

Solid Curing Agents for Polyurethane Foams: Proof of Concept of the Release Mechanism

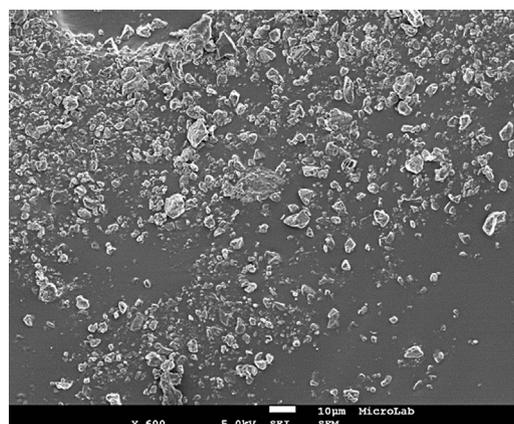
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We show the first evidence that the microporous GreenCaps organosilica microspheres, functionalized with glycerol and sprayed from a pressurized one component polyurethane foam completely break and release their functional payload, thereby noticeably increasing the rate and the extent of the foam's curing. Further positive results concerning the main froth parameters used by urethane foam manufacturers in the presence of the GreenCaps confirm the potential of these materials to cure better and greener spray polyurethane foams.

1. Introduction

Spray polyurethane foam (SPF) is a multitasking material which both air seals and insulates, reducing energy consumption in buildings and replacing in a single product for numerous other products.^[1] In addition to two-component foams, in which the chemical components that make up the foam are kept separated in different containers until mixed; urethane "one-component" foams (OCF) cured by atmospheric moisture are self-expanding, adhesive gap fillers in which the foam has already been partly mixed and partly reacted. Introduced in the early 1970s,^[2] OCF are available in pressurized cans at retail locations which are being widely utilized in construction (almost 500 million cans sold in 2013, growing at 6% annual rate),^[3] as handlers can rapidly fill all existing gaps with a foam that once fully, cured doubles its original volume.^[1]

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In general, the isocyanate containing two isocyanate groups ($R-(N=C=O)_2$) used by the OCF industry is methylene diphenyl diisocyanate (MDI, Component B) which reacts with a blend of polyols having two or more hydroxy groups per molecule ($R'-(OH)_{n \geq 2}$), in the presence of catalyst, blowing agent, flame retardant, and surfactant (Component A). The OCF producers mix the Component A and the Component B in an aerosol can which is sealed and pressurized. At first polymerization takes place with formation of a prepolymer whose monomers are linked via urethane bonds.

Upon dispensing through a valve the pressurized content, the liquid prepolymer rapidly expands into a low-density froth due to the evaporation of the blowing agent. The froth exposed to air cures by reaction of the unreacted isocyanate groups with water present in the ambient moisture (an exothermic reaction releasing 47 kcal/mol), resulting in the conversion of remaining $-NCO$ groups into linked amino groups, with concomitant CO_2 production that causes a second expansion of the froth and heat release.^[4]

The initially discharged foam thus, expands and achieves a tack-free (non-viscous) state, sealing hollow spaces (as those present when sealing windows, doors, and filling small gaps and cracks) with a low-density and eventually

rigid foam. Air insulation is so significant for effective building insulation during winter that sealed walls of the same thermal resistance (R value) perform equally well regardless of the type of insulation used, as long as effective sealing is in place.^[5]

Free MDI is toxic^[6] and since late 2010, all SPF cans commercialized in the European Union containing levels above 1% free MDI monomer (on the total amount of chemicals in the aerosol can) require a harmful warning together with the “R40” risk label (“Limited evidence of carcinogenic effect”).

When it is fully cured, the foam is stable and does not represent health and safety hazard.^[7] However, the spray foam continues to react for several hours, afterward application when uncured isocyanates can cause eye, skin, and lung irritation.^[8]

In general, a number of methods of reducing the NCO:OH ratio at the prepolymer stage exist. However, most of them, impair performance because these prepolymers have an undesired high degree of oligomerization, eventually affording, when cured, poor physical and thermal properties.

We have recently introduced the *GreenCaps* organosilica-based microspheres encapsulating glycerol (35 wt% glycerol) as new solid curing agents affording the formation of OCF of enhanced performance (higher rate and extent of curing) and better sustainability profile.^[9] In detail, mixed with the polyurethane prepolymer mixture, the ceramic *GreenCaps* (a tradename of Greenseal Chemicals) tested under standard conditions to cure one component PU formulations, showed the prolonged stability required for practical application.^[9]

It is not clear, however, whether the enhanced curing action of the microspheres is due to the action of the integer microspheres; or to the rupture and release of the entrapped glycerol, especially considering that the *GreenCaps* were recently shown to break upon decompression/compression cycle during advanced measurements of their textural properties.^[10] We now show evidence that the *GreenCaps* sprayed from a pressurized OCF can do indeed break and release the valued payload, thereby increasing the rate and the extent of urethane foam curing.

