Microcapsules Characterization
for Polyurethane One Component Foam Systems

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Chemical Engineering

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To my aunt,

Helena

Acknowledgements

Abstract

This work for dissertation has the purpose of characterizing microcapsules, developed at Greenseal Research Ltd., to be incorporated in one component polyurethane foam systems, so they can accelerate the curing process of the as-sprayed foam, by releasing their content during the spraying stage. These capsules have polyurethane/polyurea (PU), polyamide and silica-based shells. They encapsulate components exhibiting hydroxyl groups (such as diethylene glycol and glycerol), which will react with the isocyanate groups of the foam.

Thermogravimetric Analysis and Differential Scanning Calorimetry have been used to characterize the capsules, with the main purpose of quantifying the core, while Fourier Transformed Infrared Spectroscopy has been used to study the molecular structure of the shell obtained from different synthesis protocols. The other procedures employed, have been developed at Greenseal, and consist of the leaching assessment, either in aerosol and pre-polymer environment, and foam characterization

The reinforcement of the PU shell by the use of tetraethyl orthosilicate (Si-PU MCs) proved to be the best option to a higher encapsulation and lower leaching. Regarding the polyamide shell, the best amine source is diethylene triamine in terms of leaching behavior. The addition of methyl and epoxy functional silanes to the silica-based shell gave the best results regarding leaching.

Foam formulations made with PU capsules presented a shorter curing time than the reference, in a low moisture environment, but the output was found to decrease. The quality of the cured foams was not significantly affected by the presence of the microcapsules.

Keywords: Microcapsules; Polyurethane Foams; Curing Time; Polyamide; Sol-Gel; Silica

Resumo

O presente trabalho teve por objetivo a caracterização de microcápsulas produzidas na Greenseal Research Lda., a incluir em sistemas monocomponente de espumas de poliuretano, com vista a acelerarem o seu processo de cura. As cápsulas consistem numa parede à base de poliuretano-poliureia (PU), poliamida ou sílica, que encapsula dietilenoglicol e glicerol, fontes de grupos hidróxilo que irão reagir com os grupos isocianato da espuma.

Foram usadas as técnicas de Análise Termogravimétrica e Calorimetria Diferencial de Varrimento com o intuito de apurar a quantidade de material encapsulado, bem como a técnica de Espectroscopia de Infravermelho por Transformada de Fourier, para estudar a estrutura molecular das cápsulas resultantes de diversos protocolos de síntese. Foram também usadas outras técnicas, desenvolvidas pela Greenseal, para a avaliação da tendência de libertação das espécies encapsuladas (teste de viscosidade), tanto em contacto com o pré-polímero, como em ambiente pressurizado nas latas. Adicionalmente foi avaliada a qualidade das espumas resultantes.

A presença de tetraetilortosilicato nas cápsulas de PU resultou numa maior encapsulação e menor libertação do seu conteúdo. Destaca-se também uma melhor qualidade das microcápsulas de poliamida que foram preparadas com dietilenotriamina. Por outro lado, a presença de silanos com funcionalidade metil e epóxi nas cápsulas à base de sílica levou a um melhor desempenho a nível de libertação antecipada do conteúdo.

As espumas preparadas com microcápsulas de PU apresentaram tempos de cura inferiores aos da referência, mas o valor de output diminuiu. A qualidade das espumas como produto final não foi afetada pela presença das cápsulas.

Palavras-Chave: Microcápsulas; Tempo de cura; Espumas de Poliuretano; Poliamida; Sol-Gel; Sílica

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List of Abbreviations

DEG	Diethylene Glycol
DETA	Diethylenetriamine
DME	Dimethyl Ether
DSC	Differential Scanning Calorimetry
EDA	Ethylenediamine
FTIR	Fourier Transform Infrared Spectra
GPTMS	Glycidoxypropyl Trimethoxysilane
HLB	Hydrophilic-Lipophilic Balance
LPG	Liquefied Petroleum Gas. In this work, it is considered to be a mixture of isobutane and propane of known proportions
MCs	Microcapsules
MDI	Methylene Diphenyl Diisocyanate
MTES	Methyltriethoxysilane
OCF	One Component Foam
PA	Polyamide
PU	Polyurethane-Polyurea
RH	Relative Humidity
SG	Sol-Gel
SPF	Spray Polyurethane Foam
TEOS	Tetraethyl Orthosilicate
TGA	Thermogravimetric Analysis
TMC	Trimesoyl Chloride
TMP	Trimethylolpropane

1. Introduction

As the human quality of life increases and the manufacture industries evolve, the materials used in buildings or factories construction need to evolve as well. The demand is for high resistance materials that are easy to apply. Urethane one-component foams (OCF), a semi-rigid foam, is self-expanding and self-adhesive and they can be applied in fissures and in between materials (even if the materials are wet), such as door and window frames, filling the gaps in roof construction, fix polystyrene and polyurethane panels to walls and also as building insulation, and others to prevent the thermal losses and increase the efficiency of the energy used [1] [2]. It also improves air quality, since it prevents allergens to get in. Also, their great advantage comparing with other materials, is that when the foam is fully cured, it doubles its volume. So, the handler does not need to be very meticulous to fill all the gaps, because the foam will do it by itself.

Polyurethane foams can be made with different hardness or density and can be used in a huge amount of applications, as in adhesive sealants, appliances, automotive, binders, construction, coatings, elastomers, footwear and furniture and bedding [3]. This work will be focused on the foams used for structural applications and insulation, contained in aerosol cans, in the building construction sector. OCF were discovered in 1970, and they cure by the atmospheric moisture.

According to Portuguese authorities, in 2010 about 29% [4] of the total energy used in the country was for domestic purposes and 10% [5] of those were to heat or cool down the household environment. This represents a huge amount of energy that has been lost alongside with the costs that it takes. Figure 1.1 shows that the price of the energy, namely electricity, has increased so there is a need to reduce energy spending to sustainable values.
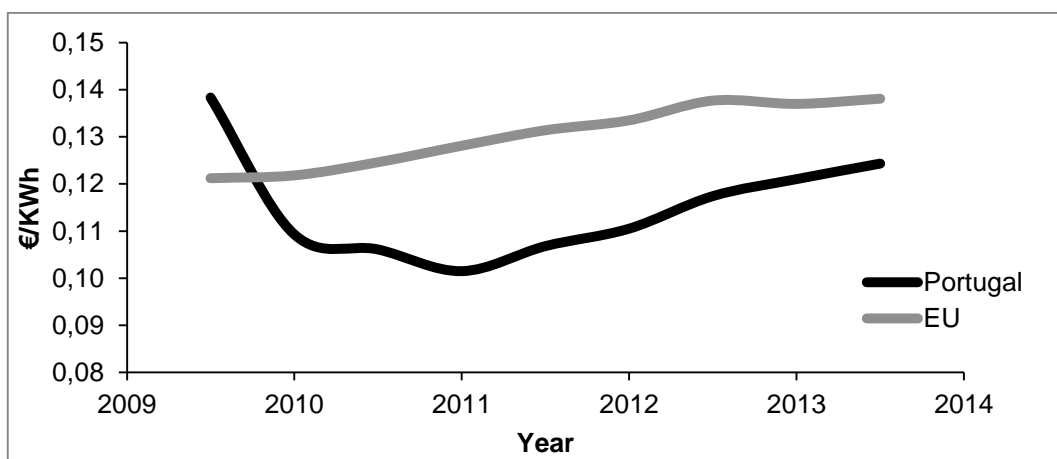
Figure 1.1: Evolution of electricity prices in the last 5 years, for Portugal and European Union. [6]

If houses, public service buildings, shopping malls and other types of buildings had more energy efficiency, costs concerning this issue would decrease. This translates into a growing demand for spray polyurethane foams, due to their thermal insulation ability [7] [8].

To promote energy saving, buildings are being certified by their energy efficiency. A higher rating building has its market value increased and utility costs would be lower since less energy is needed to keep a comfortable temperature. And one more advantage is added to the role: with an efficient use of energy, the environment impact is reduced, which is another topic that society is getting more concerned with.

The global market for OCF is expected to grow 6% per year, and in 2011 about 400 million cans were sold [9]. We can conclude that is a lucrative market with a wide range of expansion and research. A big OCF producer nowadays is Dow.

Greenseal Research is a company working on Polyurethane OCF systems aiming to produce chemical compounds for high quality foams with less impact to the environment.

This work has been carried out in parallel and in collaboration with that of Carmen Matos (chemical engineering Master student at IST) entitled "Microcapsules Synthesis for Polyurethane Foams", *Síntese de Microcápsulas para Espumas de Poliuretano*.

1.1 Motivation/Purpose

The current OCF systems take typically 24 hours (in bid form) to fully cure and get into the final shape and volume. Until that, if the froth/foam is touched or manipulated, will not serve its purpose because the foam cells will collapse and not expand in the proper way. In building construction industry, time is crucial and 24 hours sometimes can be too long. If the curing time is reduced, it will be a huge positive point when compared with other competitive products. Costumers would prefer a foam that takes less than half the time to cure, so they can proceed faster with their work.

Microcapsules containing OH groups in the core (which are stable within the aerosol can, but will burst upon spraying the foam, releasing their content) are potentially the solution to accelerate the curing process of PU foams, even in low moisture environments (weak source of OH groups). For this reason, these capsules can be seen as agents to self-curing PU OCF systems.

In the OCF field, microcapsules development is expected to increase the product value in the market, along with sales and income.

These types of microcapsules and their purpose are new to the market and no similar work has been found in the state of the art. *Greenseal* is pioneer in this field.

This thesis has three main goals:
1. Assess if the synthetized microcapsules are viable for this application;
2. Establish the conditions that lead to better microcapsules;
3. Conclude on their roles in terms of shortening the curing time of the foams.

For such, the appropriate characterization tools have been employed.

1.2 Outline

This thesis is divided into chapters. Chapter 2 includes a brief historical content of the subjects and the theoretical explanation behind them.

Chapter 3 gives an explanation of the laboratory procedures and the most important facts about microcapsules synthesis, concerning Carmen's work.

The results and their discussion are presented in chapter 4 and at last, the conclusions of the present work are described in chapter 5.

2. Background

This chapter aims at explaining the chemistry of polyurethane foams and the reactions behind the microcapsules formation as well as the theoretical concepts for the analytical techniques that have been employed to accomplish the final results (TGA, DSC and FTIR).

2.1 Polyurethane Foams

Polyurethane was first synthesized by Otto Bayer in 1937 [10]. Big companies started doing business directly or indirectly related to Polyurethane, like Dow, BASF or DuPont. By the 60's it was already being largely used as insulation material and for body car parts. Nowadays, PU is among the top five prime polymeric materials [11].

Polyurethane is made by reacting polyisocyanate (e.g. methylene diphenyl diisocyanate, MDI) with polyols, such as a diol. The reaction is shown in Figure 2.1 [12], where MDI is representing the polyisocianate and ethylene glycol is representing the diol (two OH groups). Depending on the end product desired, different combinations of polyols, monols and isocyanate compounds can be used. Besides that, the foam formulations contain catalysts, surfactants, blowing agents and fire retardants [3].

One component foam has its designation due to the fact that the reactants that will produce foam are mixed inside the can, so that a polyurethane pre-polymer, with excess of NCO groups, is formed inside the can. It will be further polymerized after spraying the content of the can, by reaction of the NCO groups with the OH groups from the moisture in the environment or from other sources.
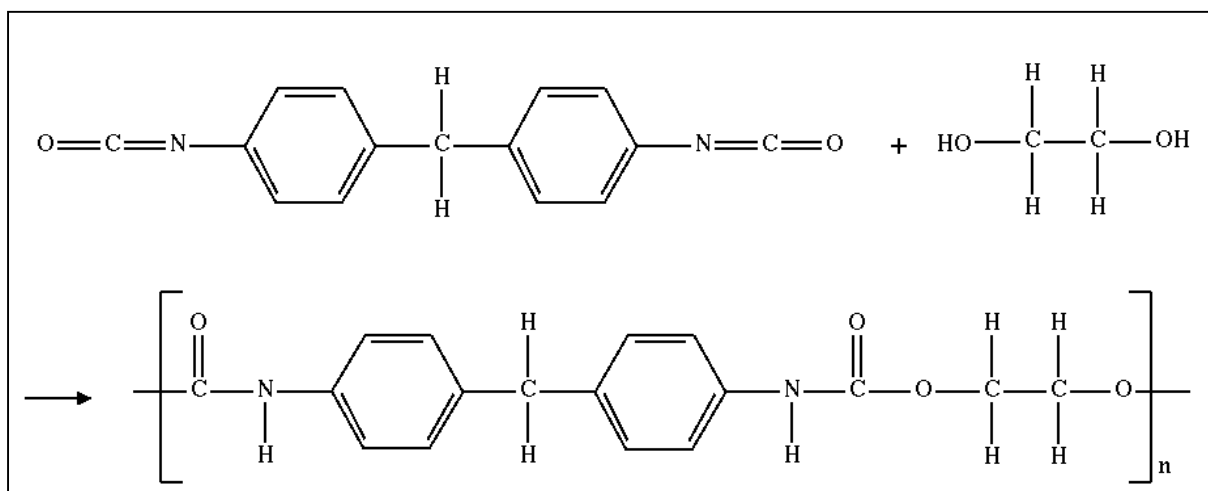
Figure 2.1: Reaction of Polyurethane.

Figure 2.2 shows the electronic behavior and the resonance structures. N=C undergo nucleophilic attack by OH group [13]. Groups electron accepters bonded with the NCO, increase its reactivity

towards nucleophilic attack. This is the reason why aromatic compounds (MDI) are suitable for this type of reactions.
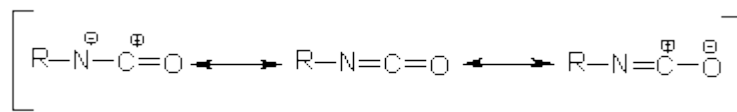
Figure 2.2: Canonical forms of cyanate group of MDI

2.2 Microcapsules

Microcapsules are small particles that contain an active reagent or a core material surrounded by a coating, membrane or shell [14]. Microencapsulation technology can be used in different applications like paper industries, food industries, pharmaceutical, cosmetics, adhesive materials and coating industries. [15].

Since 1980, the microcapsules have attracted more attention. They were prepared with phase change materials as the core content and applied for insulation purposes into polyurethane foams and other materials [14].

The present work deals with one more application for microcapsules (MCs): their use in polyurethane (PU) foams to reduce their curing time. They are supposed to break their shell when they are sprayed out and release their core. Aqueous solutions of diethylene glycol (DEG) or glycerol are used to form the core of the capsules. An extra source of hydroxyl groups into the foam will lead to a faster cure, since the reaction kinetics of PU formation is changed.

However, it is crucial that the core content does not leach when the MC are still inside the can. This case scenario would not be suitable for can bottling since it would start producing foam (Figure 2.1) and CO_2 and polyurea (Figure 2.3). It should be noted that the release of CO_2 inside the aerosol can would result in can instability due to pressure increase. Also, the microcapsules have to last in perfect conditions through the time the can in predicted to stay in the shelf, for sale (typically 12 months, maximum).
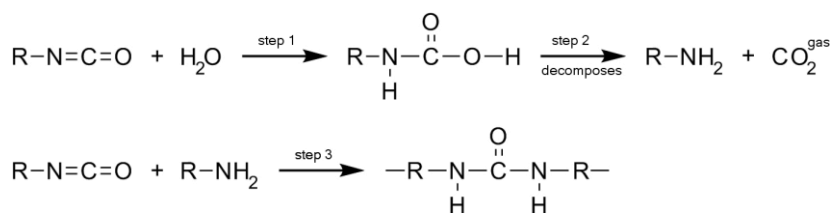
Figure 2.3: Reaction of NCO group with water.

2.2.1 Polyurethane-Polyurea (PU)

Although the reaction mentioned above (Figure 2.3) can not occur inside the aerosol can, it takes part of the PU MCs production. Concerning reactions in Figure 2.1 and Figure 2.3, polyurethane and

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polyurea will be the main shell material for the PU MCs. This will encapsulate DEG and water. The PU MCs tested in this work have been prepared by the microemulsion/interfacial polymerization method while a silane has been used to add extra mechanical resistance to the MCs through the Si-O-Si bonds formed within the shell. The diameter of this particles was between 100 and 400 μm.

2.2.2 Polyamide (PA)

Polyamide MCs are also prepared by microemulsion/interfacial polymerization method. They result from the reaction of an amine and acyl chloride, like in Figure 2.4, that shows the formation of the amide monomer. To make polyamide, the reactant should have more than one amine, and by using different reactants, different polyamides can be obtained. One famous example is *Kevlar*.

A surfactant may be added to this type of MCs for the same reason as for PU MCs.
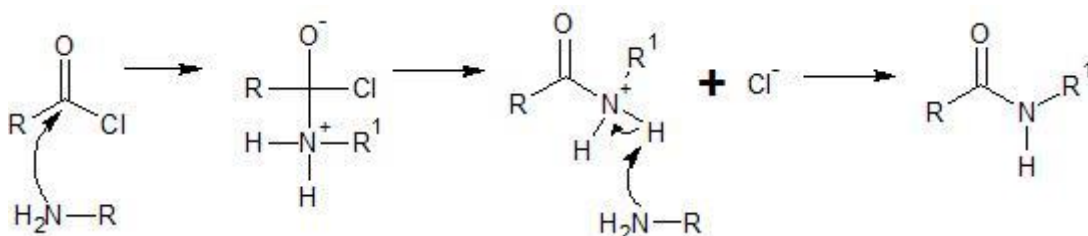
Figure 2.4: Reaction of amide. [16]

2.2.3 Sol-Gel (SG)

Sol-Gel (SG) is a technique with a wide range of applications and processes. Among those are films and coatings, fibres and monosized powders[1] [17]. A sol is a colloidal suspension of solid particles in a liquid and a gel is the particulate sols that stick together, forming a network.

To understand the further work regarding sol-gel MCs, it is important to briefly explain in this section the process behind it. Microemulsion/Sol-Gel process is divided in two steps: first, a water-in-oil microemulsion is formed with decalin, (Figure 2.5) as a solvent in the continuous phase and a solution of water and glycerol (Figure 2.6), or another alcohol, like DEG, as the disperse phase.
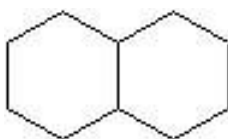
Figure 2.5: Decalin structural formula.

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[1] Used to produce polycrystalline ceramics, catalysts, pigments, abrasives, etc.
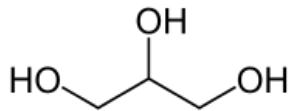
Figure 2.6: Glycerol structural formula.

