



## Organically-modified silica based microspheres for self-curing polyurethane one component foams



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### ABSTRACT

Hybrid organosilica microspheres (MSs) doped with aqueous glycerol are tested as enablers for self-curing polyurethane one-component foams (OCF). The MSs have been characterized by Scanning Electron Microscopy, Fourier Transformed Infrared Spectroscopy, Thermal Gravimetric Analyses and leaching test. Shaking rate, of the pre-polymer inside the aerosol can, and curing speed tests of the sprayed foam, in a low moisture environment, were performed in order to evaluate the effect of the MSs on the OCF can's lifespan, as well as their contribution to the PU foam's curing process. The organic functionality of these silica-based MSs (methyl and glycidyl groups) was found to be responsible for a reduced leaching and low water absorption tendency, which is critical for a longer shelf life of the product required for commercial applications. In addition, the methyl functional MSs presented a significant increase in the curing rate of the PU foam.

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## 1. Introduction

Encapsulation of different compounds is an evolving area in chemistry with a significant importance in many industrial sectors, such as pharmaceutical, agrochemical, food, textile and cosmetic industries [1]. Microcapsules and microspheres (MSs) are used as carrier systems for a wide variety of applications storing and protecting functional compounds, either gases or liquids, until controlled release of their valued payload.

Organic compounds have been widely used as encapsulating material, but polymer-based MSs normally suffer from poor chemical and physical stability [2]. Therefore, a great deal of research has been devoted to sol-gel microencapsulation in

inorganic metal oxide microparticles, which allows to conjugate robustness, thermal and mechanical stability, chemical resistance and the ability to easily incorporate additional functional groups [3,4].

One area in which the use of hybrid inorganic-organic MSs with an encapsulated curing agent has been heavily investigated is one component polyurethane foam (OCF) formulations [5]. Methylene diphenyl diisocyanate (MDI)-based OCF is a self-expanding, self-adhesive, moisture-curing filler and adhesive bonding quickly to a variety of substrates including wood, masonry, metal and plastics, eventually hardening into a rigid plastic foam that prevents air and moisture infiltration [6]. Accordingly, polyurethane OCF aerosol cans are used across the world to reduce air leakage in buildings by sealing air infiltration points as well as to fix polystyrene or polyurethane insulating panels.

In two component PU foams, both components, isocyanate and polyols, are not mixed together until the spraying of the foam. To the contrary, in OCF formulations, polyols are stored together with isocyanates (in excess), in a pressurized aerosol can or vessel fitted with a dispensing device, along with the propellants, so that a

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(quasi) pre-polymer is formed and remains liquid until sprayed [5,7].

When the device is operated, the discharged fresh foam (froth) expands to fill all hollow spaces, and starts to harden on contact with the air's humidity resulting in conversion of the remaining –NCO groups into amino groups (with production of CO<sub>2</sub>) up to the state in which no free –NCO groups are present in the final rigid foam. Owing to their versatility and surging demand from the construction market, about 600 million number OCF cans were marketed in 2015, developing at 7% annual growth rate [8].

Typically, time for fully curing a one-component spray foam is 24 h, depending on the foam thickness (the thicker the foam, the longer it takes to cure) and site conditions (especially temperature and humidity). If the froth is touched or manipulated during the curing process, it will not serve its purpose because the foam cells will collapse and not expand in the proper way.

Unfortunately, MDI is toxic and the curing time relatively long, so that the development of solid curing agents to be incorporated in polyurethane OCF formulations for faster and self-curing 2nd generation aerosol can systems is highly desirable.

In 2014, we have shown that 5% methyl-modified organosilica MSs doped with glycerol, an abundant renewable by-product of biodiesel and oleochemicals manufacturing [9], provide a slight improvement of the curing speed [10]; and subsequently that said MSs burst upon depressurization [11], breaking and releasing their functional payload [12].

Larger reduction in the curing time, however, is required prior to practical application of said MSs along with further reduction in leaching of the encapsulated glycerol and partial moisture adsorption, which both result in undesirable rise of viscosity of the pre-polymer inside the aerosol can, and thus in a reduced shelf life of the product (12 months at room temperature is the minimum shelf life required).