2. Experimental Section

We have reported elsewhere^[11] the synthesis of the partly methyl-modified silica microparticles tradenamed *GreenCaps*. We have also extensively characterized^[10] the materials by SEM, TEM, DRIFT, and TGA/DSC^[12] analyses, showing evidence of glycerol effective microencapsulation (35 wt%) within the inner microporosity of organosilica microparticles of perfectly spherical morphology, about 60 μm in size. The foam was investigated by SEM using a JSM7001F microscope (JEOL, Tokyo, Japan), in secondary electron mode, operated at 10 kV.

The *GreenCaps* were washed twice with hexane (vacuum filtration), dried (in an oven at 60 ° for two days) and tested under the same standard test conditions developed at Greenseal Research Portugal. Opposite to many other unstable polymer capsules, and in agreement with the known excellent mechanical and physicochemical properties of sol-gel silica microencapsulants,^[13] the sol-gel microspheres are physically and chemically stable and do not need any special handling such as being stored into a solvent or kept in moisture-free environment.

First, an isocyanate blend (polymeric MDI, Ongronat 2500)^[14] was mixed with 5wt% *GreenCaps* (related to the polyol blend weight) using a spatula for 2 min at room temperature until the microspheres were uniformly dispersed. The mixture was then left without stirring at room temperature, measuring viscosity at selected times. The viscosity of the mixture was monitored (via a REL cone and plate viscometer) every 30 minutes for 6 h; and then once per day (at least) until a *plateau* was reached. Then, the aerosol can was filled with a Greenseal's proprietary PU prepolymer mixture, consisting of component A followed, in order, by the *GreenCaps* and by component B. The can was then sealed and the mixture was added with the blowing gas (a mixture of a blend of propane/isobutane and dimethyl ether, added in proprietary amount) until reaching the pressure typically employed in commercial OCF cans (6 bar). The aerosol can was then vigorously shaken for around 1 min. Similarly, the shaking rate (SR) of the aerosol cans was frequently assessed during the first 3 d until reaching a constant value which indirectly indicates that there is no increase in viscosity inside the can (and thus absence of leaching and curing). A thermometer applied to the can outer surface did not show any increase of temperature at any time.

All these outcomes indirectly exclude any catalytic effects of the microparticles acting as Lewis acidic sites.^[15]

Remarkably, after 1 month of ageing at room temperature (23 °C) all the cans were still shakable (shaking rate SR~1, compared to SR~4 of the reference can without microspheres) meaning that

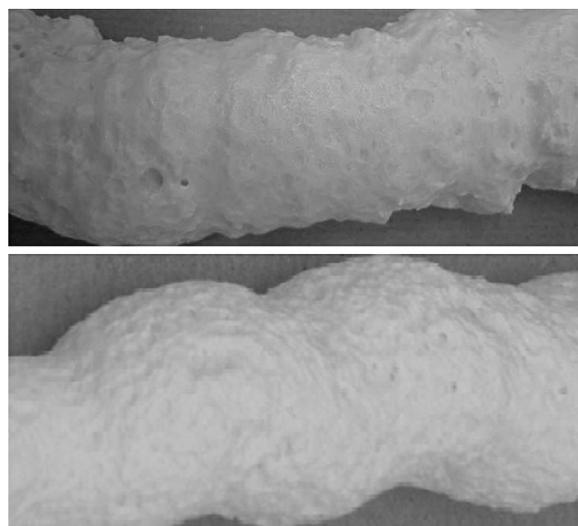


Figure 1. Foam obtained after spraying the reference OCF mixture 456 (top) and the 456 blend added with 5 wt% *GreenCaps* (bottom).

Table 1. Curing speed of PU foams sprayed from different cans at 23 °C and 40% RH

Foam #	String time [start] (min)	String time [end] (min)	Tack free time (min)	Cutting time (h:min)	Output at 5 °C (g/s)	–NCO in the froth (%)	SR at 5 °C (h)
456 (no GreenCaps)	2	19	35	1:50	7.3	8.9	3
591 (456 with 5 wt% GreenCaps) [*]	0	16	29	n/m	6.2	7.9	3

^{*}Related to the polyol blend weight.

there was a low increase in viscosity, but the can content remained liquid and, therefore, sprayable.

The prepared cans were submitted to a series of tests, which include the spray and the evaluation of the foam properties at 23 °C, when dispensed from the can in a low moisture environment. The string time (the time for which strings start to be pulled from the foam), tack-free time (the time when the final foam has lost its tackiness and can then be handled if required) and cutting time (the time it takes for the foam to become hard enough and dry to be cut with a knife), were measured for each froth sample in order to evaluate the curing speed and foam quality.

