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# Microcapsules Characterization for Polyurethane One Component Foam Systems

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## ABSTRACT

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This work has the purpose of characterizing microcapsules developed at Greenseal Research, Ltd., to be incorporated in one component polyurethane foam (OCF) 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 (PA) and silica-based shells. They contain components exhibiting hydroxyl groups (such as diethylene glycol, glycerol and water residues), which will react with the isocyanate groups.

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) have been used to characterize the samples, as well as Fourier Transformed Infrared Spectroscopy (FTIR). TGA and DSC have the main purpose of quantifying the core, while FTIR allows to know how the molecular structure of the shell is affected by the different components used in the production. 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, including curing time measurement.

The reinforcement effect of tetraethyl orthosilicate on the PU microcapsules shell proved to be the best option for a higher encapsulation (at least 50%) and to prevent the leaching. Regarding the PA shell, the best amine source is diethylene triamine in terms of leaching behavior. On the other hand, the employment of methyl and epoxy functional silanes in the silica-based shell synthesis by sol-gel, gave the best results regarding leaching and encapsulation.

Foam formulations made with PU capsules presented a shorter curing time (one day less) than the reference, in a low moisture environment. However, the output was found to decrease, suggesting some leaching occurrence within the pressurized environment of the aerosol can. The quality of the cured foams, was not significantly affected by the presence of the microcapsules.

## 1. Introduction

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, furniture and bedding [1]. This work will be focused on the foams used for structural applications and insulation, contained in aerosol cans, in the building construction sector. They can be applied in fissures and in between materials, such as door frames, filling the gaps around windows and so many others to prevent the thermal losses and increase the efficiency of the energy used. It also improves air quality, since it prevents allergens to get in.

The global market for OCF is expected to grow 6% per year, and in 2011 about 400 million cans were sold [2]. We can conclude that it is a lucrative market with a wide range of expansion and research.

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

Microencapsulation technology can be used in different applications like paper industries, food industries, pharmaceutical, cosmetics, adhesive materials and polymer and coating industries [3], and, more recently, Greenseal has been exploring it for polyurethane OCF systems

Since 1980, microcapsules (MCs) have attracted more attention. They have been prepared with phase change materials as the core content and applied for insulation purposes into polyurethane foams and other materials [4].

The present work deals with one more application for MCs: their use in polyurethane foams to reduce their curing time. They are supposed to burst (by pressure drop) when they are sprayed out and release their core. Aqueous solutions of diethylene glycol (DEG) or glycerol consist of the core of the

capsules. An extra source of hydroxyl groups into the foam (froth, or uncured 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 MCs are still inside the can. This case scenario would not be suitable for can bottling, since the contact of the isocyanate groups with water would result in CO<sub>2</sub> release and pressure build-up inside the can. Also, the MCs have to remain in perfect conditions through the time the can is predicted to stay in the shelf, for sale (typically 12 months, maximum).

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. Customers would prefer a foam that takes less than half the time to cure, so they can proceed faster with their work.

MCs 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.

Within the OCF field, MCs development is expected to increase the formulation value in the market, along with sales and income.

These types of MCs 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 work was aimed at assessing if the MCs synthesized are viable for this application. In particular, it was developed to assist the MCs production, in what regards processing parameters optimization. Finally, it allowed to establish the

conditions that lead to better MCs and to understand their role in the self-curing phenomenon of polyurethane foams.

## 2. Experimental

MCs production were made by Carmen Matos. PU and PA capsules were prepared through microemulsion/interfacial polymerization methods. However, a silane has been used to add extra mechanical resistance to the PU MCs through the silica network formed within the shell. Silica-based MCs were achieved by microemulsion/Sol-Gel processing techniques.

The characterization techniques presented in this work were crucial to select and fine-tune the best production parameters employed in MCs preparation.

### 2.1 Materials

DEG (99%) was purchased from Alfa Aesar. Ongronat2500 was from BorsodChem and Span80 from Merck. Surfactant DC193, tetraethyl orthosilicate, TEOS Z-6697, methyltriethoxysilane, MTES Z-6370 and glycidoxypropyl trimethoxysilane, GPTMS Z-6040 were received from Dow Corning. Glycerol was provided by Cmd Chemicals and Trimethylolpropane (TMP) by Resiquímica.