In this work we investigate the effects of methyl and glycidylxyloxy (epoxy) organic functionalization of the hybrid MSs on i) the morphology, molecular structure and glycerol leaching behavior of the organosilica-based MSs, ii) the nature and amount of micro-encapsulated species, and iii) the PU foam curing speed, or self-curing capability.

## 2. Experimental section

### 2.1. Materials and methods

#### 2.1.1. Materials

Tetraethyl orthosilicate (TEOS, 99%), Methyltriethoxysilane (MTES) (99.5%) and (3-glycidylxyloxypropyl)trimethoxysilane (GPTMS) (>98%) were purchased from Dow Corning. Glycerol (87%) was received from VWR. Decahydronaphthalene, (mixture of *cis* and *trans* isomers, 99%) and Span 80 (99%) were purchased from Merck KGaA. *n*-hexane (99%) was obtained from LabChem, and ethylenediamine (99.5%) from Sigma-Aldrich. All chemicals were used as received, without further purification.

#### 2.1.2. Synthesis of the microspheres

**2.1.2.1. Silica microspheres.** Deionized water and glycerol were stirred at room temperature with a magnetic stirrer, in a weight proportion 2:1, until a clear solution was obtained. The resulting solution was mixed with a solution of decalin and Span 80, and then homogenized at 9200 rpm using an Ultra-Turrax (IKA) dispersing device affording an emulsified solution 30 wt% in glycerol.

An aqueous mixture of water and TEOS was stirred at 100 rpm for 1 h at room temperature. Both the emulsion and the pre-hydrolysis solution were mixed in a reaction balloon at 600 rpm with a mechanical stirrer for 1 h at room temperature. Afterwards,

the temperature was increased first to 60 °C and then to 80 °C, stirring for 1 h at each step. The white MS precipitate was filtered through a paper filter, and extensively washed with *n*-hexane. The MSs were then dried at 45 °C for 48 h, and stored in a moisture-free environment.

**2.1.2.2. Hybrid microspheres.** Hybrid MSs were obtained following the same protocol of the SiO<sub>2</sub> MSs varying only the amount and type of silane precursors in the pre-hydrolyzed mixture as shown in Table 1.

MSs with epoxy resin rich regions in the organosilica shell were also synthesized, by adding, to the TEOS and GPTMS mixture, ethylenediamine (EDA).

In the latter case, due to the exothermic fast oxirane ring opening reaction resulting in epoxy resin moiety formation (Scheme 1), an ice bath was used when adding the hydrolysis solution to the emulsion. Furthermore, in this case the mixture was not submitted to the heating step.

#### 2.1.3. Characterization

The morphology and size distribution of the MSs were investigated by SEM using a JEOL 7001F (JEOL, Tokyo, Japan) SEM-FEG (Field Emission Gun) microscope. The molecular structure was analyzed via FTIR spectroscopy using a Nicolet 5700 FT-IR (Thermo Electron Corporation), equipped with a Smart iTR Attenuated Total Reflectance (ATR) sampling accessory, after heating each sample to 45 °C for 24 h prior to analysis. The thermogravimetric analyses (TGA) were carried out in an air controlled atmosphere using a TGA 92 16–18 SETARAM equipment, at a temperature rate increase of 10 °C/min.

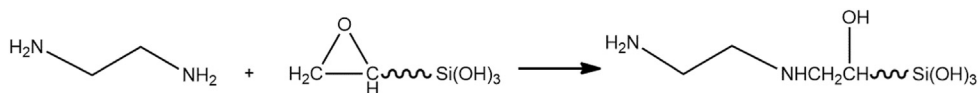
Leaching of the encapsulated glycerol through the pores of the each MS sample was indirectly assessed by monitoring the viscosity increase of an isocyanate mixture containing the MSs (leaching test). The MSs were mixed, at 5 wt%, within an oligomeric MDI solution (Ongronat 2500) and the viscosity measured over several days using a multi speed digital cone and plate viscometer with variable temperature control from REL.

Finally, typical industrial tests, such as shaking rate and curing rate determination, were conducted to determine the effect of the MSs on the polyurethane OCF curing process. One aerosol can was filled with the component B (an isocyanate-based pre-polymer), component A (composed mainly by polyols), the MSs to be tested and component C (propellant gases). The amount of MSs added to the formulation was 6.8 wt% of the A + B components mixture. A reference foam without MSs was also sprayed.