Next, a pre-hydrolysed solution of tetraethyl orthosilicate (TEOS) and other silanes is prepared and added to the microemulsion. This will be followed by an increase of the temperature under stirring, leading to polycondensation reactions and a silica-based material being formed at the droplets surface. This will result in MCs formation containing a silica-based shell and encapsulated alcohol. This hydrolysis and polycondensation reactions, which will create the silica network are exhibited in Figure 2.7. The MCs obtained were about 10 µm diameter.
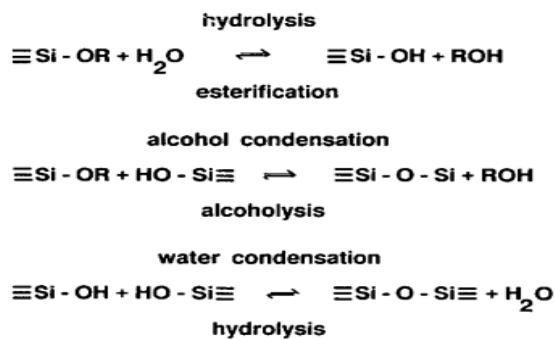
Figure 2.7: Hydrolysis and polycondensation of TEOS. [18]

2.3 Characterization Techniques

For a deeper study of the microcapsules, their compounds must be known as well as the relative amounts of each one. For that purpose, two different techniques have been used: TGA with DSC and FTIR Spectroscopy.

2.3.1 Thermogravimetric Analysis and Differential Scanning Calorimetry (TGA and DSC)

Thermogravimetric Analysis (TGA) is used to monitorize the weight of a sample through a range of temperatures (or time) under a controlled atmosphere (N_2 or air). It is used to characterize the materials structure in petrochemical, food, environmental and pharmaceutical industries, mainly.

The equipment used also provides results of DSC (Differential Scanning calorimetry) as heat flow for each temperature, which is the change in heat capacity of the material. It allows the detection of phase changes and transitions, such as evaporation, degradation, crystallization processes, etc. It also allows to determine the quantity of encapsulated alcohol and even get an idea about the cross-linking degree of the polymeric shells. With these two techniques combined, we can understand what kind of physical transformations occurs in the sample. It's expected that at lower temperatures the phenomena occurring is mainly evaporation, and at higher values, it is degradation of the material, as the molecules' bonds break.

In DSC graphs, some peaks point up and others down. This is a convention used to tell the user that the peaks pointing down are endothermic, because the sample absorb the heat so is cooler that the furnace. Peaks pointing up are the opposite, exothermic [19].

2.3.2 Fourier Transformed Infrared (FTIR) Spectroscopy

Infrared spectroscopy is a very useful technique that detects the presence of the functional groups composing the sample. Spectroscopy depends on the interaction of molecules (or atoms) with electromagnetic radiation. In this particular case, infrared radiation causes the covalent bonds to vibrate, increasing their amplitude. Said so, absorption of IR radiation will occur at different frequencies depending on the type of the atoms and their bonds. Each functional group can be identified by their position in the IR portion of the spectrum.

Fourier transform allows the spectroscopy to be much faster (there is no need to scan over a big range of wavelengths) and a bigger throughput of the infrared energy. These two facts allow spectra with no random noise and a better quality of the real signals.

The simplistic operation of the spectrometer consists in passing a beam of IR through the sample and comparing it with the one transmitted with no sample (reference).

There are a few ways a bond can vibrate. Two atoms can undergo a stretch vibration and three atoms can undergo a symmetric (Figure 2.8 and Figure 2.9) or asymmetric stretching or bending vibrations (Figure 2.10). The frequency of a given stretching bonds depends on the mass of the atoms, its geometry and the stiffness of the bond (single, double or triple bonds). Stiffer bonds give higher frequency of stretching and need more energy, since frequency and energy are proportional [16]. Stretching the bonds requires more energy than bending.
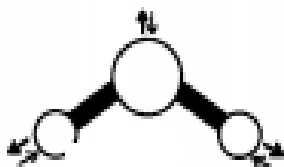
Figure 2.8: Stretching symmetric vibrations. [20]

Figure 2.9: Bending symmetric vibrations. [20]

Figure 2.10: Bending asymmetric vibrations. [20]

The resulting infrared spectrum is plotted by the percentage of transmittance (or absorbance) versus wavenumber (cm^{-1}) which is inverse to wavelength and proportional to frequency. Transmittance is the ratio of the radiant power transmitted by a sample to the radiant power incident on a sample [21].

3. Experimental Work

This chapter contains an explanation of the experimental laboratory work that was done, including the procedures and the materials used.

It will start with the production of the microcapsules, made by Carmen and hereby only the relevant production aspects for this work will be emphasized.

3.1 Microcapsules Production

Different parameters were tested in the course of the traineeship. Some of them were based on the literature search results corresponding to other types of MCs applications. Other parameters have not been evaluated using the characterization techniques because they were easily assessed, so they will not be referred in this text.

The reason why we have used the materials that were incorporated in the MCs and their effects will be explained in chapter 4.

3.1.1 PU

Polyurethane microcapsules were prepared by mixing two solutions under stirring until a "water-in-oil" emulsion were formed, followed by interfacial polymerization. The continuous (organic) phase is composed by toluene and an isocyanate based compound. The disperse (aqueous) phase is composed by DEG (Alfa Aesar, 99%) and water, together with a surfactant of high HLB value, which will stabilize the emulsion. The available options for surfactant were DC193 (Dow Corning) or Span80 (Merck).

A series of shell reinforcements strategies have been tried. Among them, there was the incorporation of alcohols with higher functionality OH as pentaerythritol and trimethylopropane (TMP), isocyanate based compounds with higher functionality NCO (distilled Ongronat2500) and the incorporation of silane species into the emulsion. The first two approaches are aimed at increasing the cross-linking of the PU shell, while the latter one leads to the formation of silica-rich regions within the PU shell.

The silanes which have been tested are TEOS (Dow Corning Z-6697) (Figure 3.1), Methyltriethoxysilane (MTES, from Dow Corning Z-6370) (Figure 3.2), and Glycidoxypropyl Trimethoxysilane (GPTMS, from Dow Corning Z-6040) (Figure 3.3).

Like in the sol-gel process (section 2.2.3) those silanes could also be previously mixed with an aqueous solution of HCl in order to hydrolyze. In this case, silanol species were added to the emulsion, instead of pure silane.
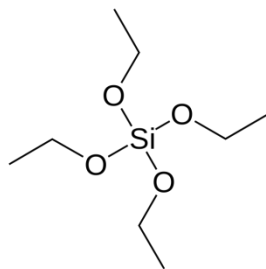
Figure 3.1: TEOS structural formula.
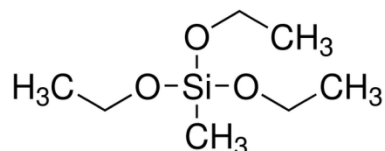
Figure 3.2: MTES structural formula.
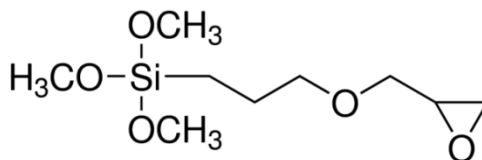
Figure 3.3: GPTMS structural formula.

3.1.2 PA

As for PU MCs, a "water-in-oil" emulsion was also prepared, followed by interfacial polymerization. The microemulsion consisted of a continuos (organic) phase of toluene and trimesoyl chloride (TMC, Figure 3.4) and the disperse (aqueous) phase contains DEG, water, a surfactant and an amine. The amines available were ethylenediamine (EDA) (Sigma Aldrich) and diethylenetriamine (DETA) (Alfa Aesar).

TMC is an acyl chloride, which reacts with amines forming amides as Figure 2.4 shows in section 2.2.2.
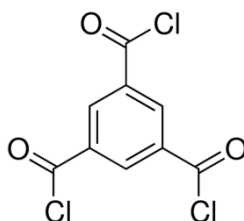
Figure 3.4: TMC structural formula. [22]

3.1.3 SG

For the preparation of the sol-gel (SG) derived MCs, the silane source (a mixture of TEOS, MTES and/or GPTMS) is previously hydrolyzed (solution one). In parallel, a "water-in-oil" microemulsion is prepared having a continuous (organic) phase of decalin solvent (Figure 2.5) with a surfactant with low HLB value and a disperse (aqueous) phase containing glycerol (Cmd Chemicals) (Figure 2.6) and/or DEG and water. Once this microemulsion is formed and stabilized, solution one is added drop by drop. Reactions of polycondensation are followed, leading to the formation of the silica-based shell.

3.2 Characterization Procedures

In this section the characterization procedures will be explained, including the viscosity test for microcapsule leaching assessment, TGA, FTIR, the preparation and assemblage of the aerosol cans with the PU formulation containing MCs and finally the several steps for foam evaluation.

3.2.1 Experimental Conditions

TGA and DSC
The experiments of TGA and DSC were made at 10°C/min, from the room temperature to 800°C, with in air environment.

FTIR
All the sample runs at FTIR were made with a *Nicolet 5700 FT-IR* (Figure 3.5) with a KBr beamsplitter plus a DTGS-TEC detector in the middle-infrared region, by Thermo Electron Corporation with a 4 cm^{-1} resolution and 128 scans, using an ATR accessory with a diamond crystal. The reflection spectra were obtained between 4000 and 600 cm^{-1}.

Figure 3.5: FTIR Equipment.

3.2.2 Viscosity Test Procedure

To assess if the microcapsules are leaching DEG and water out from the shell by the porous or even if the MCs are breaking easily, they are incorporated in pure Ongronat2500 (BorsodChem).

Viscosity test is prepared and operated by the following method:

1) For a concentration in mass of 5% of capsules, was measured 2 g of them, with less toluene as possible;
2) Next, Ongronat2500 was add, 38 g;
3) The suspension needs to be homogenized as much as possible, softly so the capsules wouldn't break;
4) Place a small amount of sample in the viscometer, enough to cover the area where the pendulum touches;
5) Start at the limit of 20P. If the value, when starting the measure comes too close of the limit, increase it to the next limit;
6) Wait 5 seconds for the pendulum to measure and take the value at the end of that time.
7) Measure the viscosity, about once a day, for approximately 500 hours.

The next figure show the equipment were this technique was performed, a cone and plate viscometer by Rel.

Figure 3.6: Cone and plate Viscometer.

3.2.3 Can Preparation

The method presented here is based on the one developed at Greenseal. It is composed by three parts: preparation of components A and B as well the MCs, filling up the cans and pressurize them, by incorporating the liquefied gas (component C).

1) Start by preparing component A which is a mixture of polyols, catalysts, plasticizers, silicones and flame retardants, according to the GreenFoam formulation;
2) Stirring component A for about 1 hour, using a mechanical stirrer;
3) Add component B (an isocyanate) to the can;
4) Add MCs;
5) Add component A;
6) Seal the can with an aerosol valve;
7) Measure the quantity of LPG and DME into the burettes;
8) Filling up the cans with the previous gases;
9) Shake the can vigorously for about 1 minute.

After the preparation, the content of the (glass) aerosol can be seen in Figure 3.7.

Figure 3.7: Content of a can after its preparation.

3.2.4 Spray Out and Output

The prepared cans are submitted to a series of tests, which include the spray and the evaluation of the foam properties at 23ºC, when dispensed from the can in a low moisture environment.

The output is a test at 5ºC, which consists of the measurement of the amount of material that comes out of the can during a certain period of spraying time (typically 10 seconds). To ensure that all the mixture inside the can is at the test temperature, the can should be at that temperature for at least 4 hours before spraying. The output value is expressed in g/s. In the present work, the output of the can was measured one week after being prepared.

In order to evaluate the quality of the foams with and without MCs (reference sample), the following tests were carried out:

(A) 23ºC / low moisture environment test: a small bid was sprayed inside a previously purged (with N_2 gas) and sealed plastic bag, until the bag is full. The foam containing bag was stored in a low moisture environment (dessicator with 10% RH). The time needed for the fully curing of the foams was recorded.

(B) 5ºC / 50% RH test: a bid of foam was sprayed on paper and left to cure at 5ºC (inside a refrigerator). The evaluated properties were: glass bubbles, curing shrinkage, cell structure, voids and pin holes, base holes, cell collapse and curing streaks.

4. Results and Discussion

The results obtained in this work and the reasons behind them will be discussed in this chapter. The outcome from the different characterization techniques will be analyzed.

4.1 TGA and DSC

4.1.1 PU Microcapsules

Figure 4.1 shows a typical TGA/DSC profile for the PU shell microcapsules. The corresponding phenomena are ascribed to each slope on the TGA curve and also to the main (endo or exothermic) transitions in the DSC curve. At lower temperatures than 100ºC, the MCs samples loose, by evaporation, the solvent where they are immersed (toluene, with a boiling point of 111ºC), water evaporation occurs at 100ºC, followed by DEG evaporation at temperatures around 200ºC. Two exotherms, a weaker one and a stronger one are observed in the DSC profiles, where the weak exotherm (300-350ºC) is due to the cleavage of meta substituted alkyl side chain of the phenyl ring (decrosslinking or post curing process), while the stronger exotherm, at 500-550ºC is due to the decomposition and desintegration of the PU resin moiety into simpler molecules [23].
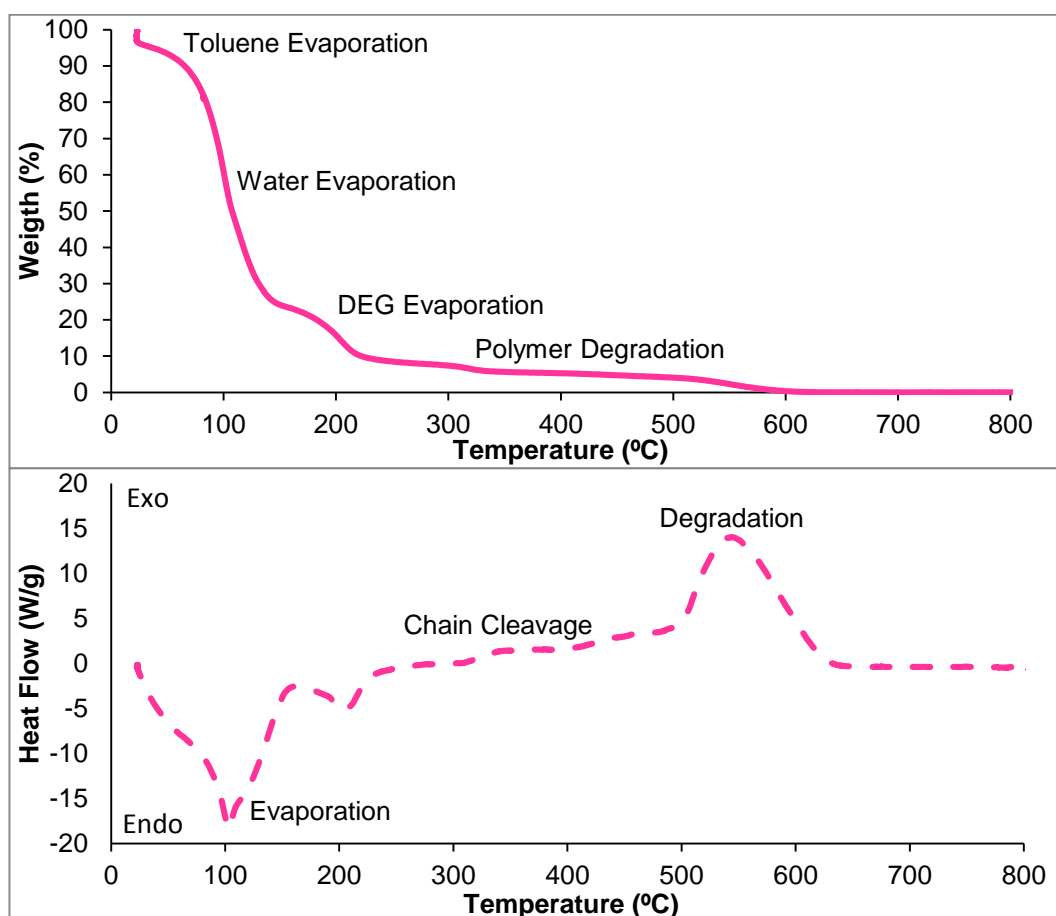

Figure 4.1: TGA/DSC of Si-PU MCs.

Figure 4.2 shows the TGA/DSC profiles for microcapsules with PU shell reinforced with TEOS not dried (Si-PU MCs) and dried (Si-PU MCs dried) at 50ºC for 24 h. These can be compared with PU shell without TEOS (PU MCs), not dried. The thermograms for DEG and TEOS are incorporated to serve as a reference.

Crossing information between both profiles, TGA and DSC, we can see that until 270 ºC, all the phenomena are absorbing heat, like evaporation or sublimation.

For the PU MCs with TEOS, the first weight loss, starting at 54ºC, is regarding the solvent evaporation, where they are immersed, or moisture at their surface. The second slope starting around 177ºC corresponds to DEG evaporation, in line with the TGA profile for isolated compound DEG. Then, the remaining sample suffers thermal degradation of the polymeric shell.

Dried microcapsules (Figure 4.2, yellow curve) as expected, exhibit a weight loss regarding the core not as evident as for Si-PU MCs (pink curve). Analyzing the TGA profile, it can be concluded that core plus the solvent around them is about 85wt% of the whole microcapsule. The dried capsules, on the other hand, exhibit a core content of ca. 50wt%. This shows that the encapsulation was quite effective. A higher encapsulation degree leads to the need of less capsules to fully cure a PU foam. As much core the capsules are retaining, the faster they will cure the foams.