### 2.2 Analytical techniques

The experiments of TGA and DSC were performed at 10°C/min, from the atmosphere temperature to 800°C, under air environment.

The FTIR spectroscopy analyses were performed with a Nicolet 5700, by Thermo Electron Corporation, with a KBR beamsplitter plus a DTGS-TEC detector in the middle-infrared region, using a 4 cm<sup>-1</sup> resolution and 128 scans, and an ATR accessory with a diamond crystal. The reflection spectra were obtained between 4000 and 600 cm<sup>-1</sup>.

### 2.3 Viscosity test

Blends of MCs and Ongronat2500 (at 5% (m/m) MCs) were prepared, and right after this preparation, the viscosity was measured once a day, for about a month, in a cone and plate viscometer from Rel.

### 2.4 Can assembling, output and foam characterization

4% (m/m) of MCs were added into the aerosol cans containing a polyurethane formulation (GreenFoam), proprietary to Greenseal. The can was then pressurized with liquefied petroleum gas and dimethyl ether and sealed with an aerosol valve.

The output is a test at 5°C, 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. In the present work, the output of the can was measured one week after being prepared.

After the output test, in order to evaluate the quality of the foams with and without MCs (reference sample), a small bid was sprayed inside a previously purged (with N<sub>2</sub> gas) and sealed plastic bag, until the bag is full. The foam containing bag was stored in a non-moisture environment (desiccator). The time needed for the fully curing of the foams was recorded. Also, at 5°C a bid of foam was sprayed on paper and left to cure inside a refrigerator.

## 3. Results and discussion

### 3.1 PU

Figure 1 shows the TGA/DSC profiles for MCs with PU shell reinforced with TEOS, not dried (Si-PU MCs), i.e. in a slurry with toluene, and dried (Si-PU MCs dried) at 50°C for 24 h. These can be compared with PU shell without TEOS (PU MCs), not dried.

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

For the PU MCs with TEOS, the first weight loss, starting at 54°C, is regarding the solvent evaporation, where they are immersed, or moisture at their surface. The second slope starting around 177°C 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 MCs, as expected, exhibit a weight loss regarding the core not as evident as for Si-PU MCs. 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 encapsulated aqueous DEG (core) plus solvent residues around them. However, 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 (551°C) when silane is incorporated within the shell than when it is not (500°C). So, this silica/PU hybrid system exhibits a 50°C 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

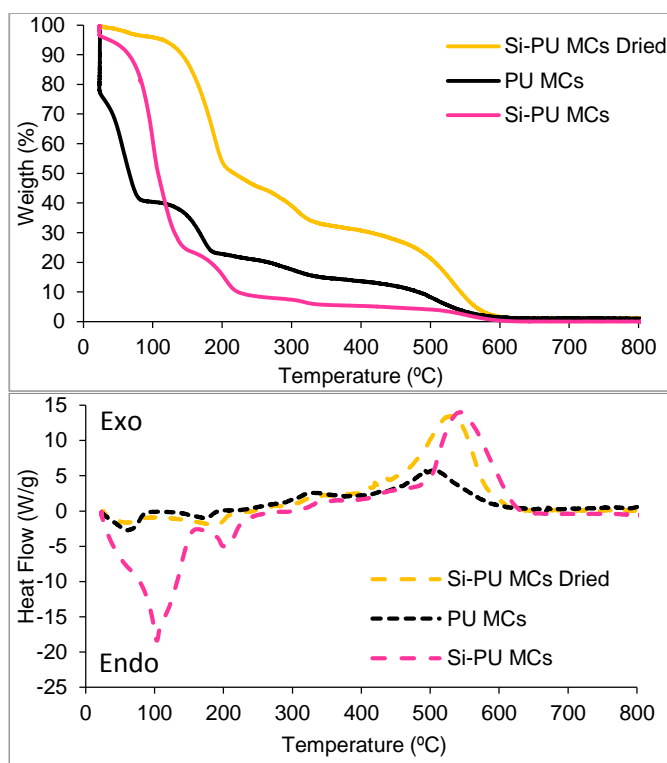


Figure 1: TGA/DSC profiles for PU MCs.