The shaking rate test comprises monitoring of the pre-polymer shaking level inside the can, for several days after preparing the aerosol can. In case of glycerol or water leaching, the viscosity would increase and shaking level would decrease. The scale in this test goes from 5 to –5, with 5 assigned to a good agitation (low viscosity pre-polymer) and –5 ascribed when the material inside the can becomes so viscous that it almost does not move any longer when shaking the can.

**Table 1**  
MS samples nomenclature and composition.

| Sample         | Silanes in the pre-hydrolyzed solution (mol%) |      |       |
|----------------|-----------------------------------------------|------|-------|
|                | TEOS                                          | MTES | GPTMS |
| 100T           | 100                                           | 0    | 0     |
| 46T:54M        | 46                                            | 54   | 0     |
| 53T:47G        | 53                                            | 0    | 47    |
| 53T:47G (+EDA) | 53                                            | 0    | 47    |



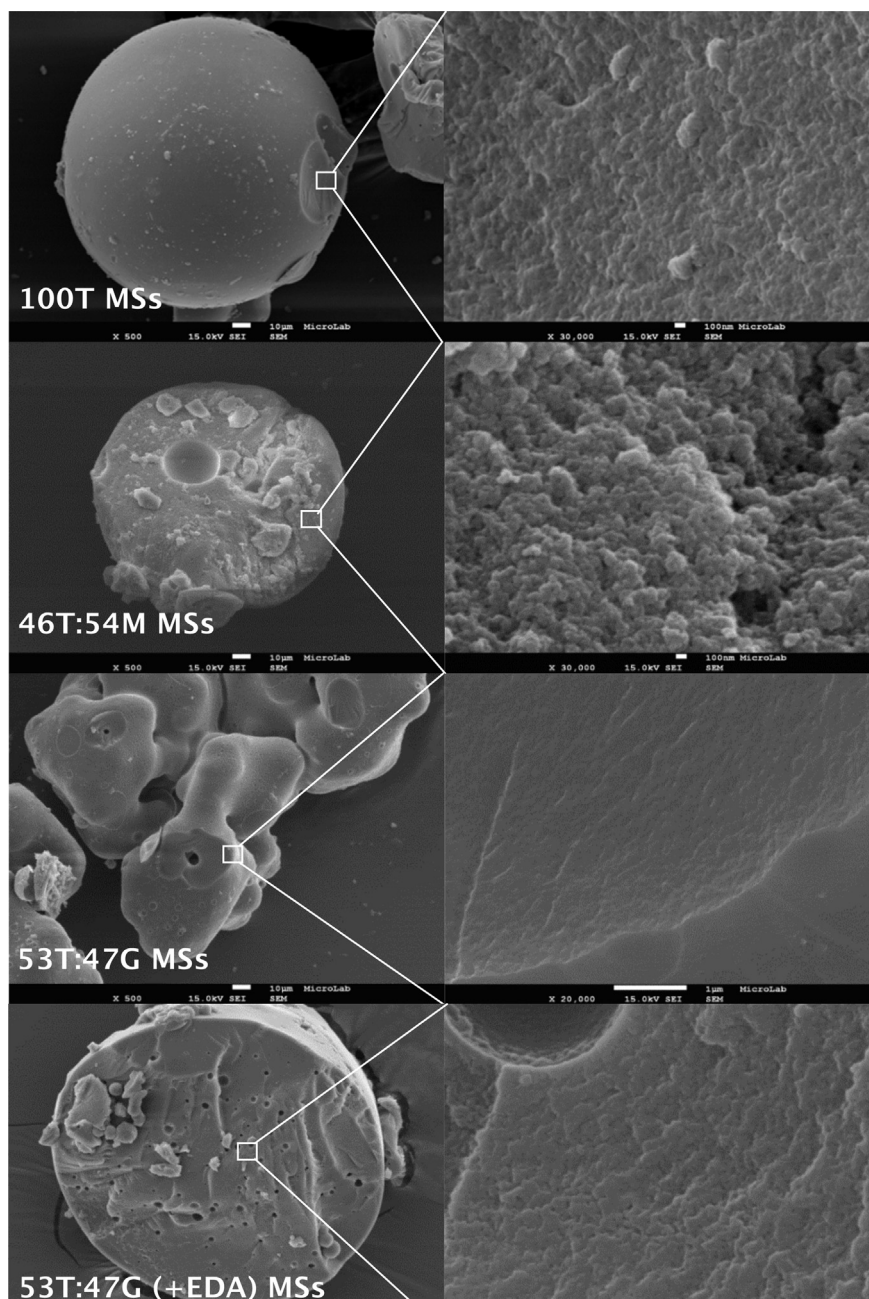
**Scheme 1.** The oxirane ring opening reaction between EDA and GPTMS.