Regarding the MCs without TEOS, they are found to exhibit ca. 79wt% of aqueous DEG encapsulated plus the shell residues, but the major difference observed when comparing it with the same MCs sample but with TEOS (Si-PU MCs), lays on the DSC results where we can see that the polymer degradation occurs at higher temperatures (551ºC) when silane is incorporated within the shell than when it is not (500ºC). So, this silica/PU hybrid system exhibits a 50ºC increase in the onset degradation temperature, meaning that it is indeed more thermally stable when compared to the unmodified PU shell MCs. This fact can be explained by the extra thermal stability that the silica network adds to the shell structure, resulting from the limited mobility of the PU chains in the presence of the silica network.
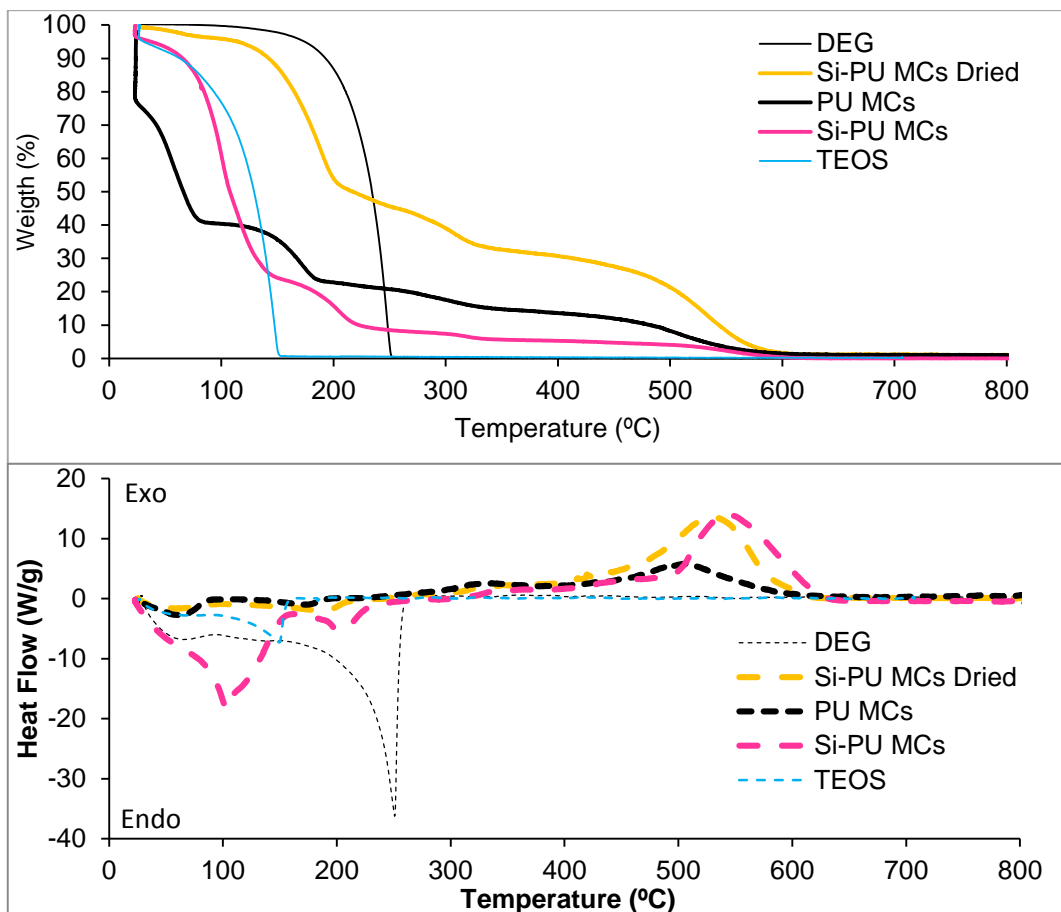
Figure 4.2: TGA/DSC profiles of PU sample and isolated compound DEG.

4.1.2 SG Microcapsules

Figure 4.3 shows the TGA/DSC profiles of different compounds used in the SG production. TEOS starts losing its mass at 80ºC, and quickly 100% of the sample is gone when the temperature reaches 155ºC. Water has most weigh loss around 100ºC as expected and glycerol at 240ºC. MTES mass loss is at 116ºC and that of GPTMS is at 200ºC, and at higher temperatures it suffers thermal degradation. The curve belonging to both glycerol and water, clearly show two slopes, one for water at 110ºC and another one for glycerol at 230ºC

MTES TGA profile shows a big slope at 30ºC and a weight loss of 10%. This may be caused by the presence of volatiles, such as methyl alcohol, because this silane is not pure, as stated in its technical datasheet.

Water and TEOS have identical evaporation temperatures, so they are covering each other at the TGA profile, however the DSC profile shows that the heat flow (endothermic peak) intensity is much higher for water.
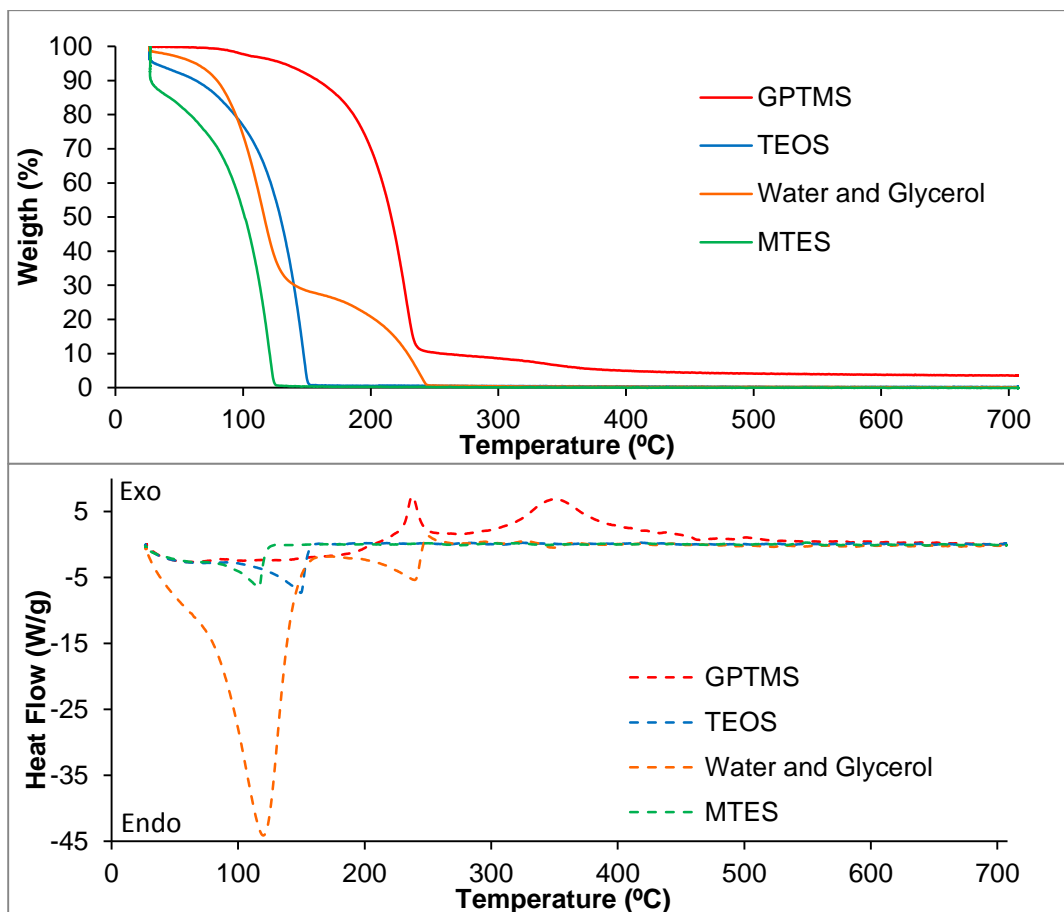
Figure 4.3: TGA/DSC profiles of isolated compounds, for SG MCs.

The following Figure 4.4 shows the TGA/DSC profiles for the different SG-derived MCs, encapsulating aqueous glycerol. This set of capsules consists of a systematic study where the amount of methyl functional silane (MTES) is increasing (none, 4g and 10g), in order to synthesize MCs shells with an increasing hydrophobic character. The presence of epoxy functional silane (GPTMS) was also studied (10MG-SG MCs). It is observed in the TGA profile of GPTMS that it suffers thermal degradation at higher temperatures, compared to TEOS and MTES, and presents a higher char yield.

The major difference when comparing the sol-gel derived MCs with the PU MCs is the char yield. These sol-gel samples (based on silica) do not lose their mass completely, as the temperature increases and reaches 900ºC. For instance, at 700ºC, still more than 40% of the silica based capsules remained. This is due to the inorganic SiO_2 network that was formed by polycondensation of the Si-OH groups [24].

Analyzing the DSC results, all the samples have a very similar, but low intensity, endothermic peak at ca. 100-150ºC, except the sample 10MG-SG. All of them exhibit clearly less than 5wt% of water in their core content, except the one without MTES (0M-SG MCs), and the one with more glycerol entrapped is the 10M-SG, where aqueous glycerol accounts for ca. 35wt%. SG MCs are poly-nucleated since their core is dispersed into multiple pores on the spherical shell.

Besides this, the DSC curves exhibit very strong exothermic peaks. The different peaks for all the samples above 270ºC are due to different networks created by different silanes and amounts of them.

The weight loss observed below 400°C results from the removal of unreacted -OEt groups and condensation of residual Si-OH groups in the gel. Subsequent loss above 400°C derives from combustion of the bound methyl groups or/and epoxy groups depending on the silane combination used. (Figure 2.7) [24]. It should be noted that the presence of epoxy groups (derived from GPTMS alkoxide) delays the thermal degradation, as shown in the DSC profile (green line) and might be the reason for such a higher char yield observed for the MCs (10MG-SG MCs), in the TGA profile. Also, for these samples, the release of glycerol is suggested to occur at higher temperatures (is delayed), which might be due to the higher thermal resistance of the shell, and/or to a lower porosity, but such must be confirmed by e.g. N_2 adsorption/desorption measurement.
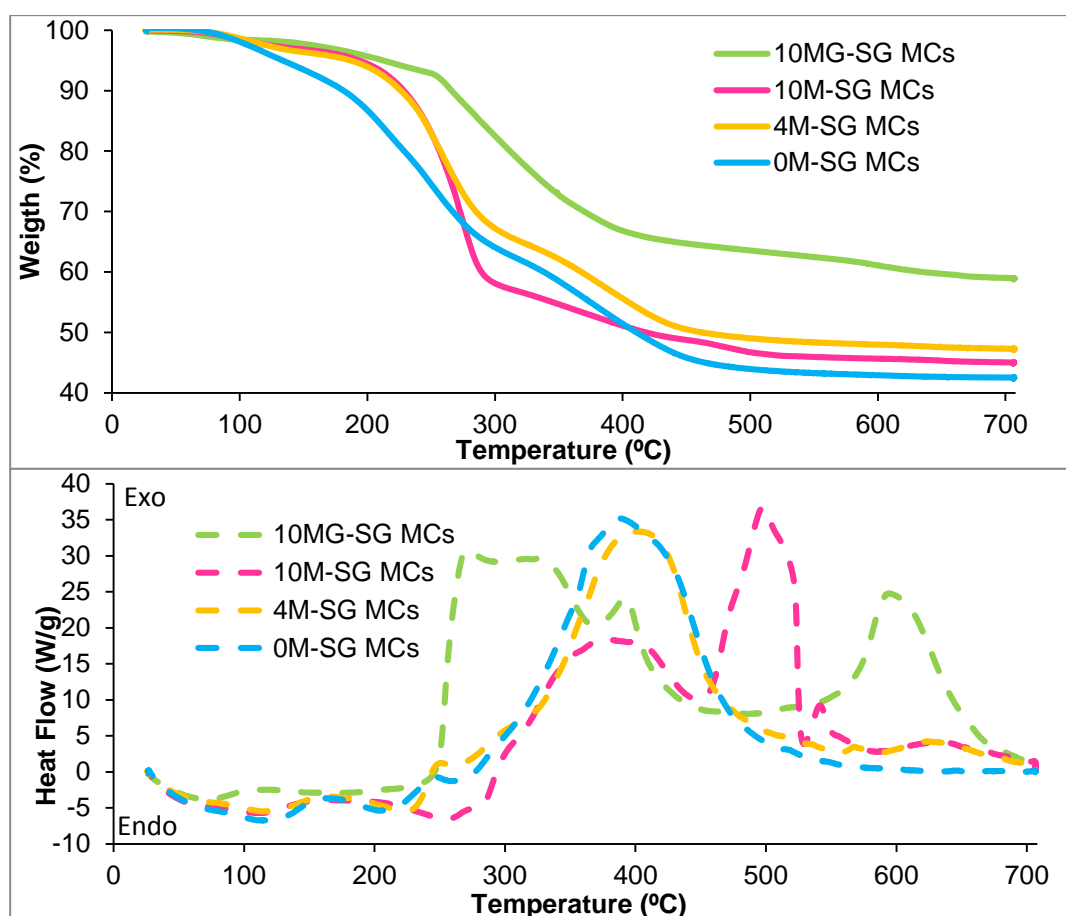
Figure 4.4: Graph of TGA and DSC of SG MCs made with different amounts of silane.

Figure 4.5 resumes the phenomena occurring at different temperatures SG MCs (made just with TEOS)
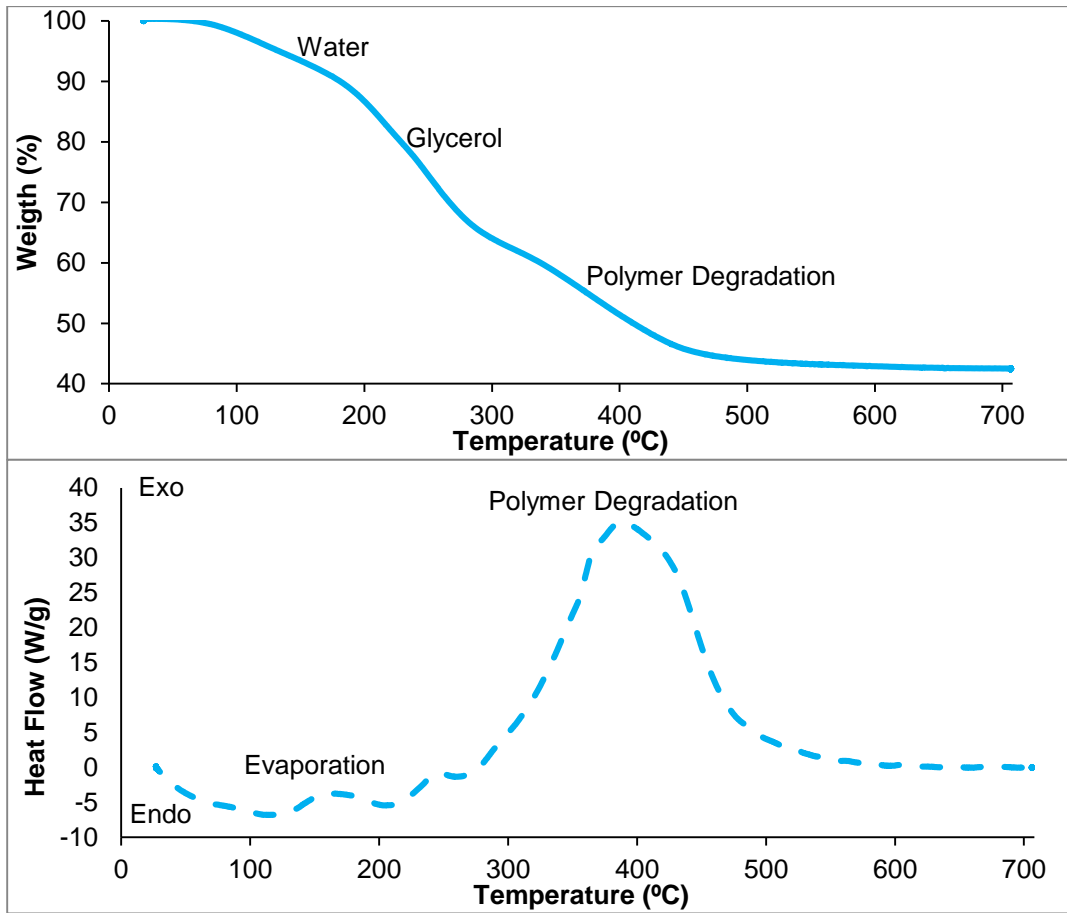
Figure 4.5: Graph of TGA and DSC for SG MCs, made with only TEOS.

4.2 FTIR Spectroscopy

All the relevant products/reagents used in the MCs preparation have been analyzed by FTIR, as well as the samples. The purpose is to assist in the spectra analysis of the MCs.

As an example, the spectrum of the surfactant DC193 is shown in Figure 4.6, and the corresponding peak analysis is in Table 4.1.
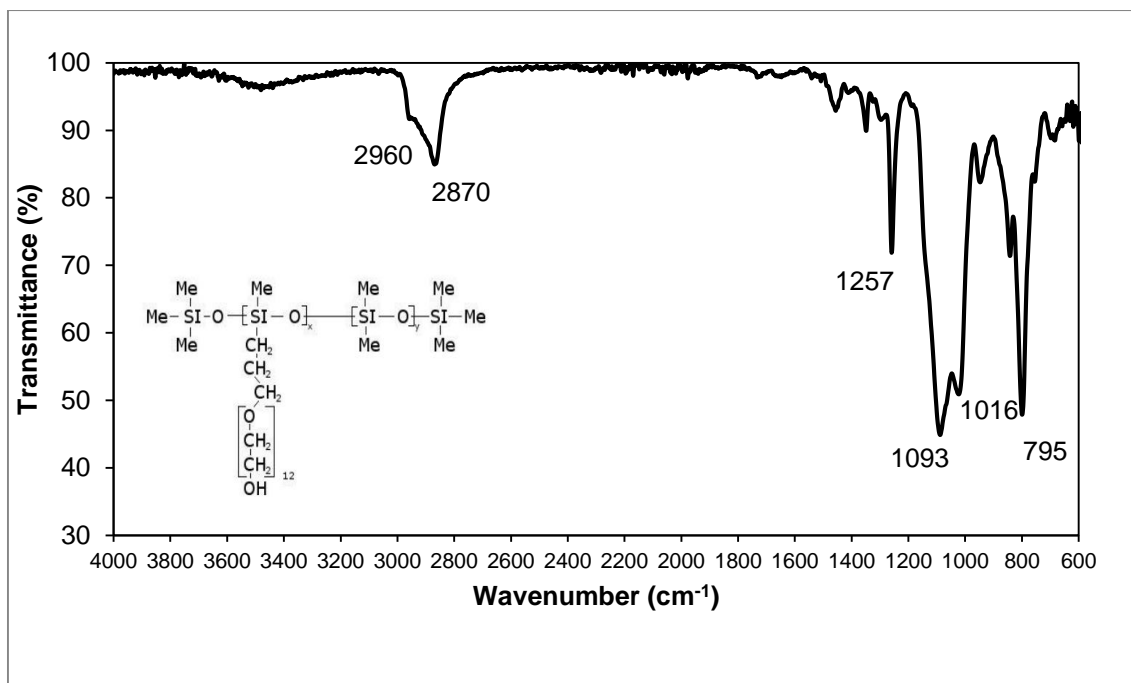
Figure 4.6: FTIR Spectrum of DC193.

Table 4.1: FTIR Spectrum analysis of DC193.