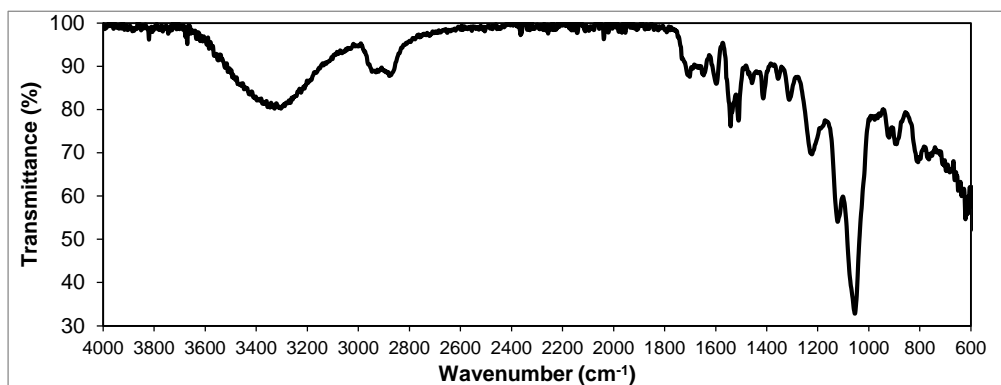


Figure 2: FTIR spectrum for Si-PU MCs dried.

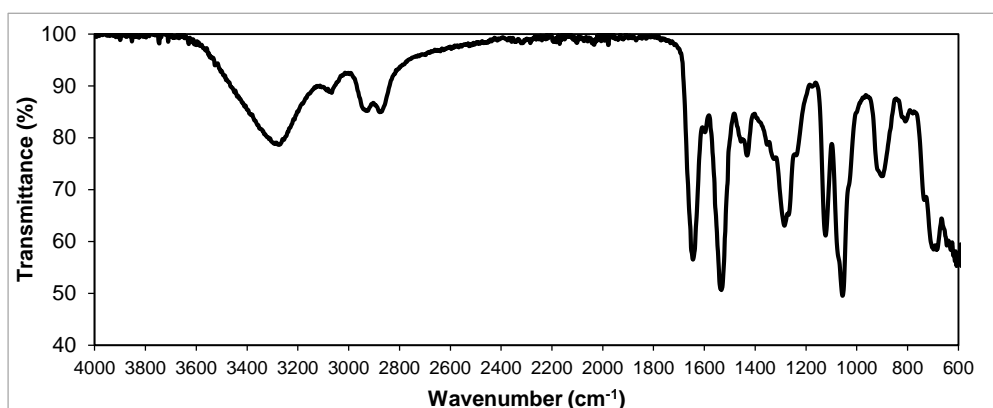


Figure 3: FTIR spectrum for PA MCs.

the limited mobility of the PU chains in the presence of the silica network.

Figure 2 shows the FTIR spectrum for Si-PU MCs dried. Its main peaks correspond to aqueous DEG, present in the core, namely the large band at 3000-3600  $\text{cm}^{-1}$  (OH stretching) and the peak at ca. 1055  $\text{cm}^{-1}$  (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.

The peak at 960  $\text{cm}^{-1}$  (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  $\text{cm}^{-1}$  [5].

There is no trace of the intense peak of Ongronat2500 at 2237  $\text{cm}^{-1}$  assigned to the isocyanate N=C=O bonds, because these groups have reacted to form the polyurethane-polyurea shell. 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 amide (N-H stretch) band at 3200-3450  $\text{cm}^{-1}$  and at 1510  $\text{cm}^{-1}$  (N-H bending), carbonyl groups at ca. 1700  $\text{cm}^{-1}$  (C=O from urethane) and at 1660-1690  $\text{cm}^{-1}$  (C=O from urea), carbamate groups (CN-H) at ca. 1600  $\text{cm}^{-1}$ , C=C at ca. 1522  $\text{cm}^{-1}$  (aromatic ring) and C-O-C at ca. 1214  $\text{cm}^{-1}$ , which indicate the presence of urethane linkages in the PU, as well as some evidence of polyurea [6]. Moreover, one can also distinguish a small contribution to the spectrum from the Si-O-Si asymmetric stretching at ca. 1070  $\text{cm}^{-1}$ , Si-O at ca. 960  $\text{cm}^{-1}$  and the symmetric stretching of the bridging oxygen at ca. 800  $\text{cm}^{-1}$  [7]. This group of peaks suggests the presence of silica domains in the PU shell, which resulted from the hydrolysis and polycondensation reactions of TEOS.