An analogous scale is used for the curing rate. A small amount of the aerosol can comprising the MSs is sprayed inside a plastic bag previously purged with  $\text{N}_2$  gas and immediately sealed, in order to avoid air's entrance. The bag was then stored in a desiccator with maximum 10% relative humidity. The resulting foams were evaluated in the above scale of –5 to 5, with –5 assigned if the sprayed foam remains in liquid state and 5 if the foam is completely cured (solid).

### 3. Results and discussion

Fig. 1 shows the SEM photomicrographs of the MSs samples, at different degrees of magnification.

All samples, apart from 100T, are comprised of mesoporous MSs, with the 46T:54M organosilica showing the largest porosity, where glycerol can be encapsulated to a large extent. The glycidyloxy-containing ORMOSIL 53T:47G particles show both lower porosity



**Fig. 1.** SEM photomicrographs of the glycerol-doped MSs at different magnifications.

and irregular shape, likely resulting from an unstable emulsion during the sol-gel processing. Remarkably, when adding the curing agent EDA to the synthesis with TEOS and GPTMS it is possible to obtain spherical MSs, as observable in Fig. 2, with a higher porosity, similar to the silica MSs.

The FTIR spectra in Fig. 3 clearly show the presence of water and glycerol via the band located at ca.  $3300\text{ cm}^{-1}$ , which is correlated with the presence of O–H groups (O–H stretching), derived from the encapsulated glycerol, the presence of remaining water and possibly some uncondensed Si–OH groups. Another evidence of the glycerol's presence is the C–H bending modes band between about  $1500\text{ cm}^{-1}$  and  $1300\text{ cm}^{-1}$ . The presence of water can also be inferred from the peaks located at  $1640\text{ cm}^{-1}$  and ca.  $650\text{ cm}^{-1}$ , due to H–O–H bending. Indeed, the highly hygroscopic  $\text{SiO}_2$  xerogel sample (100T) presents the highest intensity peak at  $1640\text{ cm}^{-1}$ .

The peak at  $1030\text{ cm}^{-1}$ , visible for all samples, corresponds to the asymmetric stretching of the siloxane bonds Si–O–Si (TO component), whereas the shoulder at ca.  $1200\text{ cm}^{-1}$  is related to the LO component of said asymmetric stretching. Both are typical of silica-based materials [12,13].

The organic functionality brought by MTES and GPTMS, used in the syntheses of 46T:54M, 53T:47G and 53T:47G (+EDA), as well as the presence of epoxy resin groups is evident in all said samples,

with the wavenumber of the corresponding organic groups summarized in Table 2.

The increase of the  $1500\text{--}1300\text{ cm}^{-1}$  band's intensity due to the C–H scissor mode seems to indicate that samples 100T and 46T:54M have the highest amount of encapsulated glycerol. The peaks at ca.  $3000\text{--}2750\text{ cm}^{-1}$ , mainly due to C–H stretching in  $\text{CH}_2$  moieties, present increased intensity for the samples derived from MTES, and especially for those derived from GPTMS, which is in agreement with the silanes' chemical composition.

For the 46T:54M sample, one band at around  $1270\text{ cm}^{-1}$  and another at  $770\text{ cm}^{-1}$  are ascribed to Si– $\text{CH}_3$  groups, i.e. blocks of methyl T units in the organosilicon compound. For the 53T:47G sample, the peaks at  $906\text{ cm}^{-1}$  and  $850\text{ cm}^{-1}$ , ascribed to C–O and C–O–C stretching of the epoxy (oxirane) groups confirm the presence of the epoxy (oxirane) group of GPTMS in the microparticles [14,15]. The characteristic bands of the glycidyloxy group are located at  $1250\text{ cm}^{-1}$  and  $3045\text{ cm}^{-1}$  [16].

