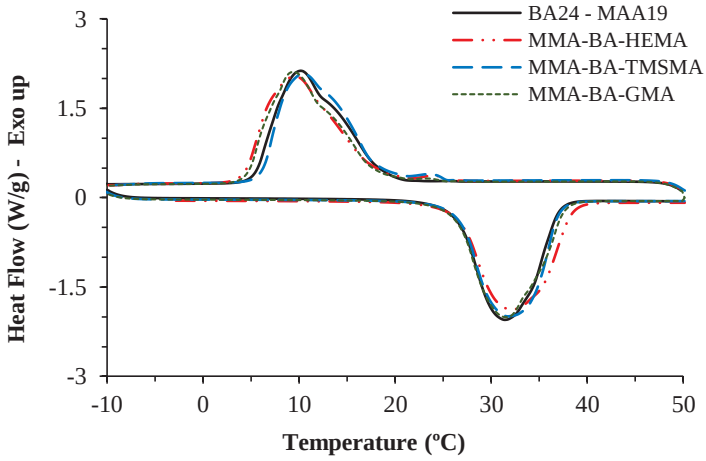


Figure D.2: DSC curves of microcapsules prepared with different dual reactive monomers.

Table D.1: Thermal performance of microcapsules prepared with different dual reactive monomers (average ± standard deviation) (ΔH_m and ΔH_c: melting and crystallization enthalpies; T_{om} and T_{oc}: melting and crystallization onset temperatures; PCM content was calculated using equation (3.1)).

Sample	**T_{om}** (ºC)	**ΔH_m** (J/g)	**T_{oc}** (ºC)	**ΔH_c** (J/g)	**PCM content** (wt.%)
BA24 - MMA19	26.4 ± 0.1	176.5 ± 1.0	18.1 ± 1.5	180.0 ± 1.3	70.7
MMA-BA-HEMA	26.5 ± 0.2	177.6 ± 2.3	18.0 ± 0.1	180.9 ± 2.1	71.1
MMA-BA-TMSMA	26.4 ± 0.1	179.6 ± 3.8	19.3 ± 0.8	182.6 ± 3.0	71.8
MMA-BA-GMA	26.6 ± 0.1	182.2 ± 3.7	17.3 ±0.9	184.9 ± 4.8	72.8

Table D.2: Thermal stability of microcapsules prepared with different dual reactive monomers ($T_{5\%}$ and $T_{10\%}$: temperatures corresponding to 5% and 10% of weight loss; T_{on1} and T_{on2}: extrapolated onset temperatures of the first and second degradation stage; Weight loss: weight loss (%) in each degradation stage).

Sample	**$T_{5\%}$** (ºC)	**$T_{10\%}$** (ºC)	**1st stage**		**2nd stage**	
			T_{on1} (ºC)	**Weight Loss** (%)	**T_{on2}** (ºC)	**Weight Loss** (%)
BA24 - MMA19	197.0	208.0	214.5	68.4	377.7	30.6
MMA-BA-HEMA	165.2	180.1	188.6	68.1	359.5	31.5
MMA-BA-TMSMA	148.6	162.6	162.3	68.0	354.9	30.9
MMA-BA-GMA	150.7	162.8	169.9	68.4	350.8	31.1