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, corroborated by TGA/DSC analysis.

By analyzing the results from the viscosity test in Figure 4, we can see that Si-PU MCs is a better option than a sample made without silane reinforcement, since the viscosity values

stay much lower through the time. Cross-linking and presence of silicon atoms give MCs 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.

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 Ongronat2500, as a source of OH and NCO, respectively. They have higher functionality comparing with DEG and non-distilled Ongronat2500.

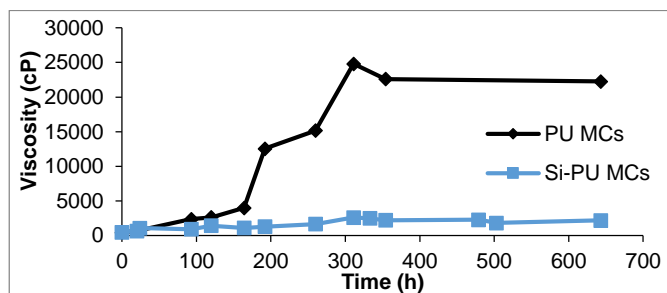


Figure 4: Viscosity evolution for PU MCs, for TEOS reinforcement.

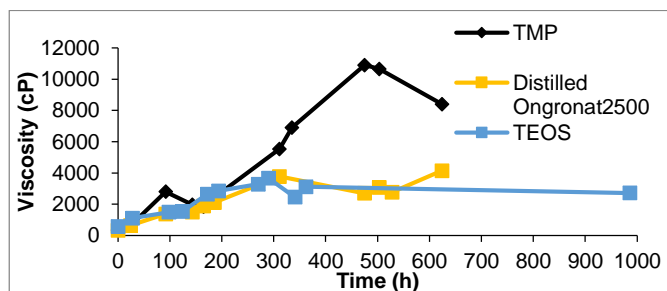


Figure 5: Viscosity evolution for PU MCs with different shell reinforcements.

As we can see in Figure 5, 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.

So, Si-PU MCs were identified as the best option in terms of functional MCs, with very limited leaching occurrence, and, therefore, they were selected for the tests carried out in real PU foam aerosol cans.

### 3.2 PA

As for PU MCs, DEG seems to be the main component for PA MCs (Figure 3), with characteristic main peaks at 3000-3600 and 1055  $\text{cm}^{-1}$ , 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  $\text{cm}^{-1}$  assigned to N-H stretch, 1644  $\text{cm}^{-1}$  for C=O stretch, N-H bending and C-N stretching, from the CNH group at 1535  $\text{cm}^{-1}$ . [8] [9]

Regarding the viscosity tests, it was found that in the majority of the cases, DETA was the amine source which led to better leaching behavior (Figure 6), probably because it contains three amine groups (while EDA contains two) and it will, therefore, result in a more crosslinked shell structure.

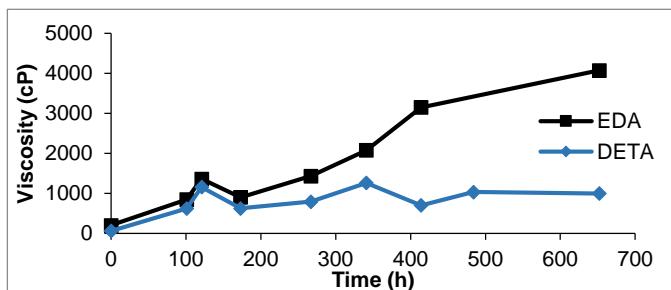


Figure 6: Viscosity evolution with PA MCs, for different types of amine (diamine and triamine).