Peaks	Bond
2960	C-H Stretch
2870	C-H Stretch
1257	C-H Bending
1093	Si-O-Si
1016	C-O Stretch
795	Si-CH$_3$

The spectra and corresponding assignment of the peaks for the isolated compounds are in Appendix A.

4.2.1 PU Microcapsules

Figure 4.7 shows the spectra for PU microcapsules, prepared with DC193 surfactant and TEOS for silane, and dried at 50ºC before the FTIR analyses (Si-PU MCs dried). The spectra for the isolated compounds are also present so the identification of each band can be associated with them.
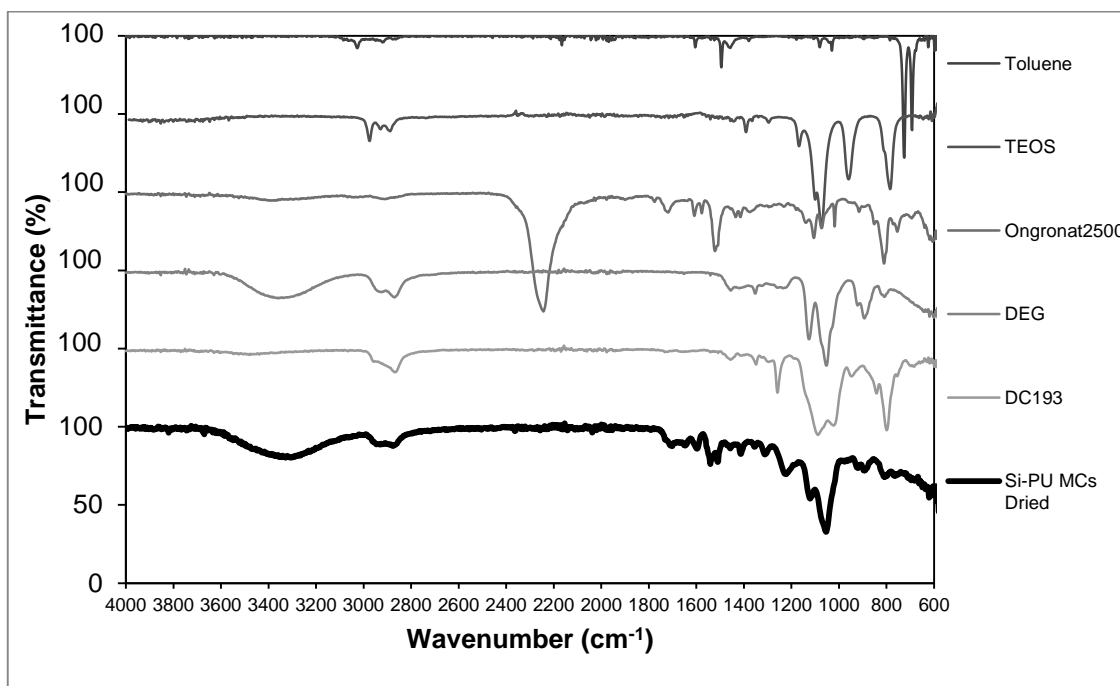
Figure 4.7: FTIR Spectra for Si-PU MCs dried and isolated compounds.

It is very clear that the Si-PU MC dried spectrum is similar to that of DEG, namely the large band at 3000-3600 cm^{-1} (OH stretching) and its main peak at ca. 1055 cm^{-1} (C-O stretching), so we can assure that it is well encapsulated, being the main constituent of the MCs and corroborating the results from TGA/DSC analyses which indicated the presence of 50% of aqueous DEG. There can be also hided bands that belong to other components but have similar peaks at the same wavenumbers, like DC193, which is expected to remain in a lower quantity than DEG.

The intense peak at 960 cm^{-1} (characteristic of Si-OEt, from TEOS) was found to strongly decrease at the MCs spectrum, because such bond is hydrolyzed with water and DEG, forming Si-OH bond, located at the same wavenumber. However, this one also tends to suffer polycondensation reactions giving a Si-O-Si network peaked at ca. 1070 cm^{-1} [25]. This group of peaks suggests the presence of silica domains in the PU shell, which resulted from the hydrolysis and polycondensation reactions of TEOS.

There is no trace of the intense peak of Ongronat2500 at 2237 cm^{-1} at the MCs spectrum because the bond N=C=O has reacted to form the polyurethane shell, as in Figure 2.1, so, there is evidence of full isocyanate conversion, into polyurethane and polyurea, at the shell of the MCs. Indeed we can confirm the presence of the amine (N-H stretch) band at 3200-3450 cm^{-1} and at 1510 cm^{-1} (N-H

bending), carbonyl groups at ca. 1700 cm^{-1} (C=O from urethane) and at 1660-1690 cm^{-1} (C=O from urea), carbamate groups (CN-H) at ca. 1600 cm^{-1}, C=C at ca. 1522 cm^{-1} (aromatic ring) and C-O-C at ca. 1214 cm^{-1}, which indicate the presence of urethane linkages in the PU, as well as some evidence of polyurea [26]. Moreover, one can also distinguish a small contribution to the spectrum from the Si-O-Si assymmetric stretching at ca. 1070 cm^{-1}, Si-O^{-} at ca. 960 cm^{-1} and the symmetric stretching of the bridging oxygen at ca. 800 cm^{-1} [27].

However, these peaks are of relatively low intensity, which shows that the core content (aqueous DEG) is present in larger amount than any of the materials composing the MCs shell.

This sample was dried before the IR characterization. So, toluene where it has been kept for preservation is not present at the spectrum, as expected.

Besides TEOS incorporation, other shell reinforcement strategies have been also tested. Their effect on the shell structure was studied by FTIR. The results are in Figure 4.8, where the spectra are shown for each reinforcement type evaluated:
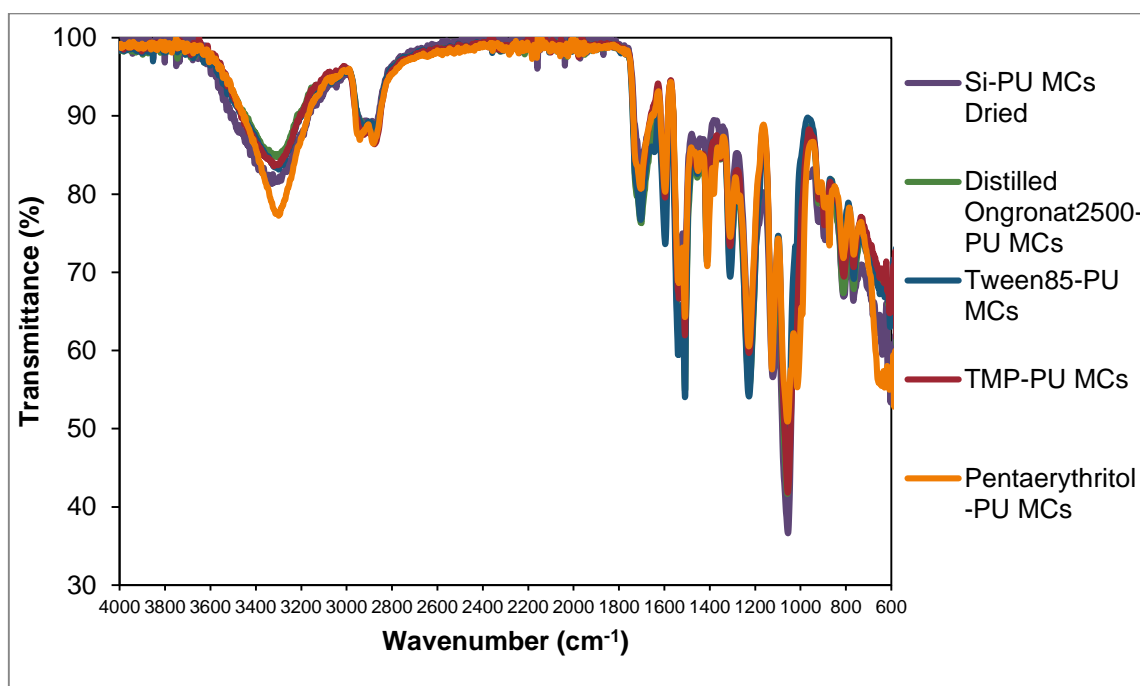
Figure 4.8: FTIR Spectra for PU MCs made with different shell reinforcements.

Although some bands of DEG may be hiding some other components such as Si-O-Si stretching at 1070 cm^{-1}, like said before, there is no relevant structural change that any of the other reinforcements are doing. The spectra are similar to the Si-PU MCs dried, with one exception: the ratio between the intensity of the peaks characteristic from polyurethane and polyurea (1700, 1600 and 1220 cm^{-1}) and the aromatic rings (1522 cm^{-1}), I_{PU}, and the intensity of the band peaked at ca. 1055 from DEG, I_{1055}, is larger than in the presence of silica. This is due to the fact that TEOS has a peak (at 1070 cm^{-1}) very close to the DEG peak and another reason can be the fact that the Si-PU MCs are able to encapsulate slightly more quantity of aqueous DEG than the PU MCs.

25

During can spraying, we came across the issue if MCs were getting stuck at the bottom of the can and if they had a homogenous distribution in the foam. The solution found was to coloring the MCs so they can be seen in the foam. To assess if the dye was affecting somehow the shell structure, a sample with no dye and other with an orange one were compared by FTIR (Figure 4.10). Other dyes were tried, Figure 4.9, but had no distinct results worthy of being included in this work. The yellow sample is the original color of PU based MCs.

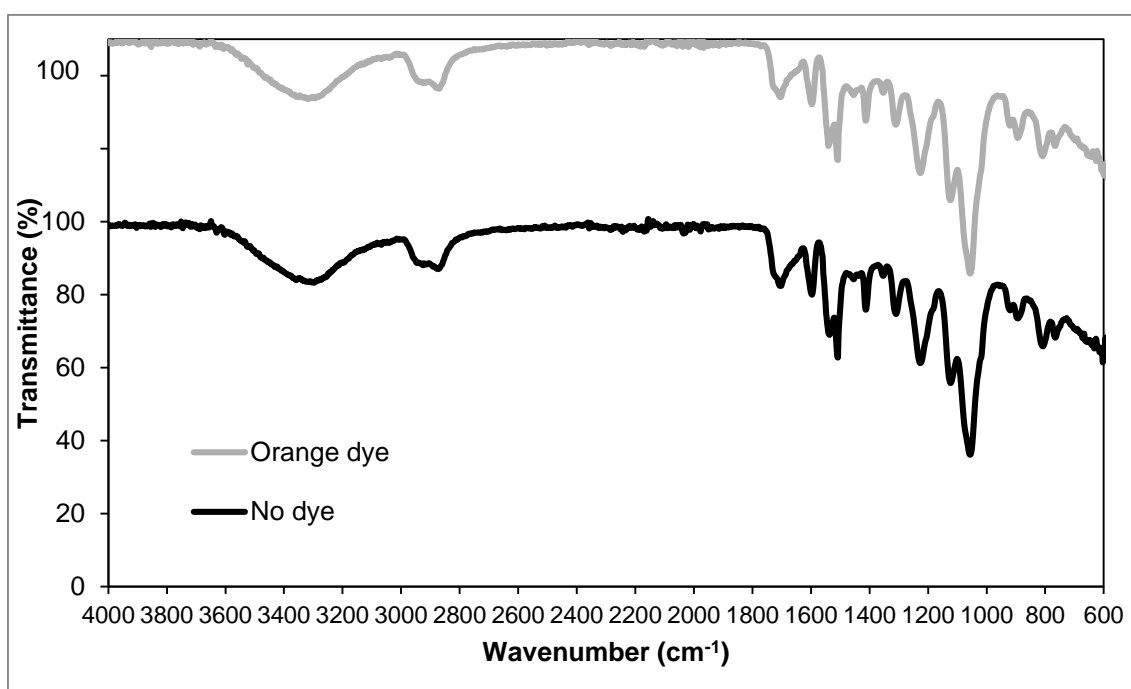**Figure 4.9: Dye options used during the work.**

Figure 4.10: FTIR Spectra for PU MCs with dye.

From the previous discussion, we can conclude that there is no structural changes associated to including a dye in the MCs.

4.2.2 PA Microcapsules

In Figure 4.11 is the same comparison that was made with the PU, this time with PA: microcapsules and the isolated compounds.
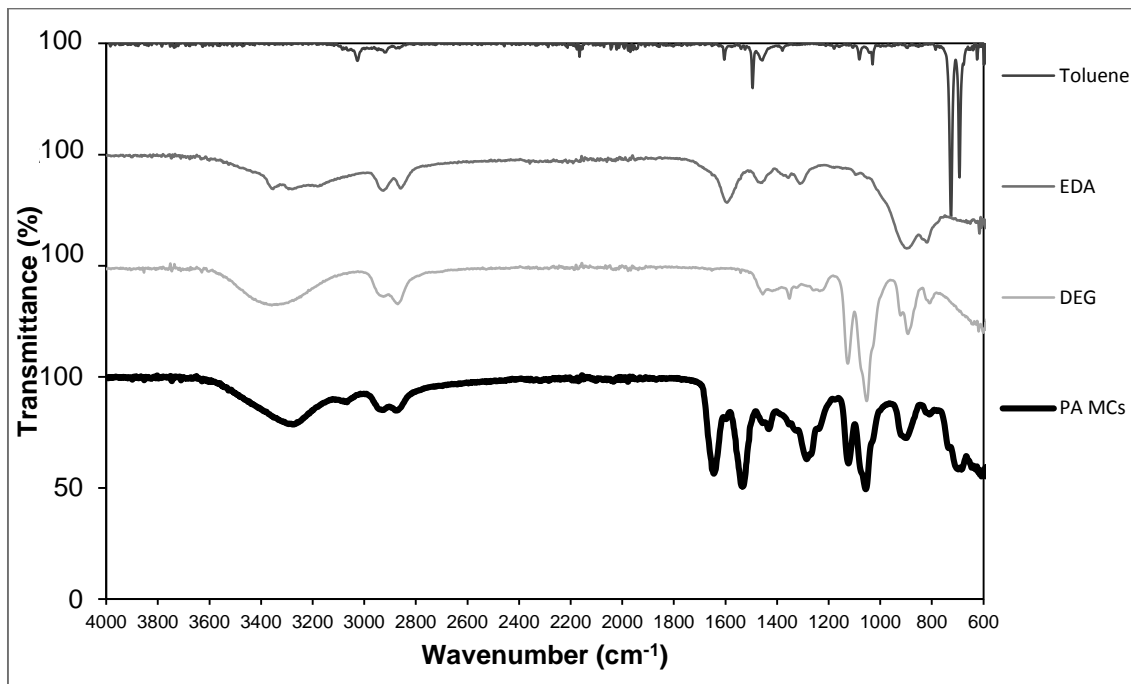
Figure 4.11: FTIR Spectrum for PA MCs made with EDA.

As for PU, DEG seems to be the main component for PA MCs, with characteristic peaks at ca. 1128, 1055 and 885 cm^{-1} (Table 7.4), as well as the typical bands characteristic of amide groups. Indeed, the PA MC spectrum exhibited the following main peaks, which confirm the significant presence of polyamide in the MCs shell: 3270 cm^{-1} assigned to N-H stretch, 1644 cm^{-1} for C=O stretch, N-H bending and C-N stretching, from the CNH group at 1535cm^{-1} [28] [29].

After the MCs preparation, they had to be washed and filtered, in order to wash away DEG and water from their surface, as well as other contaminants. Two available options were tested: vacuum filtration with toluene and vacuum filtration with toluene followed by ethanol. In Figure 4.12, it can be observed that there is no significant difference when PA MCs are washed through these two different methods. And ethanol is known to be a better dispersant solvent than toluene, which might promote less agglomerated MCs.

Figure 4.12: FTIR Spectra for different PA MCs washing method.

The biggest concern with the method that included a second wash with ethanol was that this solvent was degrading the shell and washing away 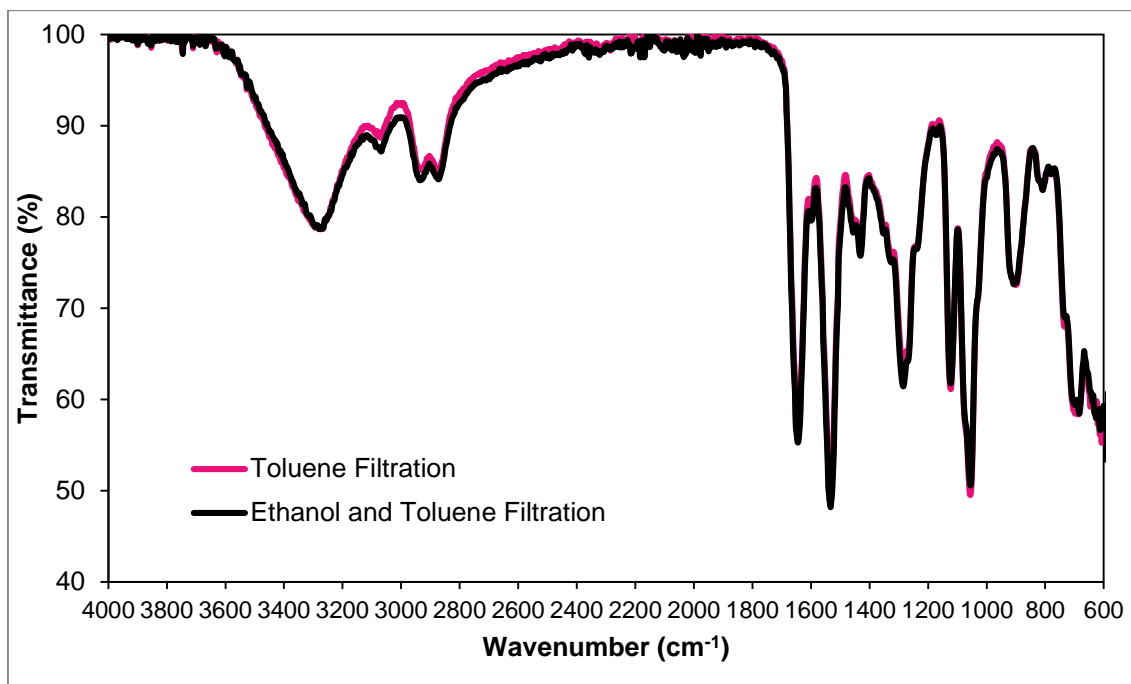the core from the inside of the capsules. This would compromise the functionality of them. But peaks are the same for samples washed both ways, so ethanol is not negatively affecting the microcapsules. It has only a positive effect, as we will see further in this work, is effectively washing the residues on the shell, which can improve the stability of the MCs inside an aerosol can.