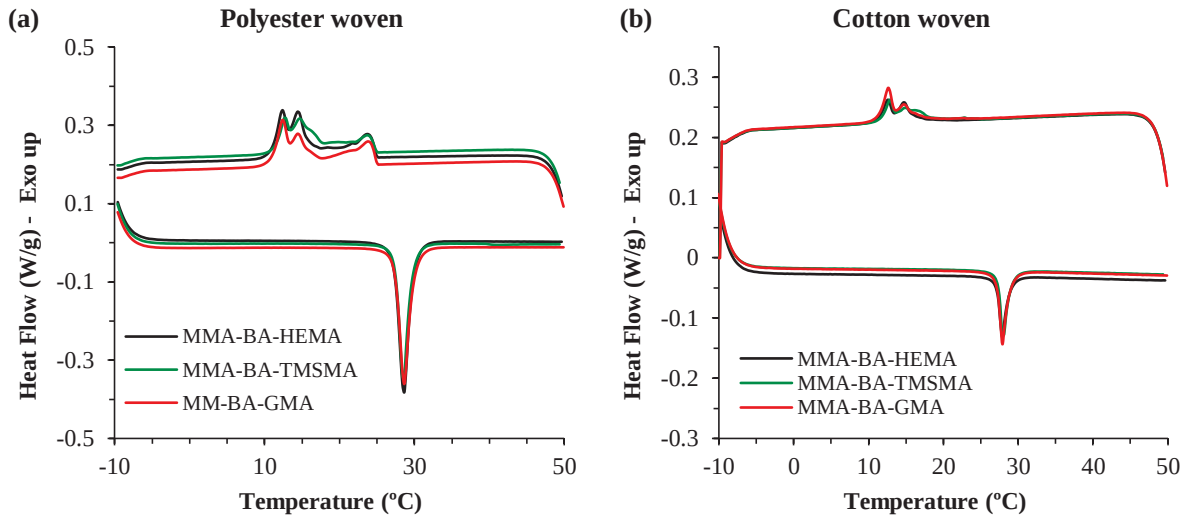


Figure D.3: DSC curves of treated woven with microcapsules MMA-BA-HEMA, MMA-BA-TMSMA and MMA-BA-GMA on (a) polyester woven and (b) cotton woven.