As expected, the intensity of the bands typical of the epoxy group decreases with the addition of EDA (53T:47G + EDA), confirming epoxy ring opening polymerization in the presence of the curing agent, EDA. Finally, the presence of newly formed NH groups is revealed by the appearance of a peak at  $1570\text{ cm}^{-1}$  ascribed to N–H bending [17]. This reveals the formation of epoxy resin moieties within these MSs' shell. The corresponding N–H stretch peak is, however, masked by the band at  $3300\text{ cm}^{-1}$  due to O–H groups. Peaks corresponding to  $\text{NH}_2$  groups are not visible, which might indicate that both  $\text{NH}_2$  groups, from EDA, might have reacted with GPTMS' epoxy rings.

Thermograms in Fig. 4 and results in Table 3, reporting the calculated percentage of glycerol, which is considered lost until  $300\text{ }^\circ\text{C}$ , and water content for each MS sample, show that the 46T:54M sample exhibits the highest amount of encapsulated glycerol (36.4%), significantly higher than the remaining MS samples, and fully consistent with the results obtained so far with MS encapsulating this polyol [18]. In agreement with the FTIR results, the 53T:47G sample presents the lowest amount of encapsulated glycerol (17.9%), whereas the silica (100T) sample has the highest water content (10.2%). It is important to stress that the glycerol is only physically entrapped in the MSs core and in its inner porosity, since glycerol is not reactive with the shell. It is possible that some water is present in the MSs' surface, not due to a chemical reaction but because of the shell's hydrophilicity which leads to moisture adsorption on the surface. The desired decrease of the water amount with the addition of MTES and GPTMS to the sol-gel synthesis is clearly observed. With the addition of EDA to the 53T:47 G MS synthesis, no water is detected any longer from TGA analysis. In the latter sample, the residual weight after heating at  $400\text{ }^\circ\text{C}$  is the lowest, which is probably related with the presence of the epoxy resin network formed through the reaction of GPTMS with EDA.

The amount of water entrapped in the methyl-modified microparticles 46T:54M is more than halved, when compared to the  $\text{SiO}_2$  sample, and no water is left in the organosilica microparticles obtained via addition of EDA to the 53T:47G mixture.

The leaching tests performed with the oligomeric isocyanate blend, Ongronat 2500, assess the occurrence of glycerol (and water) release through the MS porosity and also the effect of adsorbed moisture species for those MS with higher hygroscopic nature.

In full agreement with previous results [9], Fig. 5 indicates a noticeable viscosity increase for the silica sample (100T), leading to the highest and fastest increase of the mixture viscosity.

After 7 days (168 h) the Ongronat 2500 mixture in the aerosol can was already solid, making glycerol-doped silica MSs incompatible with the final application, as they would lead to a strong decrease of the product shelf life.

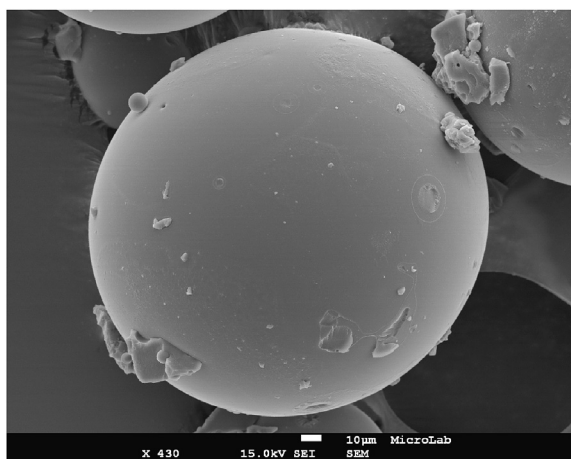


Fig. 2. SEM photomicrographs of the glycerol-doped 53T:47G (+EDA) MSs.