For each sample, the amount (%) of unreacted –NCO groups on the froth was assessed according to well established standard method,^[16] along with the output at 5 °C. From a technical viewpoint, the froth output is acceptable when it is above 4 g/s (for a 395 mL can). The output value expressed in g/s and measured at 5 °C, consists of the measurement of the amount of material exiting the can during a certain period of spraying time (typically 10 s). 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 h before spraying. Here, the output was measured one month after preparation of the can.

3. Results and Discussion

Compared to the conventional foam, the more viscous froth obtained from the precursor mixture added with 5 wt% *GreenCaps* leads to formation of a “dog-tail” shaped foam

(Figure 1). This is the first, visual sign of formation of a foam of enhanced quality.

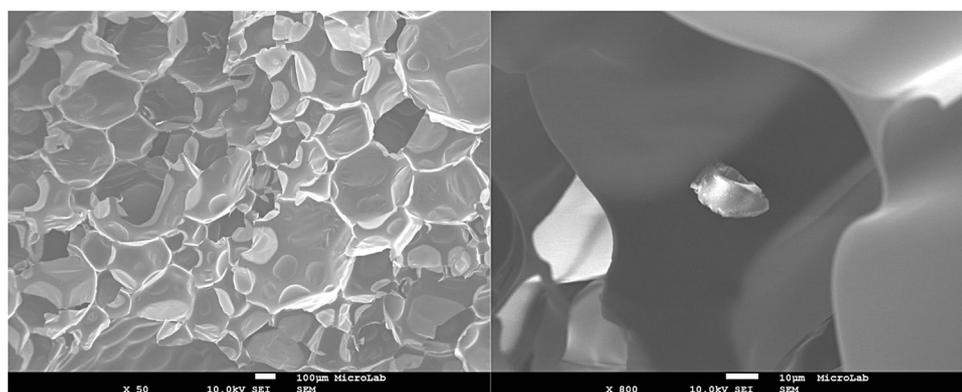
To quantify improvement, Table 1 shows the three parameters for curing speed evaluation (string time, tack-free time, and cutting time), which are provided to end users by OCF manufacturers.

Results in Table 1 show that the foam obtained from the aerosol can including 5 wt% *GreenCaps* microspheres (related to the polyol blend weight) has a distinctly lower string time and a lower tack free time when compared to the reference foam (456) with no added microspheres.

Contrary to the foam obtained with no *GreenCaps*, the foam containing the microencapsulated curing agent starts to cure immediately after spraying, and the overall curing process is faster, with a tack free time of 29 min versus 35 min for the reference sample. Furthermore, the amount of unreacted –NCO groups in the froth is 11% lower (Table 1, column 7). The reduction in the output from 7.3 to 6.2 g/s is acceptable, especially when considering that no difference in the shaking rate at 5 °C was observed (Table 1).

As mentioned above, the dried *GreenCaps* microspheres added to the isocyanate + polyol blend formulation 456 and pressurized, remained leach-proof for more than one month. Hence, the content was sprayed and the foam analyzed by SEM microscopy to identify the status of the sprayed *GreenCaps*.

No microspheres were observed in the foam. We rather observed just a piece of a broken microsphere (Figure 2,

**Figure 2.** Foam obtained after spraying the reference OCF mixture 456 added with 5 wt% *GreenCaps* (left). Magnification (right) shows evidence of a broken *GreenCaps*.

right), containing Si in its composition, inside an open cell of the foam structure. This showed the first evidence of the *GreenCaps* rupture as, indeed, the single microscopic piece of glass was atomically analyzed revealing its silicate nature (Si and O main components).

In order to therefore understand whether the pressurized *GreenCaps* break or do not break upon spraying at room temperature, an aerosol can containing only the microspheres and the propellant (blowing component) was prepared. The can was pressurized at 6 bar and sprayed directly onto the sticky part of a plastic tape, where the integer or broken *GreenCaps* would remain attached.

To our delight, Figure 3 shows that along with a few partly broken and deformed microspheres, the vast majority of the *GreenCaps* were ruptured affording small pieces of the original microspheres; a finding in full agreement with rupture and release of the payload recently observed upon pressurization-depressurization cycles of the *GreenCaps*.^[11]

4. Conclusions

We have shown evidence that the *GreenCaps* organoglass (methylsilica) microspheres functionalized with glycerol break and release their content upon spraying the microporous microspheres from an aerosol can pressurized at 6 bar, namely the pressure of commercial OCF cans.

Along with several other advantages,^[17] these materials offer the prolonged chemical and physical stability required for practical application of microencapsulated curing agents. For example, the target shelf life for commercial OCF cans is 12 months.