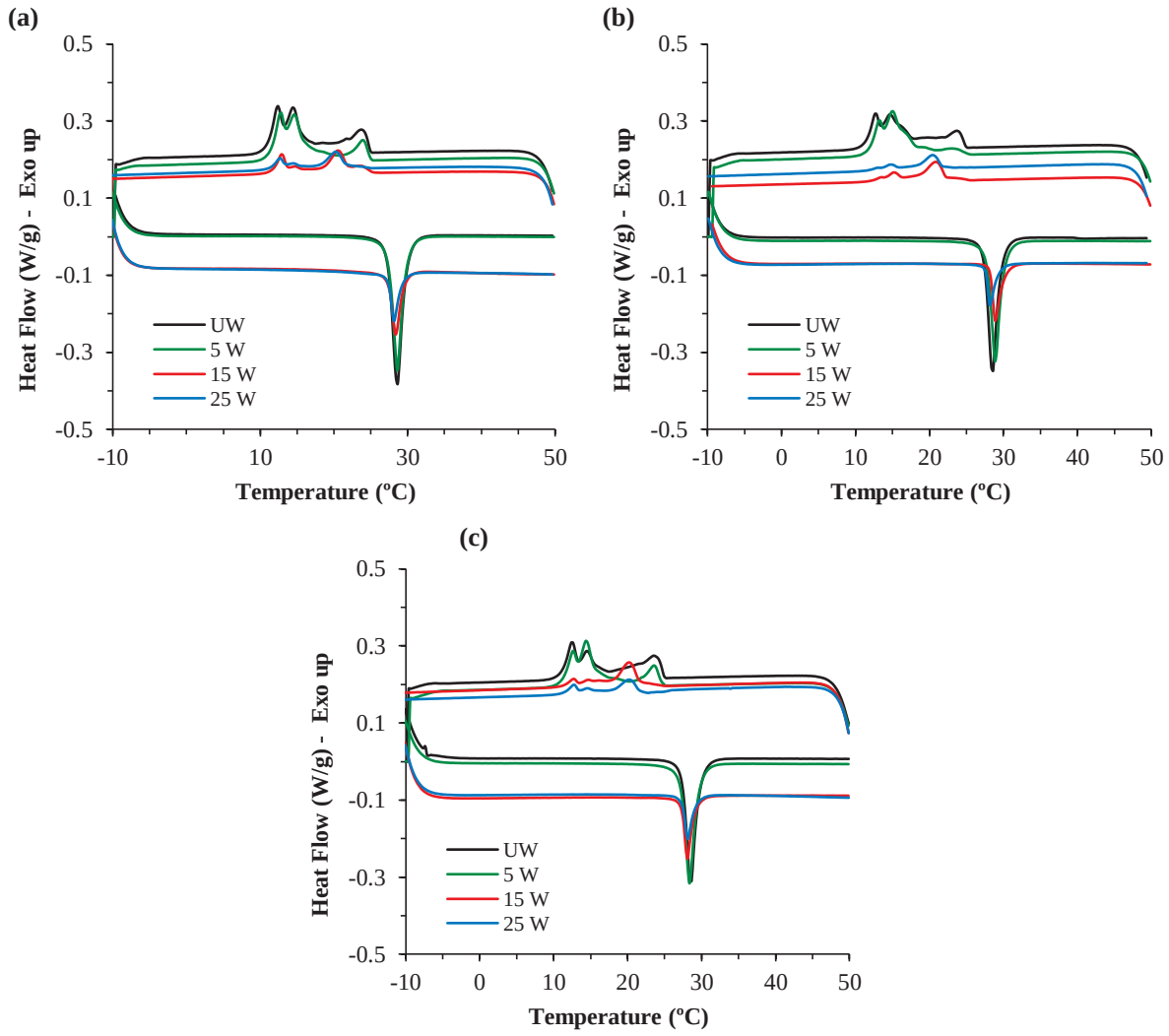


Figure D.4: DSC curves of treated polyester woven with: (a) microcapsules MMA-BA-HEMA; (b) microcapsules MMA-BA-TMSMA; and (c) microcapsules MMA-BA-GMA. Unwashed polyester woven (UW) and washed after 5W, 15W and 25W.