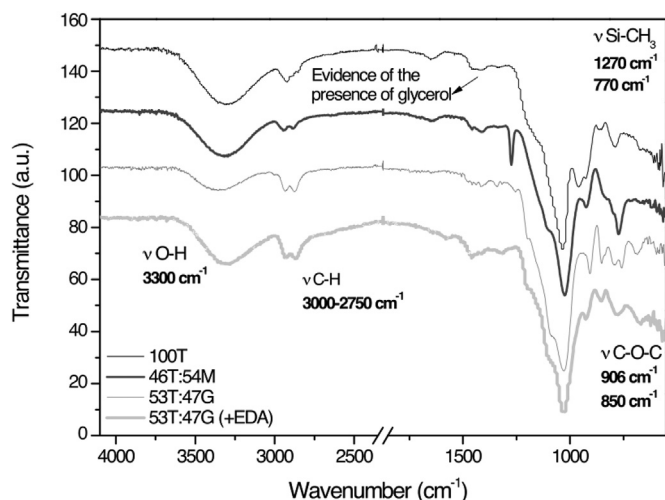
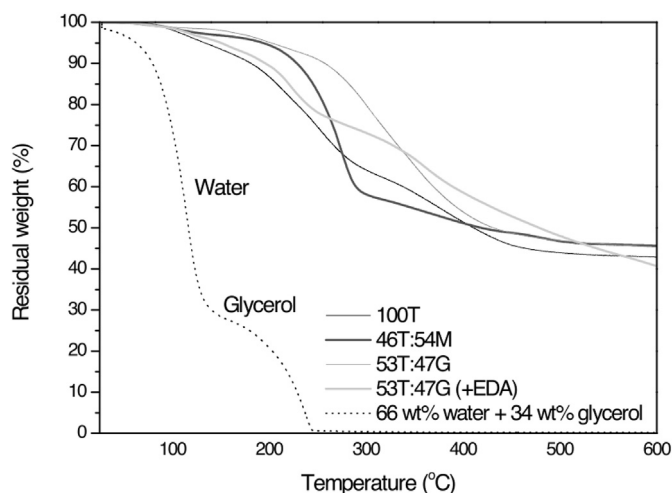


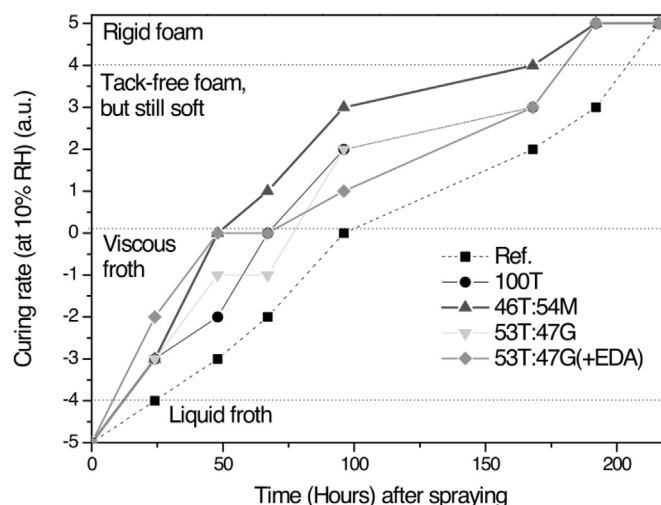
Fig. 3. Normalized FTIR spectra of the glycerol-containing MSs.

**Table 2**  
Detectable organic groups, and respective wavenumbers, for each sample of hybrid MSs.

| Sample         | Organic groups                                 | Wavenumber (cm <sup>-1</sup> )                                                        |
|----------------|------------------------------------------------|---------------------------------------------------------------------------------------|
| 46T:54M        | Si-CH <sub>3</sub>                             | 1270 cm <sup>-1</sup><br>770 cm <sup>-1</sup>                                         |
| 53T:47G        | C-O and C-O-C stretching, of the oxirane group | 906 cm <sup>-1</sup><br>850 cm <sup>-1</sup>                                          |
| 53T:47G (+EDA) | Glycidyoxy group<br>N-H bending                | 1250 cm <sup>-1</sup> and 3045 cm <sup>-1</sup> (weak bands)<br>1570 cm <sup>-1</sup> |



**Fig. 4.** TGA thermograms of glycerol-doped MSs. The TGA of an aqueous glycerol solution 66 wt% water + 34 wt% glycerol is also displayed.