4.2.3 SG Microcapsules

The FTIR spectroscopy technique allows to correlate the MCs composition with the MCs shell structure. It helps to understand how the network that is created by the silane(s) is affecting the molecular structure of the samples. It is an appropriate tool to follow the structure evolution (by observation of the spectra) with the increase of the amount of MTES (Figure 4.13), which was the strategy followed to increase the hydrophobic character of the MCs shell, useful to limit the occurrence of leaching. The number of hydrophobic Si-CH$_3$ groups, which come from the MTES alkoxide, is found to increase as the MTES content increases, as expected. This is revealed by the increase of the peaks intensity at 1270 and 785 cm^{-1}, which are ascribed to Si-CH$_3$ groups in polysiloxane network. [25] However, it is not possible to accurately discern on the encapsulated aqueous glycerol amount, between the samples with different contents of MTES (0, 4 and 10 g). It can be concluded that for such purpose TGA/DSC analyses are more recommended.
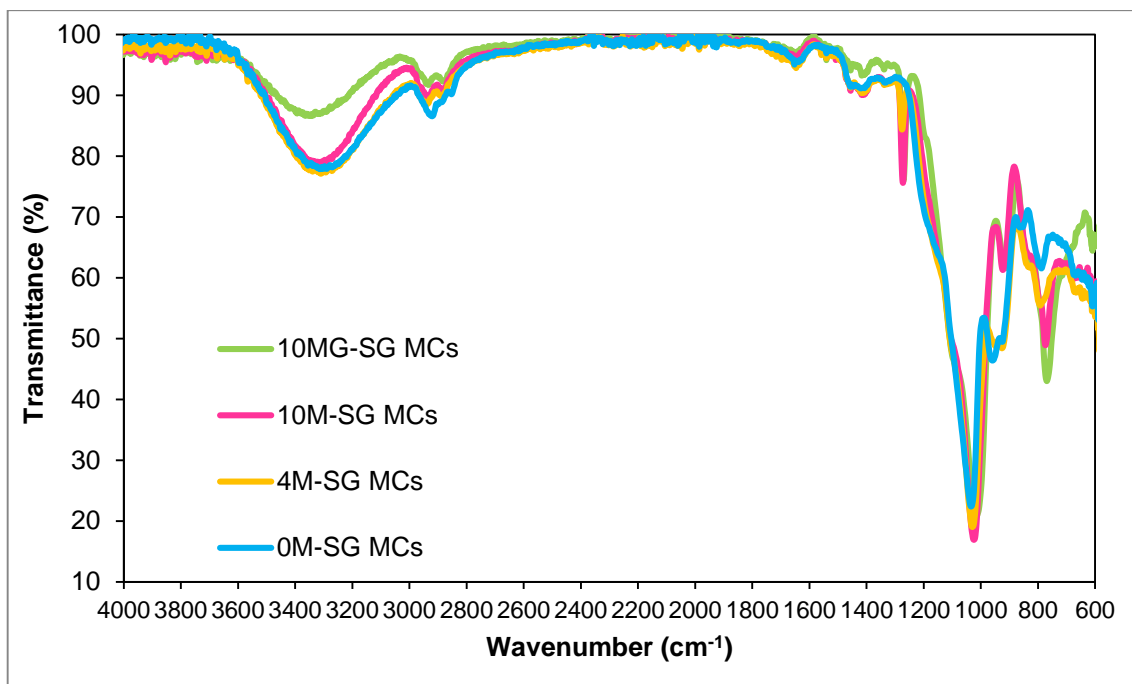
Figure 4.13: FTIR Spectra for SG MCs with different amounts of Silane.

The FTIR spectra corroborate the TGA/DSC results for the SG derived samples, since the sample 10MG-SG MCs is the one with less encapsulated aqueous glycerol, evidenced here by the lower intensity band at 3000-3500 cm^{-1}.

4.3 Viscosity Test

The viscosity test procedure developed at Greenseal allows to assess and compare the leaching tendency of the different MCs evaluated. It was considered that for a type of MCs to proceed to can bottling, the viscosity of the isocyanate blend (Ongronat2500) with MCs, should not go above 5000 cP (Figure 4.14). But higher values will be used for comparing the samples so that production parameters can be adjusted.

Higher viscosity values mean more leaching, since the core content (aqueous DEG or glycerol) by escaping through the shell will react with the isocyanate to give PU or polyurea, like in Figure 2.1 and explained in section 2.2, increasing viscosity.

The pure *Ongronat2500* (without MCs) viscosity behavior over the time is depicted in Figure 4.14. It should be noted that if Ongronat was stored in a hermetic container its viscosity would not suffer any apprecaible change.
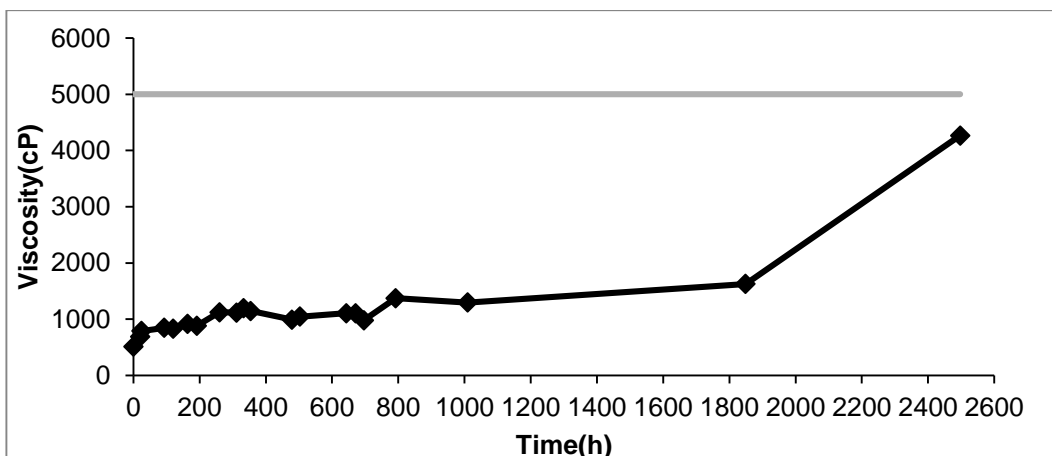
Figure 4.14: Graph of viscosity test of Ongronat2500 and acceptable higher limit.

Until 2,5 months old isocyanate (1800 hours), values are regular, increasing just a few points. After that period, viscosity increases. Aging effects and the contact with air seem to have some influence in the compound viscosity behavior. The contact with air is possible because the containers used to keep the MDI and the microcapsules are not perfectly sealed.

4.3.1 PU Microcapsules

For PU MCs as well for the other types of microcapsules made, the results from the viscosity test will be divided into types of studies. Each parameter adjusted will have a comparing graph with the different options that were considered for that parameter.

This type of leaching assessment was decisive in the optimization of the PU MCs production parameters. This was an interactive and iterative process, in the sense that the production parameters were going to be adjusted depending on the results from this evaluation technique.

- **Surfactant Type**

Two surfactants with a low and a high HLB value, *Span80* (Figure 4.15) and *DC193* (Figure 4.16) respectively, have been employed in the production protocols. It is important to know the structural formula of each compound so we can be able to understand the chemistry behind the results.
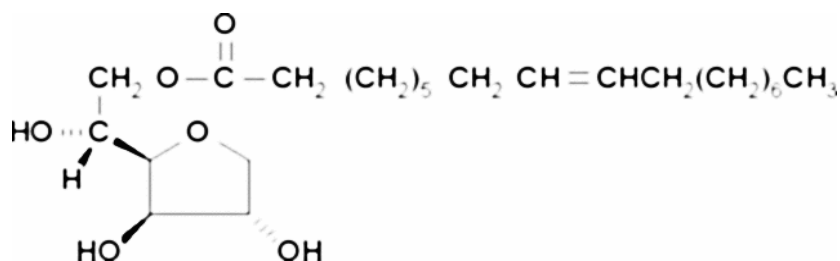

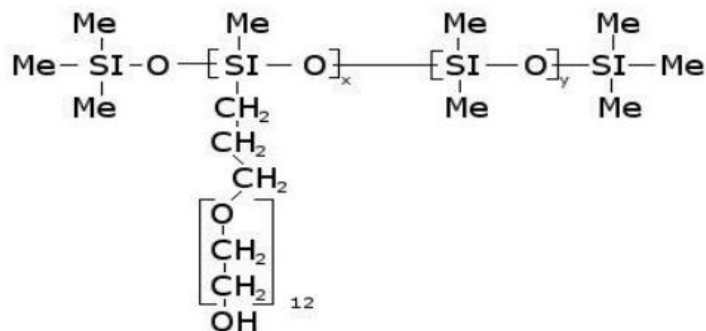**Figure 4.15: *Span80* structural formula. [30]**

Figure 4.16: *DC193* structural formula. [31]

Since Figure 4.17 shows lower values for *DC193*, we can say that it is the better surfactant to synthesize PU microcapsules.
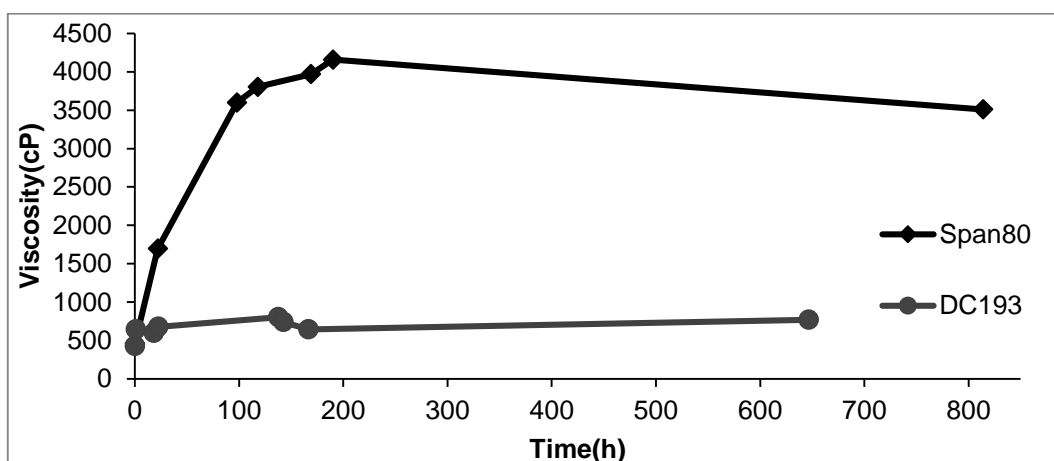
Figure 4.17: Graph of viscosity test to assess the best surfactant.

The viscosity test results for the MCs prepared with DC193 were better (lower viscosity increase over the time) than for MCs prepared with Span80. This makes sense, because in the present production protocol the surfactant is added to the disperse (aqueous) phase, and, since the HLB value of DC193 is 12 [32] this means it is more compatible with the aqueous phase than Span80 (HLB of 4,3, [33]) and is more efficient in stabilizing the microemulsion, resulting in better quality MCs.

Also, as showed in Figure 4.15 and Figure 4.16, DC193 has only one hydroxyl group on the molecule, comparing with Span80 which has two. Since isocyanate reacts with OH groups, and in case there are residues of surfactant in the shell and in the core, it is predictable an increase in viscosity if Span80 is used, for the same degree of leaching.

- **Silane type**

The purpose of adding a silane to the shell is to create a hybrid silica-PU material, which would reinforce the MCs shell.

The graph in Figure 4.18 shows that MCs made with TEOS result in almost unchangeable viscosity values over the time, followed by MCs prepared with GPTMS. Mixtures of TEOS and MTES led to the worst results in the viscosity test. Said so, leaching of DEG and water from TEOS derived MCs is less than for the other silanes.
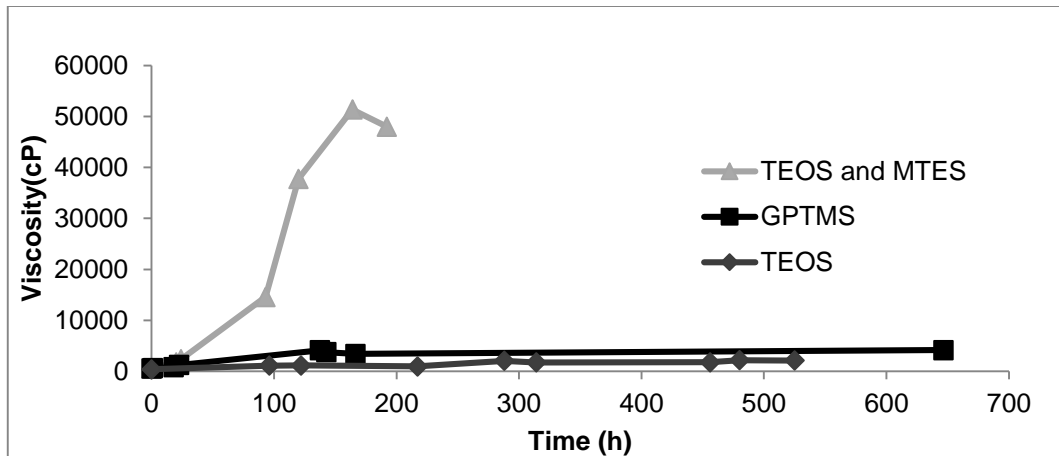
Figure 4.18: Graph of viscosity test to assess the best silane, for MCs made with surfactant DC193.

The reason TEOS is a better option is due to its symmetry, that form a very crystalline structure, with very few pores, which prevents the core to leaching out through the shell.

- **Presence of TEOS for shell reinforcement**

To assess if the presence of the silane TEOS has a positive effect preventing leaching, like it was said in the previous section, the following analysis was done, represented in the three studies/graphs below.

Figure 4.19: Graph of viscosity test to assess the effect of TEOS, with surfactant *DC193*.

Figure 4.20: Graph of viscosity test to assess the effect of TEOS, with surfactant *Span80*.
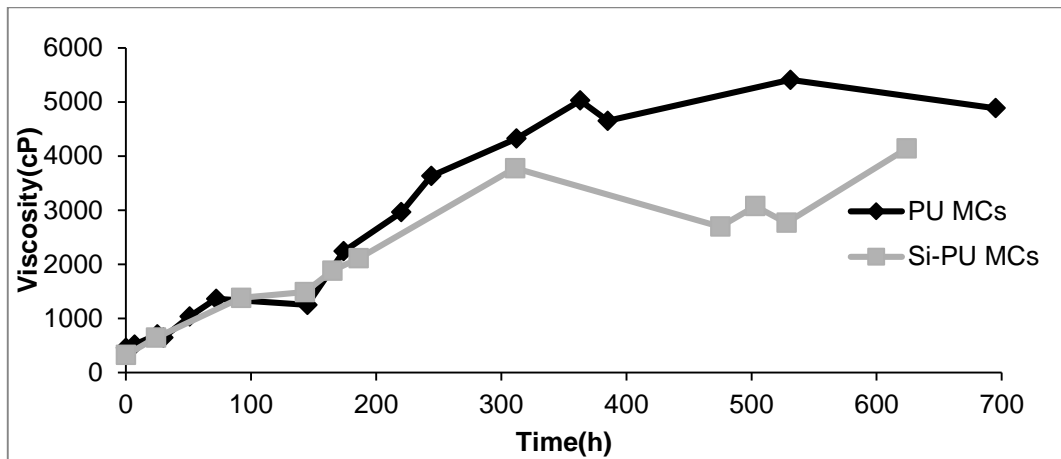
Figure 4.21: Graph of viscosity test to assess the effect of TEOS with another shell reinforcement agent, distilled *Ongronat2500*.

By analyzing the graphs, we can see that TEOS is a better option in all of three cases. Cross-linking and presence of silic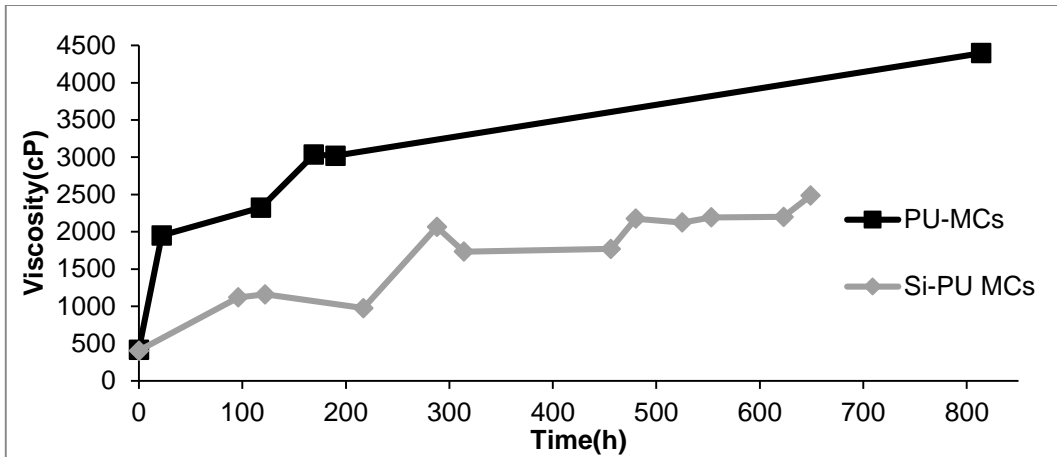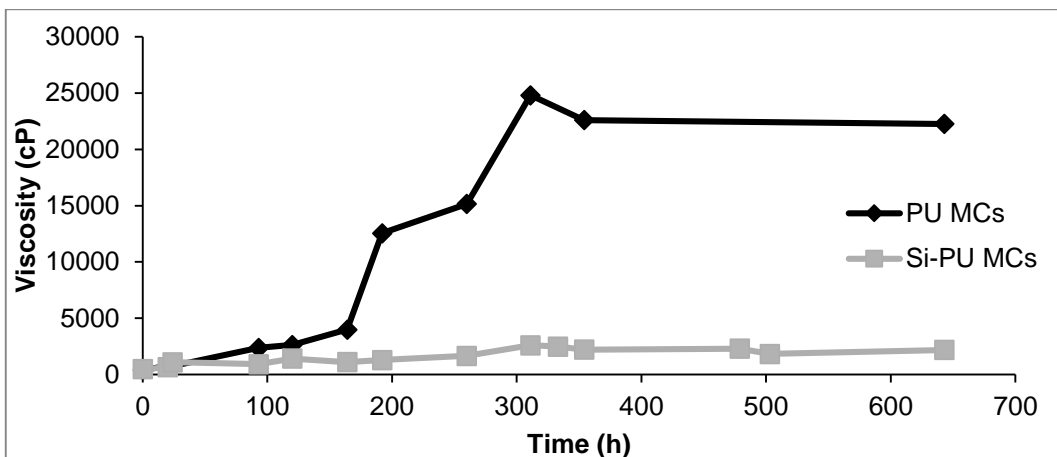on atoms give microcapsules more resilience to leaching. The presence of silica-rich domains in PU-based shells increases the mechanical, chemical and thermal resistance of the MCs shell.