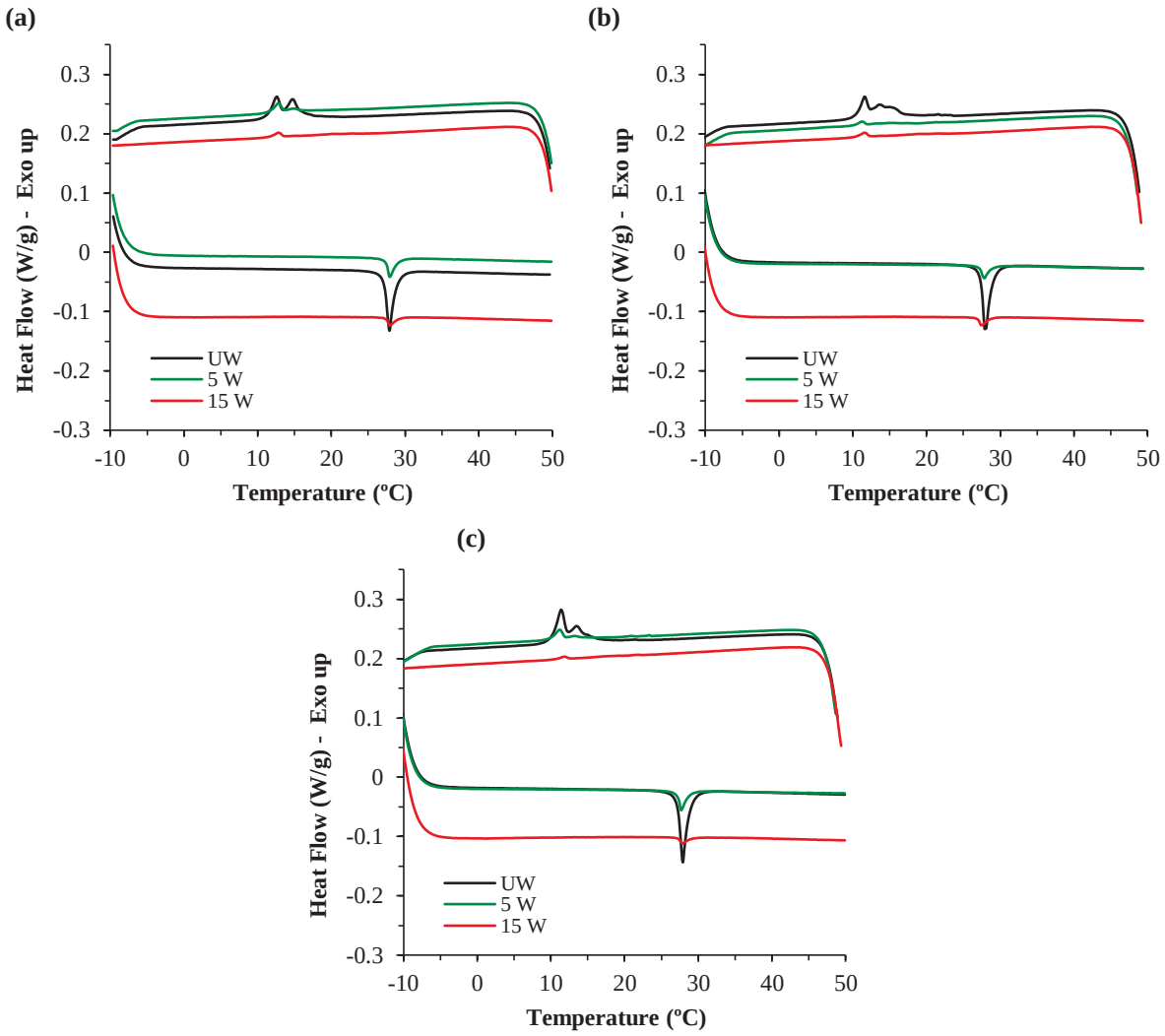


Figure D.5: DSC curves of treated cotton woven with: (a) microcapsules MMA-BA-HEMA; (b) microcapsules MMA-BA-TMSMA; and (c) microcapsules MMA-BA-GMA. Unwashed polyester cotton (UW) and washed after 5W and 15W.

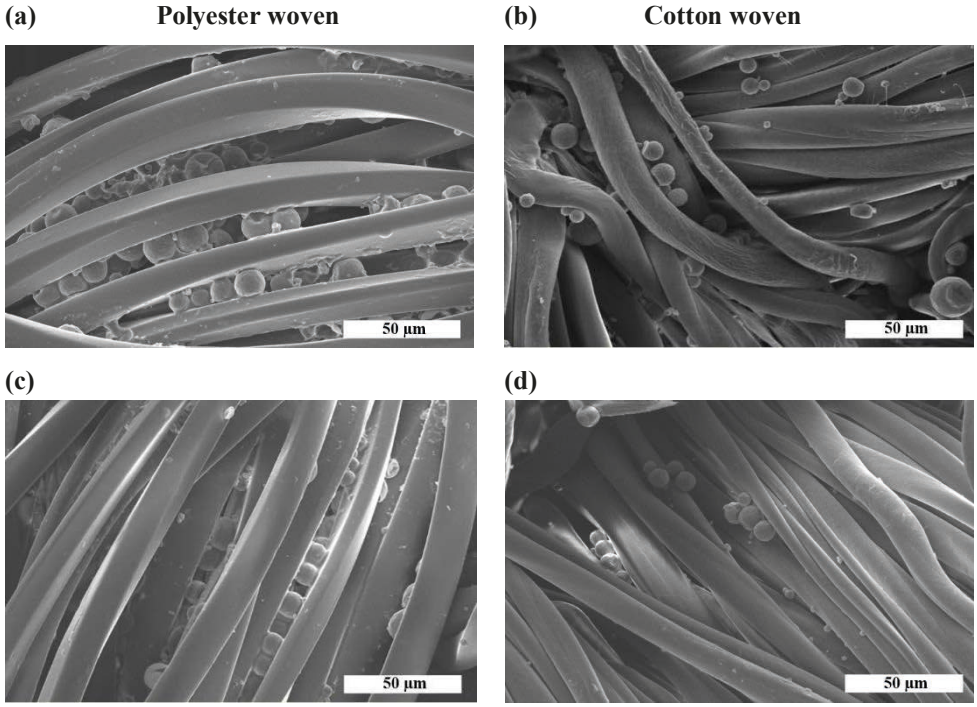


Figure D.6: SEM micrographs after washing process (5W) of treated woven: microcapsules MMA-BA-HEMA on (a) polyester and (b) cotton fibres; microcapsules MMA-BA-GMA on (c) polyester and (d) cotton fibres (magnification x600).