### 3.3 SG

Figure 7 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 from 0g to 4g and 10g MTES (0M-SG, 4M-SG and 10M-SG MCs, respectively), 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 should be noted that GPTMS is the silane which experiences mass loss at higher temperatures (ca. 200°C), followed by MTES (at 120°C) and TEOS (at ca. 80°C) (TGA profiles obtained in this work, but not shown in this paper). GPTMS, besides suffering thermal degradation at higher temperatures, compared to TEOS and MTES, also presents a higher char yield. Water has most weight loss around 100°C as expected and glycerol at 240°C.

The major difference when comparing the sol-gel derived MCs with the PU MCs is the char yield obtained at higher

temperatures. These sol-gel samples (based on silica) do not lose their mass completely, as the temperature increases and reaches 900°C. For instance, at 700°C, still more than 40% of the silica based capsules remained. This is due to the inorganic  $\text{SiO}_2$  network that was formed by polycondensation of the Si-OH groups [10].

Analyzing the DSC results, all the samples have a very similar, but low intensity, endothermic peak at ca. 100-150°C, except the sample 10MG-SG MCs. All of them exhibit clearly less than 5wt% of water in their core content, except the one without MTES (0M-SG MCs), which is more hydrophilic. The sample exhibiting 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 270°C 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 [10]. 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.

The FTIR spectroscopy technique allows to correlate the MCs composition with the MCs shell structure. It helps to

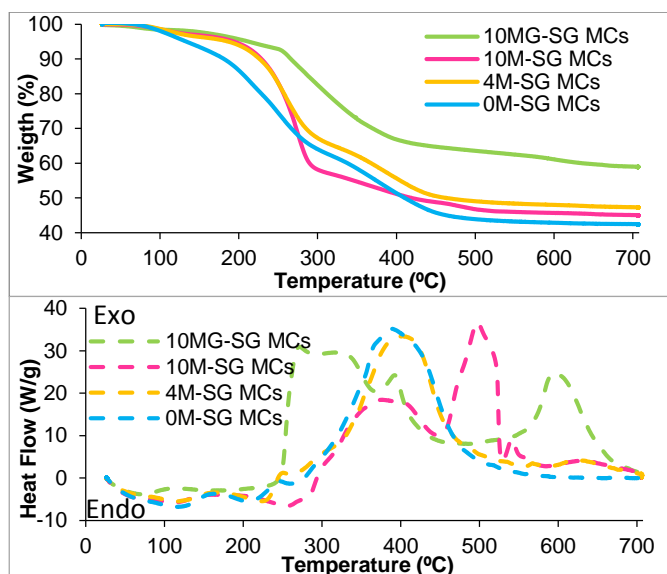


Figure 7: TGA/DSC profiles for SG MCs.

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

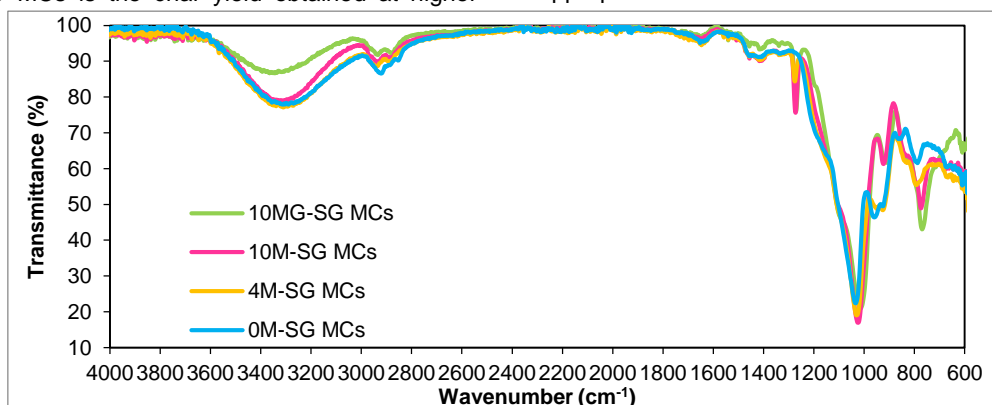


Figure 8: FTIR spectrum for SG MCs.



observation of the spectra) with the increase of the amount of MTES (Figure 8), which was the strategy followed in this work to increase the hydrophobic character of the MCs shell, useful to limit the occurrence of leaching. The number of hydrophobic Si-CH<sub>3</sub> 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<sup>-1</sup>, which are ascribed to Si-CH<sub>3</sub> groups in polysiloxane network [5].