- **Pre-hydrolyzed TEOS**

It should be noted that TEOS is added directly to the continuous (organic) phase, but when TEOS is previously hydrolyzed it is added to the dispersed phase. The pre-hydrolysis procedure results in the formation of silanol Si-OH species, like explained before in section 2.2.3. Since these species are more prone to condense and forming the shell, we thought that this would reinforce more the MCs shell.

The results did not turn out to be the way we expected, maybe because the addition of the pre-hydrolyzed solution negatively impacts the stability of the microemulsion formed and the quality of the obtained MCs, or the unreacted silanol species which remain in the shell material will contribute to the increase of viscosity (Figure 4.22) due to the reaction with the Ongronat2500 NCO groups.
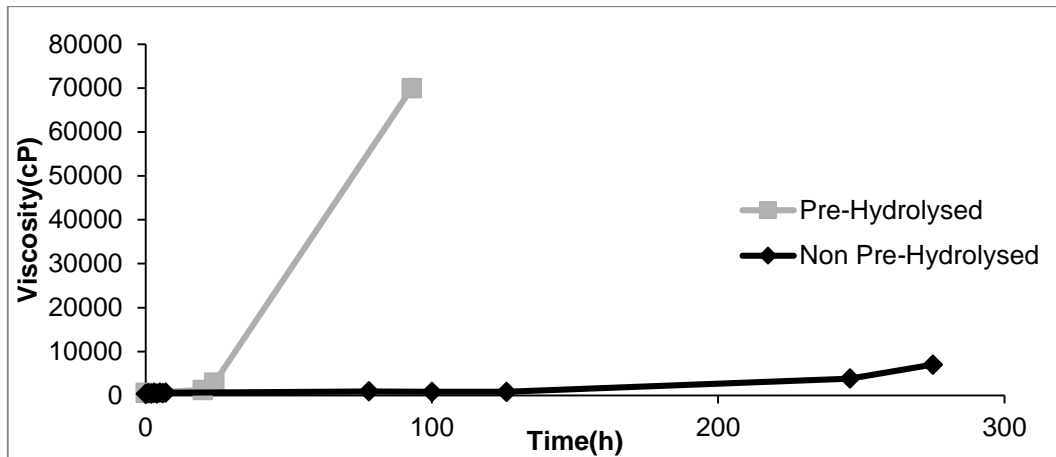
Figure 4.22: Graph of viscosity test to assess the presence of Hydrochloride, with surfactant DC193.

- **Higher functionality OH and NCO groups for shell reinforcement**

Different types of shell reinforcement were used in order to make the MC endure and, once again, prevent leaching. The only ones that have produced reliable results were TMP and distilled MDI (distilled Ongronat2500), as a source for OH and for NCO, respectively. They have higher functionality comparing with DEG and non-distilled Ongronat2500. The results are shown in Figure 4.23.
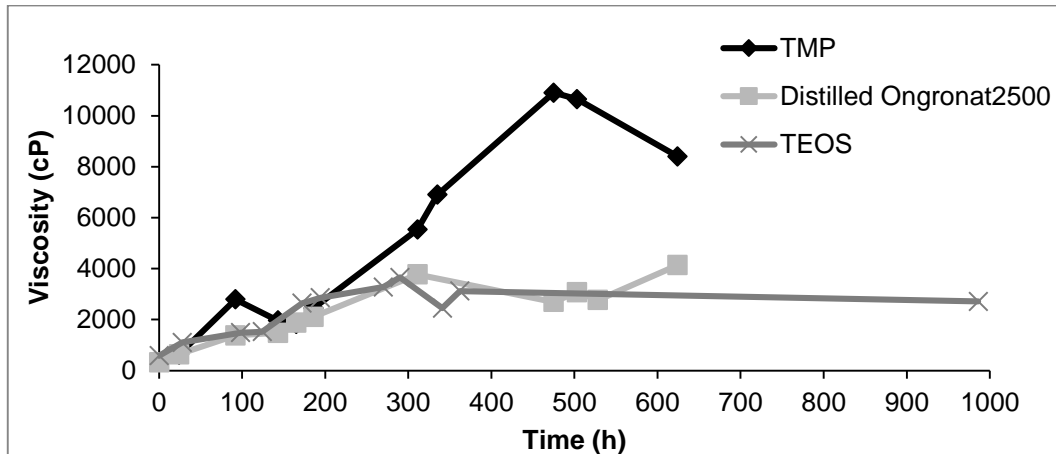
Figure 4.23: Graph of viscosity test to assess the effect of different approaches for shell reinforcement.

As we can see in the previous graph, TMP does not bring any advantage in terms of leaching behavior, on the contrary. On the other hand, the effect of a higher NCO functionality (distilled Ongronat2500) is very similar with the effect of adding TEOS.
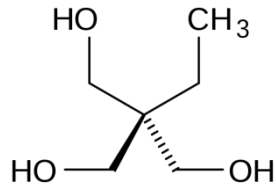
Figure 4.24: TMP structural formula.

- **Washing method**

Like for PA MCs (section 4.2.2), PU MCs were also washed and filtered with toluene or toluene and ethanol. The evidence that a second filtration with ethanol is a better method is on Figure 4.25 and Figure 4.26. However, it should be stressed that after filtration with ethanol the MCs must be stored in toluene, otherwise there might occur shell degradation, and even core leaching.
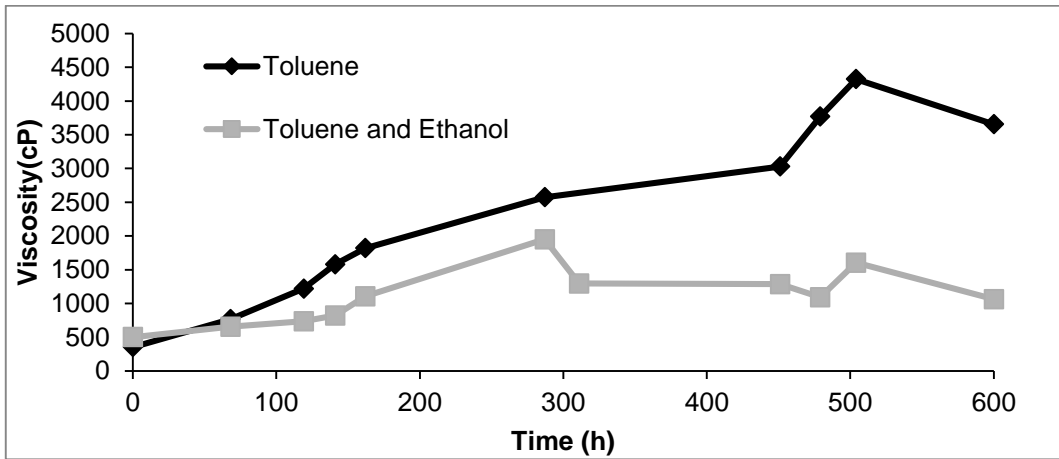
Figure 4.25: Graph of viscosity test to assess the best washing method, for MC made with distilled *Ongronat2500*.
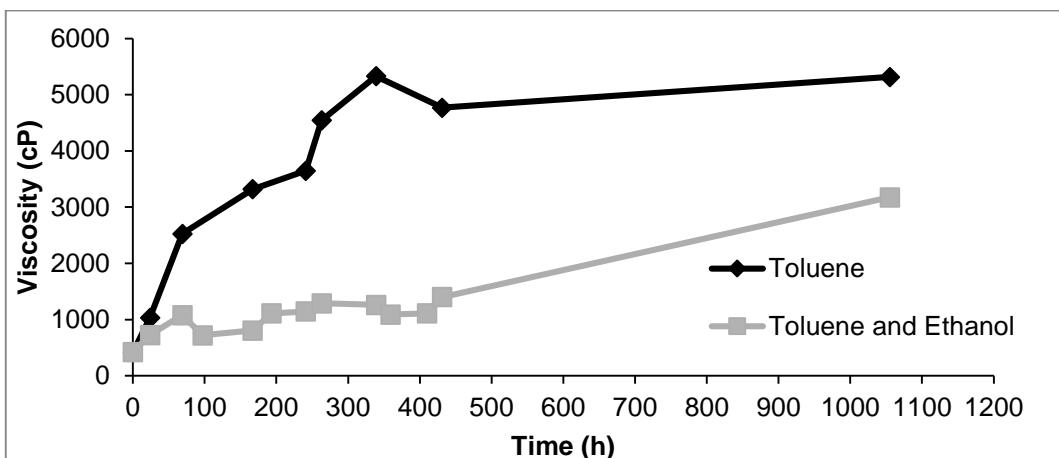
Figure 4.26: Graph of viscosity test to assess the best washing method, for MC made with silane TEOS and dye.

The graphs clearly show that ethanol has an important role diminishing viscosity, probably because it avoids the MCs agglomeration and is effective in the washing of the residues at the MCs surface.

4.3.2 PA Microcapsules

- **Amine Type**

In order to choose the best amine to make this kind of MCs, two options have been tested: EDA (Figure 4.27) and DETA (Figure 4.28).
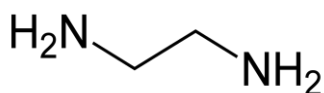
Figure 4.27: EDA structural formula.
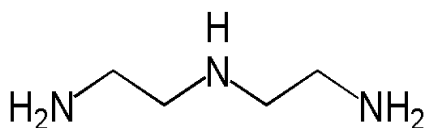
Figure 4.28: DETA structural formula.

In Figure 4.29, Figure 4.30 and Figure 4.31 viscosity test reveals DETA to be more efficient in leaching prevention.
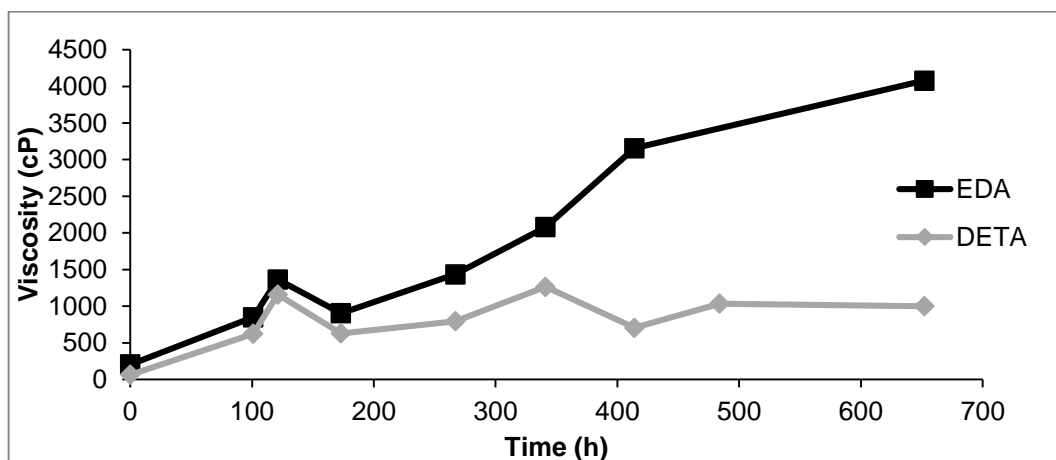
Figure 4.29: Graph of viscosity test to assess the best amine, for MCs washed with ethanol and toluene.
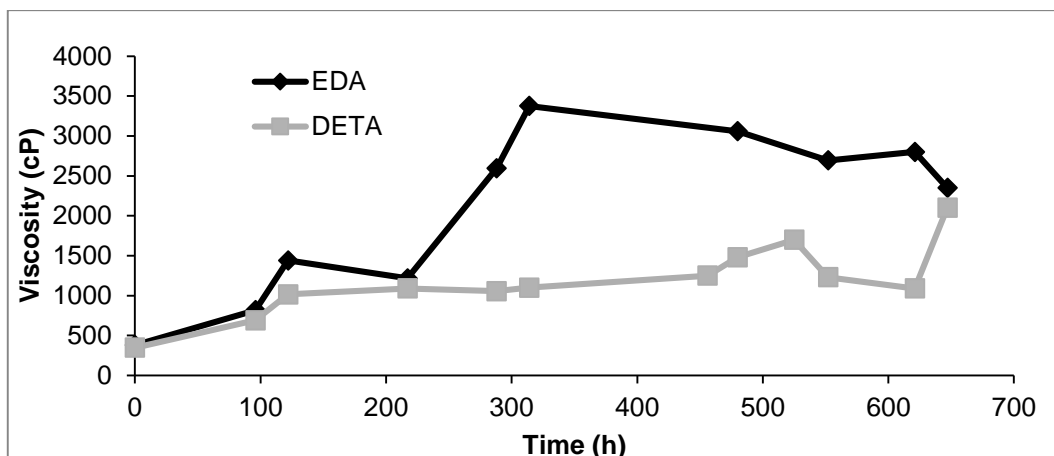
Figure 4.30: Graph of viscosity test to assess the best amine, with 1600 rpm.
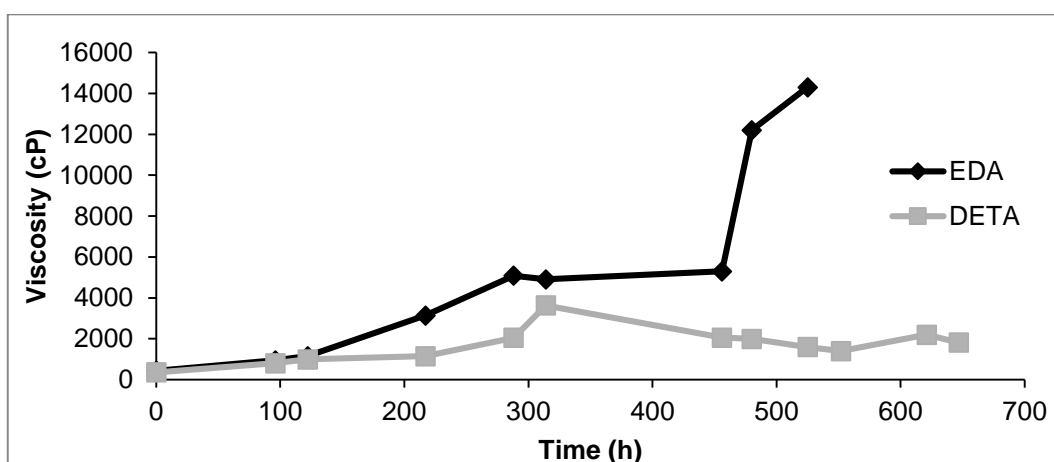
Figure 4.31: Graph of viscosity test to assess the best amine, with 5000 rpm.

The results concerning the two types of amines were not very regular. For some cases, MCs with EDA had a better viscosity behavior. But, in the majority of the cases, DETA was the amine source which led to better leaching behavior, possibly because it contains three amine groups (while EDA contains two) and it will, therefore, result in a more crosslinked shell structure.

- **Stirring Speed**

For each amine, microcapsules were prepared using different rotation speeds: 900, 1600 and 5000 rpm. The results are shown in the figures below.
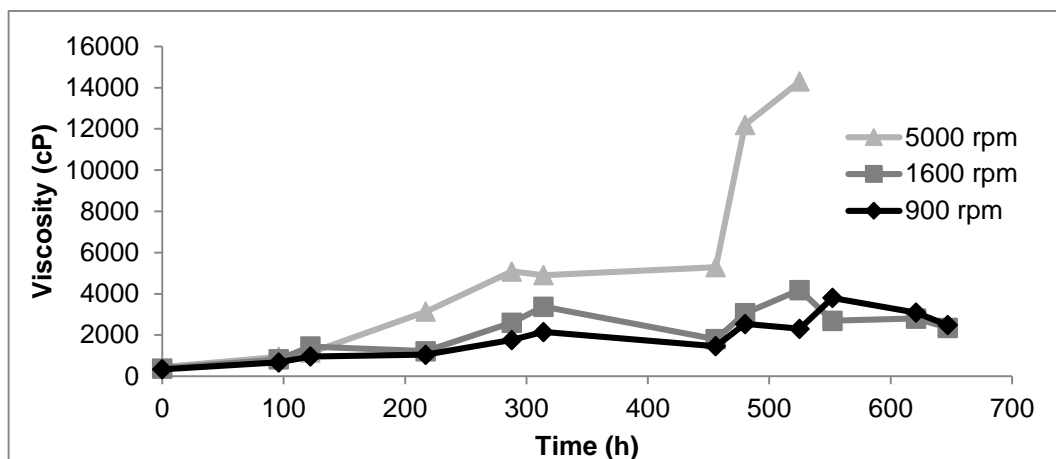
Figure 4.32: Graph of viscosity test to assess the best stirring rotation, for MCs made with EDA.
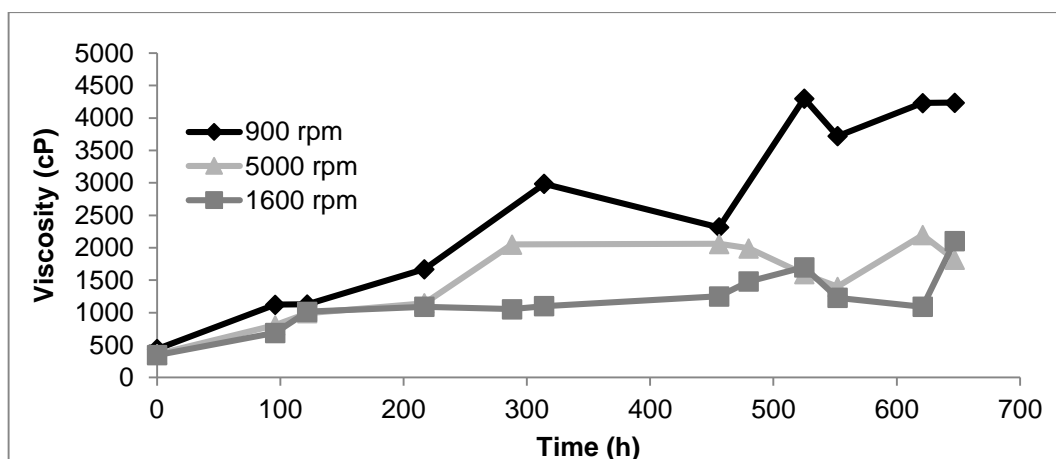
Figure 4.33: Graph of viscosity test to assess the best stirring rotation, for MCs made with DETA.

The results are not similar for the two amines. However, for 1600 rpm, viscosity values are low for both cases, and since we assumed that DETA is the best amine, 1600 rpm is the best stirring speed that fits different scenarios.