**Fig. 5.** Leaching test results for 100T, 46T:54M, 53T:47G and 53T:47G (+EDA) MSs.

The viscosity increase was found indeed to be mainly correlated with the hydrophobicity of the MSs' shell. A more hydrophilic shell contributes to a higher viscosity increase, mainly resulting from reaction of adsorbed moisture species with NCO groups of Ongro-nat 2500, as well as some leaching of glycerol and some possible remaining water. Since the MSs' shell composition interferes with this behavior and all the MSs herein present show a different composition, it was not possible to infer about the effect of the porosity in the leaching behavior, i.e. there is a mix effect coming from the shell composition, and corresponding hydrophobicity behavior, and porosity.

A decrease in the leaching tendency with the addition of MTES in the silane precursor formulation is clearly observed. The hydrophobic methyl groups from MTES tend to decrease the affinity to water species at the surface of the MSs. The MSs composed of GPTMS-derived organosilica, as well as those derived from GPTMS and EDA, hardly show any leaching. The MSs composed only by GPTMS, as well as those with GPTMS and EDA, hardly show any leaching. Indeed, the FTIR analysis demonstrates that the 53T:47 G MSs contain the lowest amount of encapsulated glycerol, suggesting the lowest observed leaching. However, it is not the case for 53T:47G (+EDA), since a considerable amount of encapsulated glycerol was detected. Therefore, it is possible to state that the

combination of silica/epoxy resin within the MSs' shell significantly contributed to a decrease in the leaching observed for the silica based MSs.

The shaking rate test results in Table 4 indicate that after 120 h the difference in the shaking rate between the reference aerosol can (formulation without MSs) and the one with silica MSs (100T) is remarkable (5 points in the 10 points scale), indicating a strong increase of the pre-polymer viscosity and a decrease of the shelf life to unacceptable values. On the other hand, the addition of 46T:54M, 53T:47G and 53T:47 G MSs does not seem to influence the shaking rate within such testing period.

The curing time test results in Fig. 6 show that all the tested MSs contributed significantly to the curing process, as shown by the faster curing rate in the presence of MSs. The MTES-derived MSs lead to the fastest foam curing. In detail, foams cured in the presence of these MSs become tack-free 1 day prior to foams cured with the remaining MSs, and 2 days in advance than the reference foam.

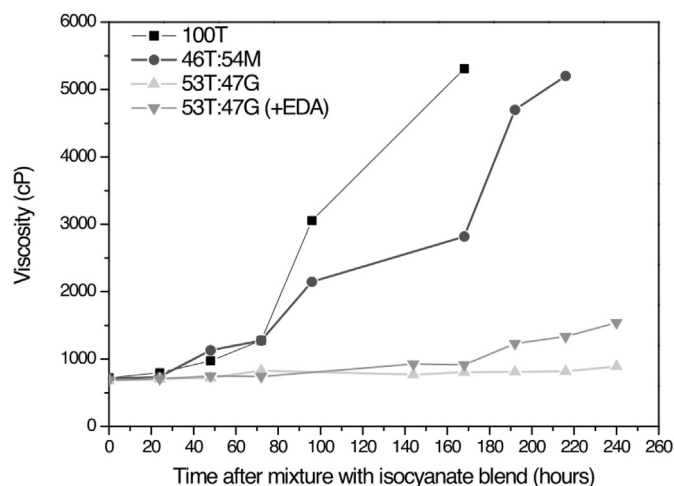
On the other hand, GPTMS-derived MSs, including 53T:47G (+EDA), displayed a poorer curing power than MTES-derived MSs. As already stated, the 53T:47 G MSs do not contain as much glycerol as the MTES derived MSs, which might limit the curing effect and the 53T:47G (+EDA) MSs, since they contain epoxy resin moieties in their composition, are expected to be stiffer, exhibiting a limited

**Table 3**  
Calculated percentage of glycerol and water content for each MS sample.

| Microspheres   | Onset Temperature °C | Average Temperature °C | Glycerol % | Water % |
|----------------|----------------------|------------------------|------------|---------|
| 100T           | 121.7                | 218.0                  | 25.2       | 10.2    |
| 46T:54M        | 184.0                | 257.0                  | 36.4       | 4.7     |
| 53T:47G        | 185.5                | 257.0                  | 17.9       | 1.7     |
| 53T:47G (+EDA) | 137.3                | 215.6                  | 26.5       | ≈ 0.0   |