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, or with less water adsorbed on the MCs surface evidenced here by the lower intensity band at 3000-3500 cm<sup>-1</sup>.

Figure 9 shows that the amount of MTES and silane combination which enabled lower viscosity values in the viscosity test, was 10MG-SG. The most hydrophilic MCs shell (0 g MTES) exhibited the worst performance in the viscosity test.

The glycidoxy group in GPTMS 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<sub>3</sub> 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 might be not as large as for 10M-SG MCs, which might have also led to a better result in the viscosity test.

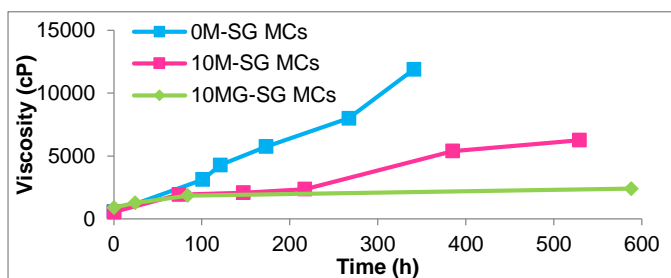


Figure 9: Viscosity evolution for SG MCs.

### 3.4 Output and curing time

The reference, i.e. a foam formulation without MCs, represents the ideal parameters that a foam with MCs should have, except for the curing time. For all the types of MCs tested the time needed for the foam to totally cure was a day less of the reference, which shows the benefit, in terms of curing speed, of incorporating MCs in the PU foam formulation.

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 microcapsules are increasing the foam viscosity, which difficults the spraying process. 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, with a negative impact on the output, suggesting that there is leaching occurring. We believe that it is the pressurized environment inside the aerosol can and the liquefied gas, which are at the origin of this leaching. After incorporating the MCs inside the aerosol can, the hydroxyl groups will slowly get dispersed into the whole can, reacting and increasing the foam viscosity with a corresponding decrease of the output value. Based on these results (decreased output) a pressurized aerosol can (with the liquefied gas) was prepared, containing the MCs (without prepolymer). 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.

Table 1 lists these results obtained for PU MCs (without silane), and for Si-PU MCs, as well as for the reference, a can with no MCs sample. It evidences the benefit of the MCs in terms of curing speed, but the drawback in terms of output and shaking rate.

As a future (on-going) work, polyamide and silica-based sol-gel derived capsules will be tested in aerosol cans, which, due to logistic issues, has still not been carried out.

Table 1: Output and curing time for PU MCs.

Type	Output (g/s)	Curing Time (days)	Shaking Rate
Reference	4,5	3	5
PU-MCs	0,3	2	-4
Si-PU MCs	1,9	2	-2

## 4. Conclusions

This work employed varied characterization techniques to assess different types of MCs prepared at Greenseal Research, and to assist on the synthesis parameters optimization. PU MCs reinforced with TEOS, consisting of silica-PU hybrid shell material, exhibited at least 50% of encapsulated core and they were the ones with better performance in terms of leaching. Moreover, they were able to significantly accelerate the curing process of the polyurethane foams, but simultaneously they led to an increase of the viscosity inside the aerosol can, with corresponding decrease of the output value.

Regarding the SG method, silica-based MCs, or multinucleated MCs, prepared with MTES presented a lower percentage of core (aqueous glycerol) encapsulated (35%) than the PU samples.

The production parameters, and shell composition, should be tuned to prevent the leaching completely, inside the aerosol can. As soon as this is achieved and the curing time is less than for regular foam, the product should start being presented to the clients.

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