Added in 5 wt% amount of the polyol blend to a proprietary PU formulation, after an initial modest increase in viscosity (which is also due to the relative humidity), the viscosity and the shaking rate remain constant for several months. No difference in the shaking rate at 5 °C between the conventional formulation and the one added with the *GreenCaps* is observed. When sprayed, the froth/foam obtained from the aerosol can including the *GreenCaps* cures at distinctly higher rate, when compared to the reference foam with no added microspheres.

These findings go beyond previous attempts aimed to develop solid curing agents for thermally expandable particles for polyurethane adhesives,^[18] core-shell graphite/melamine-formaldehyde particles as flame retardants for rigid polyurethane foam,^[19] and polydimethylsiloxane microcapsules (which, indeed, required the use of organically modified silica particles mixed into the PDMS shell to improve the mechanical properties).^[20]

To understand the practical relevance of these findings, it is relevant here to notice that the typical current OCF system takes about 24 h to fully cure. In building

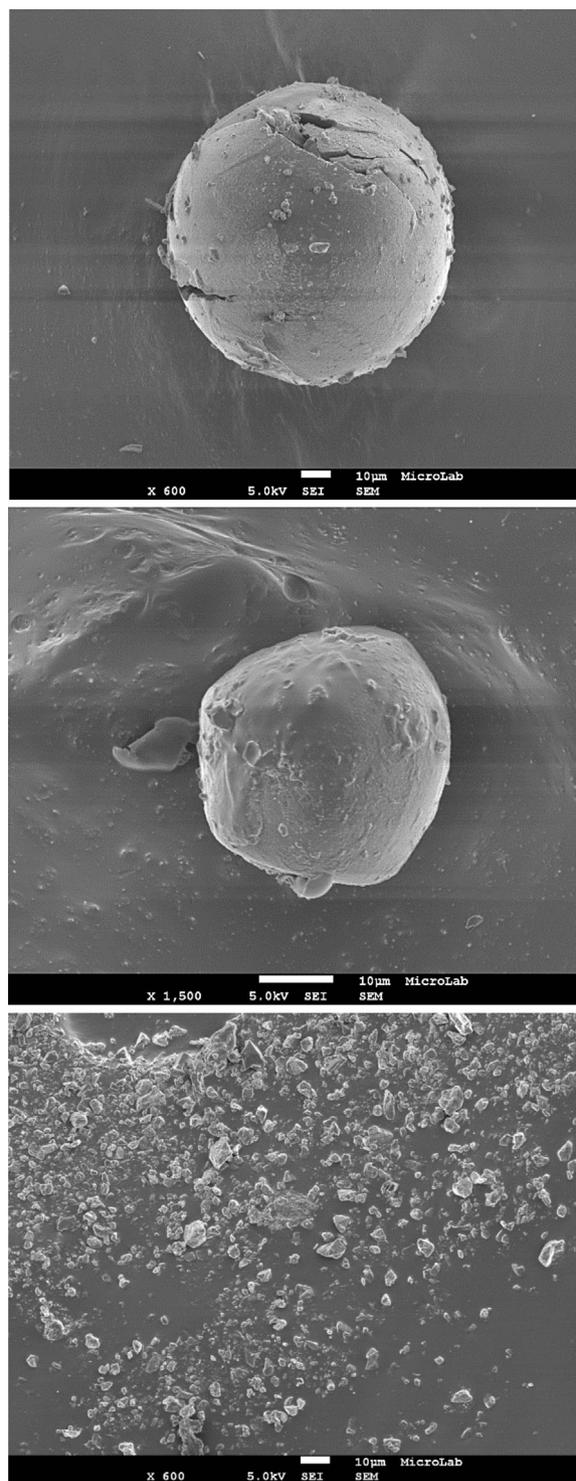


Figure 3. SEM pictures of the *GreenCaps* at sprayed at room temperature from an aerosol can pressurized at 6 bar. Besides a few partly broken and deformed microspheres (top), the vast majority of the *GreenCaps* are broken into small fragments (bottom).

construction industry, time is notoriously crucial. Reducing the curing time and improving the extent of the polymerization will translate into a huge advantage from the technical and health and safety viewpoints when compared with conventional OCF products. Users would get a foam that takes much shorter time to cure (so they can proceed faster with their work), with rapid conversion of undesirable –NCO groups in the polymer matrix ongoing formation.

The chemistry of polyurethanes is well known for its versatility,^[21] and an optimal PU precursor formulation will now be aptly developed to be used in the presence of the solid curing agents. Herein the crucial mechanism of the payload release through rupture of the pressurized microporous *GreenCaps* has been demonstrated. The route is now fully open to practical utilization of the *GreenCaps* to cure one component urethane foams, as well as other important thermoset polymers.

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