- **Surfactant quantity**

Surfactant *DC193* was the selected one used in the production of PA MCs. Its amount had to be adjusted in order to optimize the MCs quality.

The next figure shows the viscosity test for MCs made with 8,5, 6, 4, 2 and 0% of surfactant added to the dispersed phase.
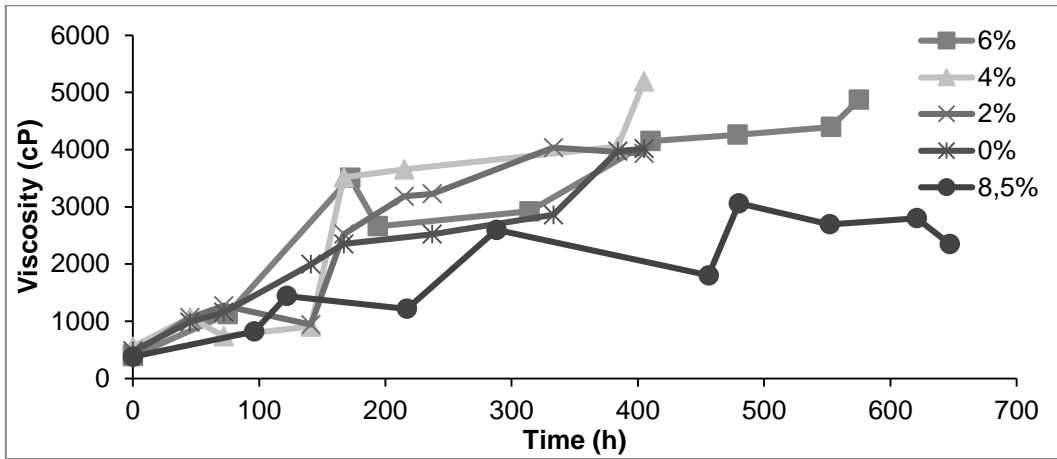
Figure 4.34: Graph of viscosity test to assess the best amount of surfactant, for MCs made with EDA.

For all curves, viscosity is below the limits (5000 cP), and 8,5% leads to the lowest values. We have also tested 11% of surfactant, but its results in this test were far beyond the accepted limits.

8,5% of surfactant DC193 was also the optimized concentration for DETA derived PA MCs, since it was the one that resulted in a lower viscosity increase over the time.
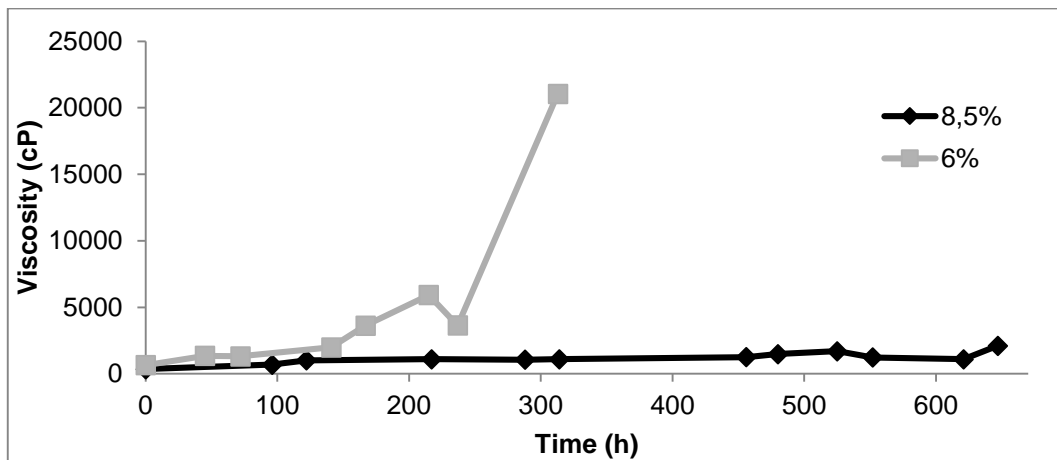
Figure 4.35: Graph of viscosity to assess the best amount of surfactant, for MCs made with DETA.

- **Presence of silane for shell reinforcement**

As for PU MCs, it was important to evaluate the effect of TEOS in the shell. The production process has been repeated several times to confirm the results, and it was concluded that, contrary to the case of PU MCs, TEOS does not improve the leaching behavior (Figure 4.36). After 400 h of testing, the viscosity values sharply increased for the MCs synthesized with TEOS.
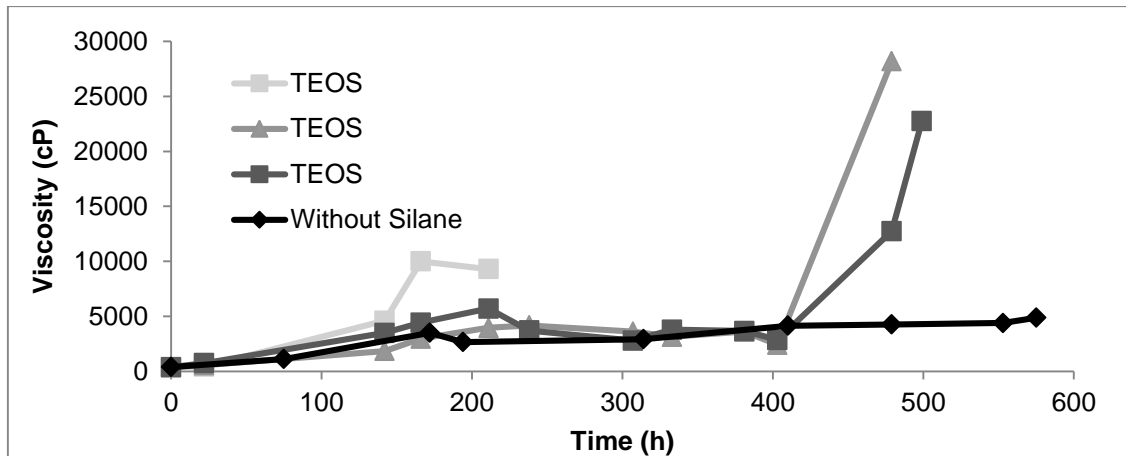
Figure 4.36: Graph of viscosity test to assess the effects of the silane TEOS, for PA MCs.

- **Washing method**

As expected, ethanol and toluene type of filtration is the best one, since ethanol promotes the washing away of DEG and water residues on the shell, preventing reactions with the NCO groups of the Ongronat2500 and, therefore polyurethane and polyurea formation (Figure 4.37).
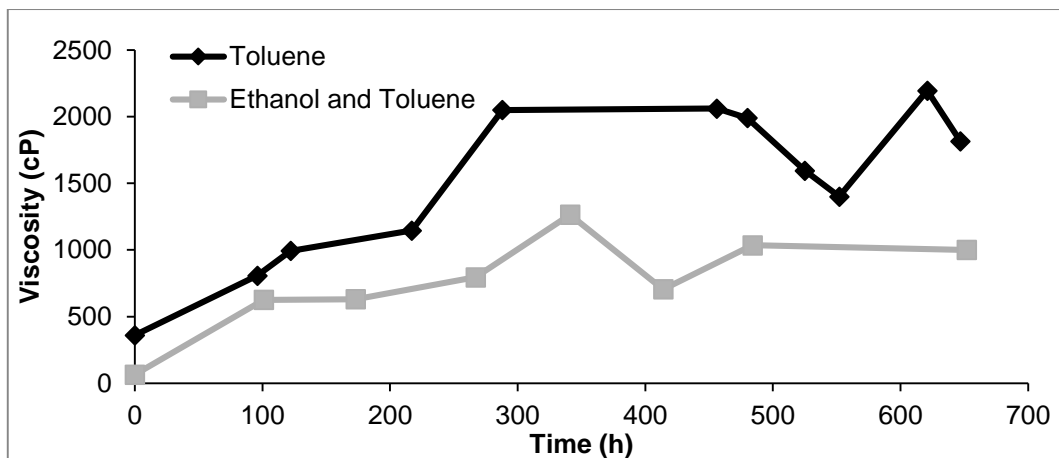
Figure 4.37: Graph of viscosity test to assess the best washing type, for MCs made with DETA.

Results obtained with FTIR, in section 4.2.2, showed no difference in molecular structure between samples washed with both products. So, it can be assumed that ethanol is not affecting the shell structure and is effective cleaning the surface.

4.3.3 SG Microcapsules

Microcapsules made by sol-gel process are able to be dried without being damaged, so they do not need to be stored in toluene or another solvent and, consequently, the viscosity values are not affected by the solvent.

- **OH source**

In order to understand what is the best OH source to be used in this synthesis, which will compose the MCs core, DEG and glycerol have been employed, and the results from viscosity test are displayed in Figure 4.38.
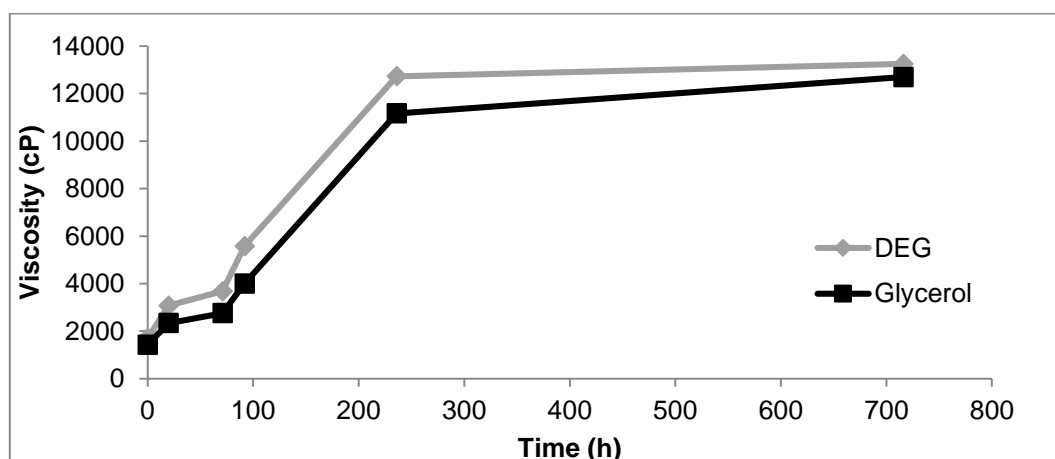
Figure 4.38: Graph of viscosity test to assess the best alcohol.

There is not much difference between the two. In fact the difference is within the typical error of these measurements (of 15%). However, glycerol was the one selected to proceed the study, because, since it has three hydroxyl groups (and DEG has only two), its hydrophilic character will promote a more stable and well defined emulsion, improving the encapsulation.

- **Silane Amount**

The silanes solutions consisted of TEOS, without MTES (0M-SG MCs), TEOS and 10 g of MTES (10M-SG MCs) and TEOS, 10 g of MTES and GPTMS (10MG-SG MCs). The effect of the silanes amount is studied in this section.

Figure 4.39 shows that the amount of MTES and silane combination which enabled lower viscosity values was 10MG-SG. The most hydrophilic MCs shell (0 g MTES) exhibited the worst performance in the viscosity test.
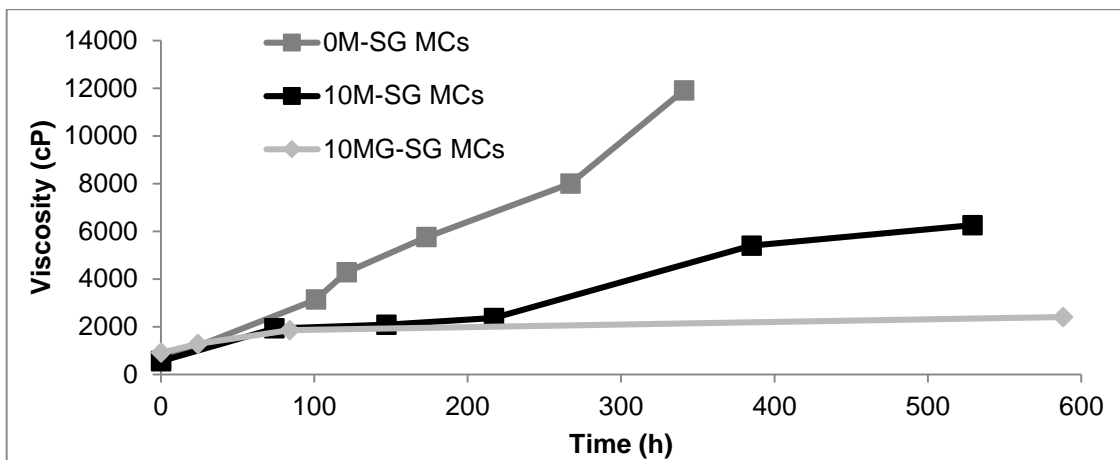
Figure 4.39: Graph of viscosity test to assess the best silane and its amount, for SG MCs.

The glycidoxy group in GPTMS (Figure 3.3) promotes the presence of hydrophilic moieties in the silane, and later on, in the pre-hydrolysis solution. This might have helped the encapsulation because these branches will gather around water and DEG molecules. Also, the resulting MCs exhibit a combination of hydrophobic character (due to the CH_3 groups from MTES) and of chemical resistance, due to the epoxy groups (from GPTMS), which might be the reason for such better result on the viscosity tests. On the other hand, their core amount is not as large as for 10M-SG MCs, which might have also led to a better result in the viscosity test. The study of SG derived MCs will be further developed.

- **Washing method**

As for PU and PA, if the samples are washed twice, the viscosity values tend to be much lower (Figure 4.40). For SG MCs the washing method consisted in a vacuum filtration with hexane. They were then left in the oven for about two days, to completely dry. Opposite to PU and PA MCs, SGs don't need to be stored into a solvent.
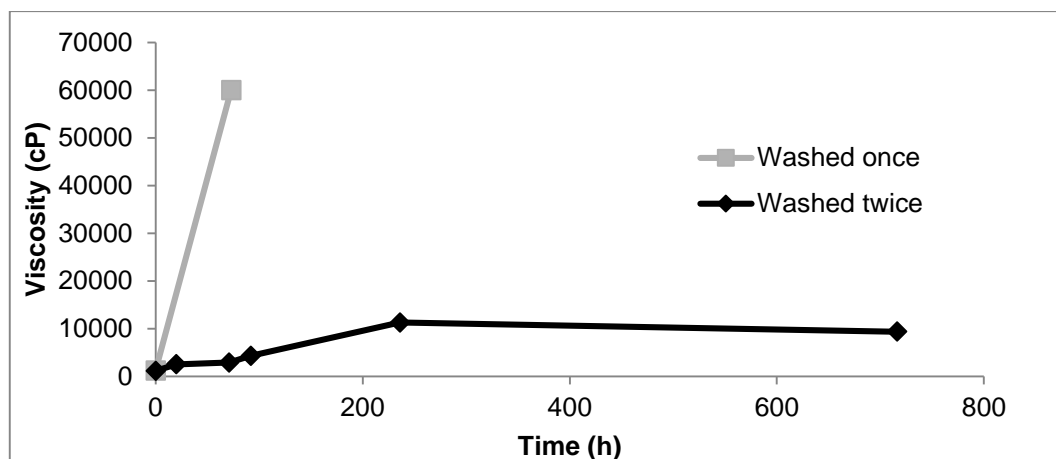
Figure 4.40: Graph of viscosity test to assess the best washing type, for SG MCs.

4.4 Output and Curing Time

To verify if the MCs are accomplishing their final purpose (accelerate the foam curing process), we compared the curing time value for foams with and without MCs. A PU OCF aerosol can (Reference) was prepared (without MCs), and in a similar way PU OCF aerosol cans containing 4% of MCs were also prepared, for comparison. The MCs tested consisted of PU shell MCs made with the surfactant Span80, another with silane TEOS and DC193 and another with pre-hydrolyzed TEOS.

The output was measured at 5ºC (as explained in section 3.2.4) and the curing speed was assessed by spraying the foam at 23ºC in a sealed plastic bag (23ºC / low moisture environment test).

The results obtained for PU MCs are summarized in Table 4.2.

Table 4.2: Foam Output and cure time, with PU MCs.

Type	Output (g/s)	Curing Time (days)	Shaking Rate
Reference	4,5	3	5
Span80	0,3	2	-4
TEOS and DC193	1,9	2	-2
Pre-Hydrolyzed	2,7	2	-4/-5

The reference represents the ideal parameters that a foam with microcapsules should have, except for the cure time. For all the types of MCs tested the time needed for the foam to totally cure was a day less of the reference.

However, there are some issues concerning the output. For the MCs tested, their output was much lower than that of the Reference, so we might conclude that MCs are increasing the foam viscosity, which makes the spraying process more difficult. Despite of the acceptable values on the viscosity tests of the Si-PU MCs and PU-MCs, there is an increase of the viscosity inside the can, and a decrease of the output, suggesting that there is leaching occurring. Some degradation might have occurred on the MCs, when exposed to the liquefied gas and to the pressurized environment inside the can. After incorporating the MCs inside the aerosol can, the hydroxyl groups will slowly get dispersed into the whole can, reacting and increasing foam viscosity and diminishing the output value. Based on these results (decreased output) a pressurized aerosol can (with the liquefied gas) was prepared, containing the MCs (without pre-polymer). After removing the MCs from the can, we have observed that the capsules were dilated and very spherical. Apparently they became harder but more fragile and were empty. It seems that the liquefied gas penetrates through the pores and promotes leaching of their content.

So, these experiments with MCs stored in a pressurized environment like the one inside the can, show that the gas and the pressure seem to be forcing the core out of the shell, which can explain why microcapsules with good results in the viscosity test are affecting so much the foam spraying process.

Moreover, it should be noted here, that the MCs with larger tendency for leaching, react easily and faster with the NCO groups, forming a hard polymer shell around them, becoming heavier and tending to go to the bottom of the can. In this case, they will agglomerate at the bottom (Figure 4.41), however they will not affect so much the remaining pre-polymer inside the can, which might explain the better output result observed for the pre-hydrolyzed TEOS PU MCs (Table 4.2).

4.1 Foam Quality

The addition of MCs to the GreenFoam formulation has no major effects on foam quality. In Figure 4.42 it is evident that the only value that is not similar for both cases in the shaking rate. Also, for the other types of MCs in Table 4.2, shaking rates are very low and the reason is the leaching occurrence due to the pressurized aerosol can environment, explained in the previous section.