**Table 4**  
Shaking rate test results for the MSs.

| Sample         | Shaking rate (hours) |    |    |     |
|----------------|----------------------|----|----|-----|
|                | 0                    | 72 | 96 | 120 |
| Reference      | 5                    | 5  | 3  | 3   |
| 100T           | 5                    | 4  | 1  | –2  |
| 46T:54M        | 5                    | 4  | 4  | 3   |
| 53T:47G        | 5                    | 4  | 3  | 3   |
| 53T:47G (+EDA) | 5                    | 4  | 4  | 2   |



**Fig. 6.** Curing rate test results for various MSs.

tendency for rupture and influencing the release of the encapsulated glycerol upon spraying.

The effect of the MSs in the curing tests is correlated not only with the amount of encapsulated glycerol, which is affected by the MSs' porosity and morphology, but also with the capability for the MSs to burst by pressure drop effect during the spraying process. This capability is not only correlated to the MSs' size, i.e. smaller MSs are more difficult to burst, but also with the stiffness of the shell material.

#### 4. Outlook and conclusions

Glycerol-doped silica and organosilica hybrid MSs obtained via template-assisted sol-gel process using TEOS, MTES and GPTMS silane precursors were synthesized and used to enhance the curing process of polyurethane one component spray foams.

The addition of methyl and glycidylxy organic functionality to the silica based MSs enabled the achievement of hybrid MSs with a decreased leaching and a reduction in the amount of water species, in comparison with inorganic silica based MSs, contributing to the product shelf-life. All the developed MSs were found to contain encapsulated glycerol and to contribute to the curing process of PU foams. Specifically, GPTMS-derived MSs synthesized with ethylenediamine, exhibit good performance in terms of glycerol encapsulation and leach-proof behavior, but reduced curing power due to high mechanical strength that prevents microparticle rupture by pressure drop at the spraying step.

The best compromise between fast curing and low leaching (acceptable shelf-life) is obtained from a mixture of MTES (54%, in molar terms) and TEOS (46%). Dubbed *GreenCaps* (a tradename of Greenseal Chemicals), these MSs contain about 36% in weight of microencapsulated glycerol and significantly contribute to

accelerate the curing process being, therefore, a promising solid curing agent for PU OCF formulations marketed in pressurized vessels.

Contrary to polymer capsules, these sol-gel MSs do not need to be stored in a solvent, which makes them easy to manipulate, while not adding any further solvent inside the aerosol can.

The scope of these findings is significant, from both health and safety, and economic viewpoints. MDI employed in most spray polyurethane foam formulations is toxic [19], and the isocyanate molar excess typically used in OCF cans affords a remaining amount of unreacted (free monomeric) isocyanates that for concentration values above 1 wt% and below 5% since May 2013 requires insertion in the can of the "Harmful" indication of danger (the St-Andrew's Cross) and of R40 and R42/43 labels ("limited evidence of carcinogenic effect" and "may cause sensitisation by inhalation and skin contact") [20].

In general, the reduction of the molar ratio NCO/OH in the aerosol can negatively impacts the foam properties. Hence, achieving free monomeric isocyanate content below 1%, but also an acceptable overall foam structure quality, a good output and a shelf life long enough (12 months of can storage at ambient temperature) is a challenge, that is being met for example by using monohydric alcohols preventing chain extension and small amounts of toluene diisocyanate [21]. Having a curing agent that accelerates and extends curing of said new formulations with ultralow values of free monomeric MDI becomes even more important.

From an economic viewpoint, it should be considered that in the construction industry, reducing building times is a crucial competitive advantage. Reducing the curing time of the foam by, for instance, 50% will have a significant beneficial impact on construction companies, so they can proceed faster with their work. Finally, the use of glycerol as curing agent, with its three hydroxyl groups, results in lower percentage of free monomeric isocyanates and higher crosslinking density of the cured foam [22], which in its turn results in less shrinkage and less outflow of the sprayed material.

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