Figure 4.41: Formulation in a glass replica of an aerosol can of PU foam with microcapsules.
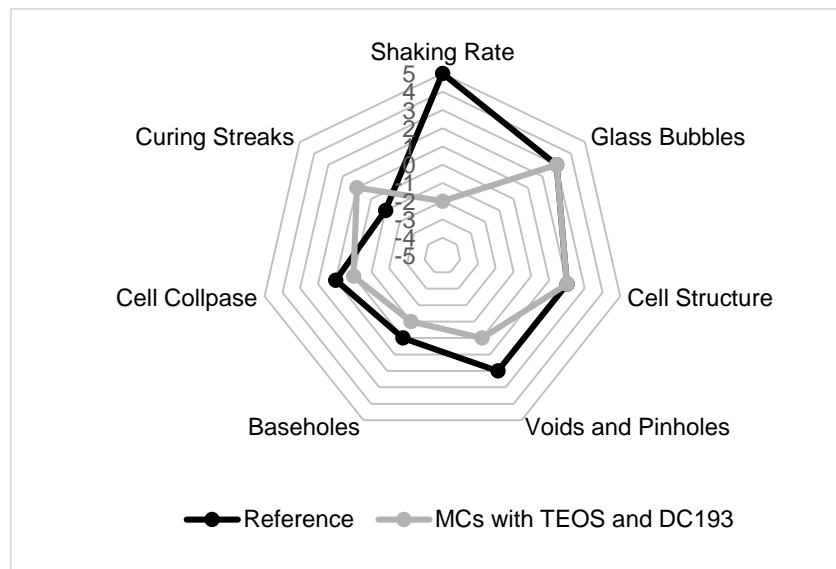

Figure 4.42: Graph for foam quality parameters, for PU MCs, at 5⁰C and in paper.

5. Conclusions

The three goals set in the beginning of this work had been successfully achieved. The outcome of this thesis was the development of a procedure to evaluate MCs to be employed in polyurethane one component foam systems, as well as functional polyurethane-polyurea (PU) microcapsules (MCs) containing hydroxyl groups that will accelerate the curing process of the foams. This was achieved, however the only capsules that were tested (PU shell) were found to lead to an increase of the viscosity inside the aerosol can, which suggests that they are being affected by the liquefied gas and the pressure inside the can.

By optical microscope observation of the PU MCs we were able to check that when they were burst they release their liquid content (aqueous diethylene glycol). Also, Thermogravimetric Analysis results proved that the encapsulation is effective and the capsules can hold the desirable core at least at 50% of their mass, being the best ones, those reinforced with tetraethyl orthosilicate (TEOS). Among the different processing parameters employed, this work allowed to select the conditions for obtaining the best performing MCs. However, it was also concluded that the PU MCs, despite their good performance in the viscosity test, lead to the decrease of the output value of the PU froth, which means that there is leaching inside the pressurized can. There is still work to be done in this field, where the leaching has to be reduced to near zero in pressurized environments, like those inside the aerosol can. This means a more rigid shell, with very small pores, some empty space inside and with a high enough ageing (chemical) resistance. The presence of silica-rich regions in the shell contributes to some of these aspects. That is why the Si-PU MCs exhibited less leaching.

For the polyamide (PA) microcapsules, the main question was the type of amine to use. The triamine compound was the one selected, due to better performance in terms of leaching, possibly due to higher crosslinking in the shell.

Regarding the sol-gel (SG) derived microspheres, or multinucleated capsules, it was observed that they contain less species encapsulated, i.e. a lower percentage of core (aqueous glycerol) encapsulated (ca. 35-40%) than the PU samples. The best result was achieved for a silane combination comprising of TEOS, methyl and epoxy functional silanes. An effort to obtain capsules, instead of microspheres should be done in the future.

Sol-Gel MCs have a great range of development and further work and still several experiments, including aerosol can preparation, must be done to complete this research. Their big advantage is that they do not need to be stored in a solvent. This means they will be easier to manipulate, they will not be affected by the storage solvent and they will not bring solvent to inside the can, affecting the resulting foam.

For Greenseal Polyurethane foams to be competitive in the market, they have to display a main characteristic that differentiates them from the rest, and turn them unique for the client. With microcapsules this can be achieved: a great foam quality that cures in less time than the competitive products.

Much work is still left to do. Since this was a first attempt to incorporate microcapsules in this type of systems, results are still not tuned and optimized. Preventing the leaching inside the aerosol can

and improving the output value is crucial, although very close to be achieved after this work in collaboration with Carmen.

This pioneer research work opens many doors for improving the production of future MCs, which may address other applications, besides polyurethane OCF systems.

I leave this work certain that I gave my contribution to help the polymer industry to evolve.

5.1 Future Work

Polyamide MCs and silica based, sol-gel derived MCs samples are still in need to be incorporated in the polyurethane foam in order to assess the output values and the curing time, as well as their leaching behavior inside the aerosol can. The next step in microcapsules development for polyurethane foams systems should be the choice of the best shell material, based on those results.

The production parameters should be tuned to prevent the leaching completely and other characterization techniques, such as N_2 adsorption/desorption measurement, Hg porosimetry, surface tension and microhardness assessment may be explored. As soon as this is achieved and the curing time is less than regular foam, the product should start being presented to the clients.

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7. Appendix A

7.1 MCs Components FTIR analyses
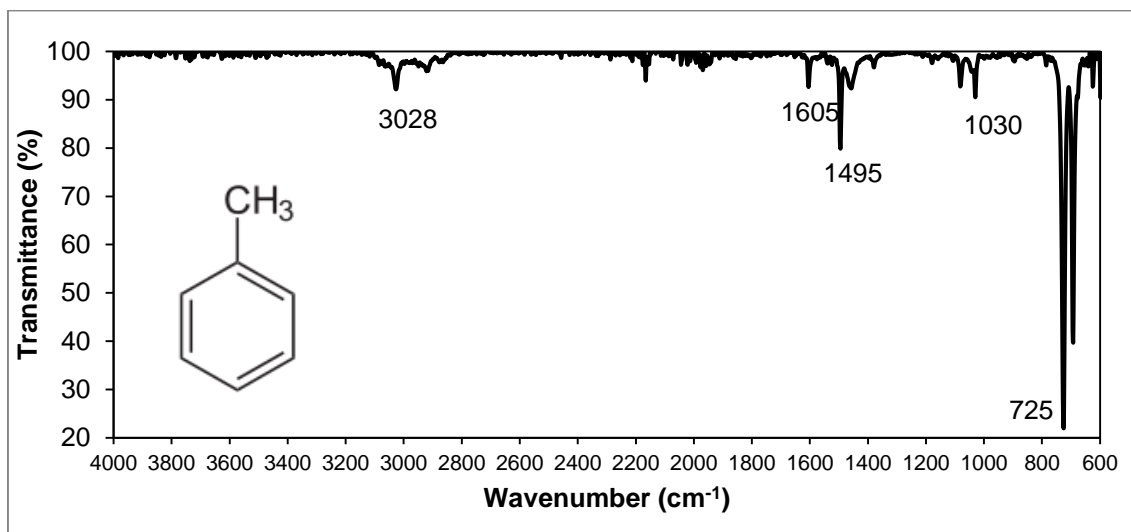
Figure 7.1: FTIR Spectrum of Toluene.

Table 7.1: FTIR spectrum analyses of Toluene

Peaks	Bonds
3028	C-H Stretch, ring modes
1605	C-C Stretch, ring modes
1495	C-C Stretch, ring modes
1030	C-H Bending
725	C-H Bending
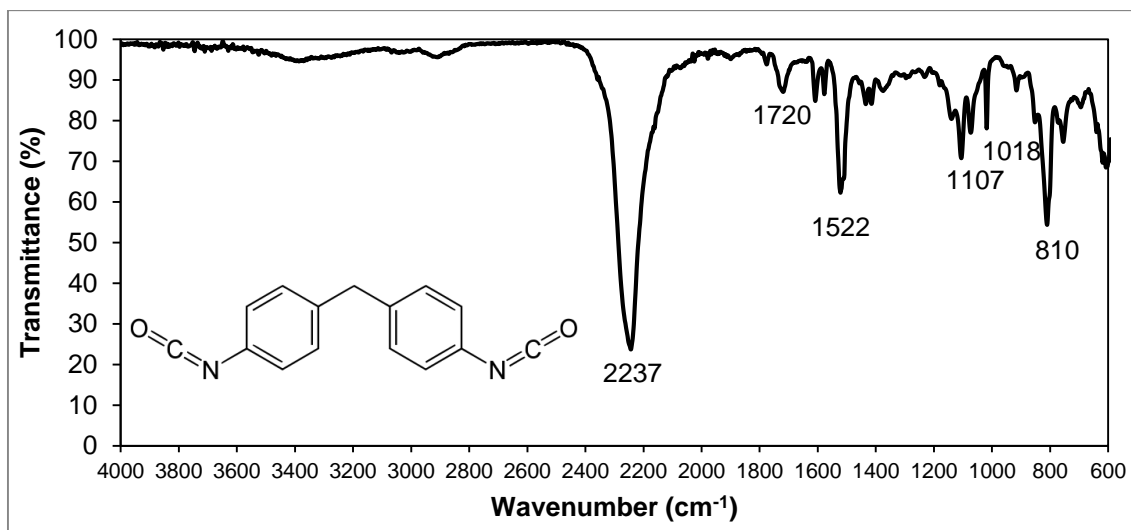
Figure 7.2: FTIR Spectrum of Ongronat2500.

Table 7.2: FTIR Spectrum analysis of Ongronat2500. [34]

Peaks	Bond
2237	N=C=O
1720	C=O
1522	C=C Stretch, ring modes
1608	C-N
810	CH, disubs ring, oop
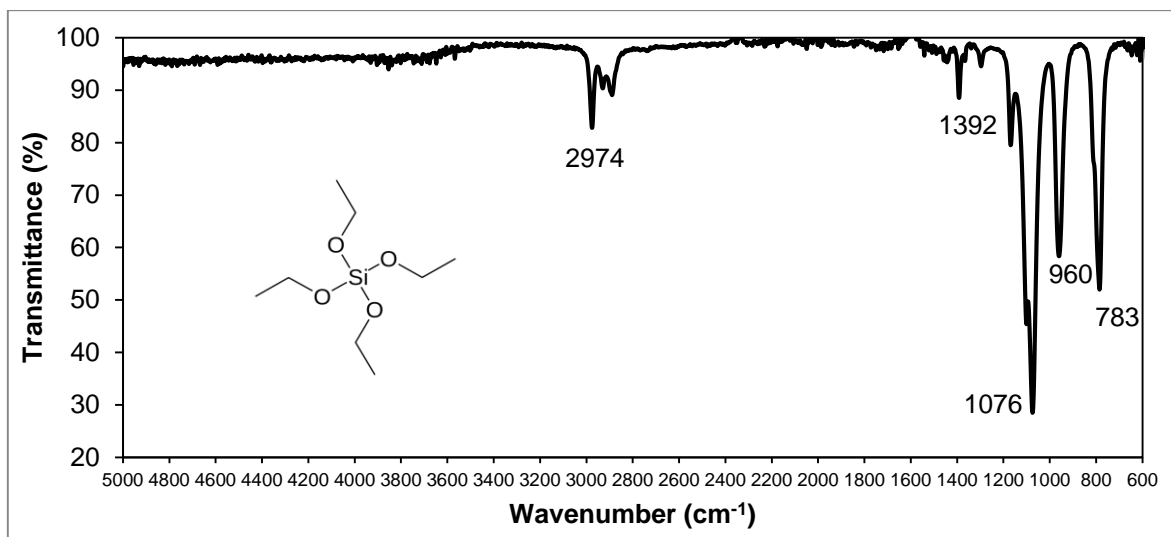
Figure 7.3: FTIR Spectrum of TEOS.

Table 7.3: FTIR Spectrum analyses of TEOS.

Peaks	Bond
2974	C-H Stretch
1392	CH_3 Bending
1076	C-O Stretch
960	$Si\text{-}OCH_2CH_3$
783	$Si\text{ -}O^-$
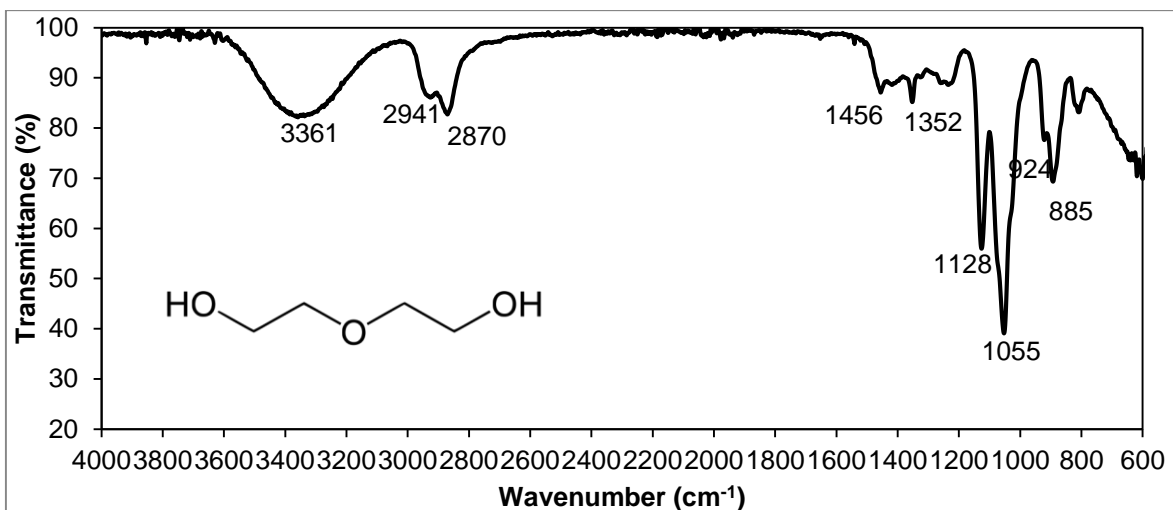
Figure 7.4: FTIR Spectrum of DEG.

Table 7.4: FTIR Spectrum analyses of DEG. [35]

Peaks	Bond
3361	O-H Stretch
2941	CH_2 Stretch, antisym
2870	CH_2 Stretch, sym
1456	CH_2 Bending
1352	CH_2 Bending
1128	C-O Stretch
1055	C-O Stretch
924	COH Stretch
885	$-OC_2H_4$
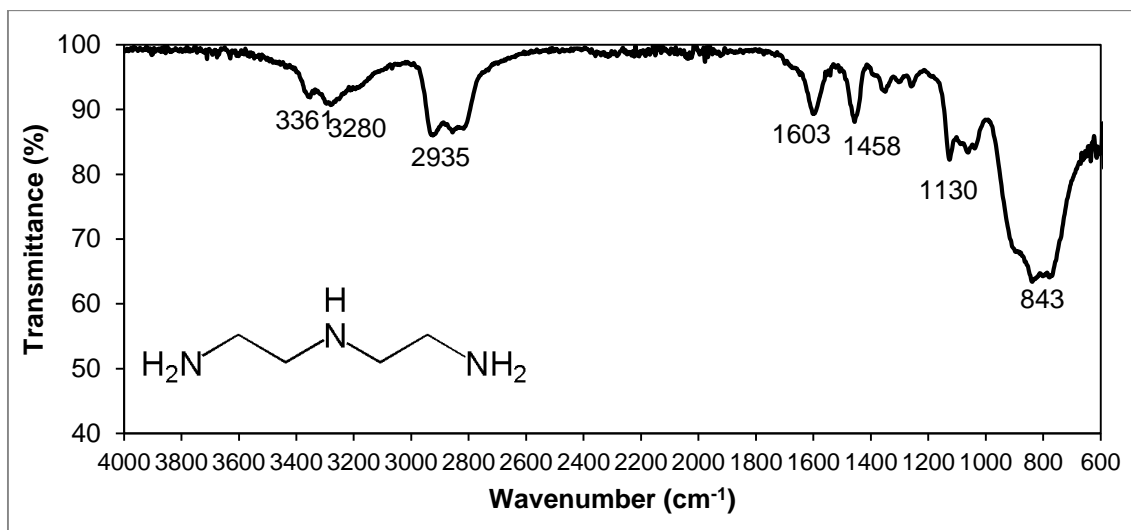
Figure 7.5: FTIR Spectrum of DETA.

Table 7.5: FTIR Spectrum analyses of DETA. [36]

Peaks	Bond
3361	NH_2 Stretch
3280	NH_2 Stretch
2935	C-H Stretch
1603	N-H Bending
1458	CH_2 Bending
1130	C-N Stretch
843	N-H Bending oop
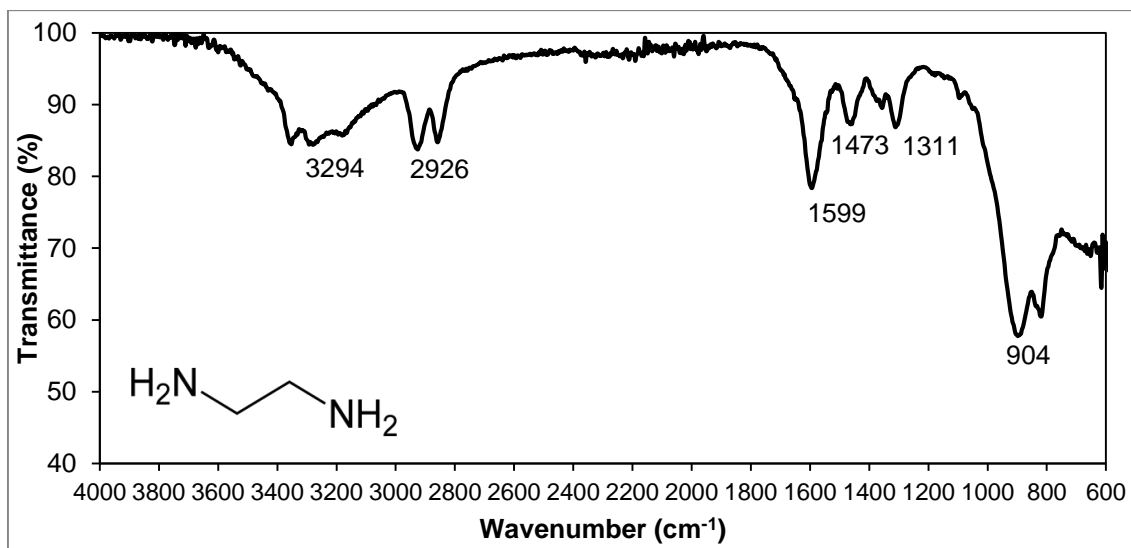
Figure 7.6: FTIR Spectrum of EDA.

Table 7.6: FTIR Spectrum analyses of EDA.

Peaks	Bond
3294	NH_2 Stretch
2926	C-H Stretch
1599	N-H Bending
1473	CH_2 Bending
1311	C-N Stretch
904	N-H Bending oop