

# Enhanced One-Component Spray Polyurethane Foams via Sol–Gel Microspheres Doped with Aqueous Glycerol

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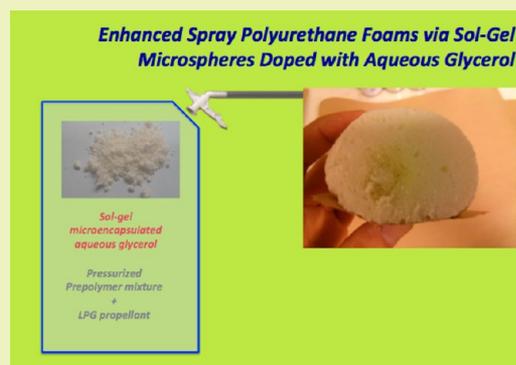
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**ABSTRACT:** The sol–gel microencapsulation of aqueous glycerol in silica-based microspheres affords functional materials that can be used to cure one-component polyurethane foams (OCF) formulations affording better and greener foam formation. These findings are important and may open the route to more sustainable materials, such as foams, coatings, adhesives, and sealants that are widely utilized in many industrial sectors.



**KEYWORDS:** Microencapsulation, Polyurethane, One-component foam, Sol–gel, Curing agent, Glycerol

## INTRODUCTION

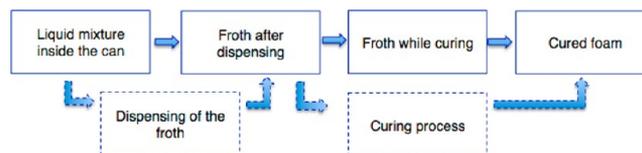
Polyurethane polymers are ubiquitous being used as foams, coatings, thermoplastic elastomers, and Spandex fibers.<sup>1</sup> In particular, urethane foams cured by atmospheric moisture (one-component foams, OCF)<sup>2</sup> are widely and increasingly utilized in the construction industry for installing door and window frames, to seal gaps in roof constructions, and to fix polystyrene and polyurethane panels to interior and exterior walls and insulate buildings.<sup>3</sup>

These spray polyurethane foams (SPF), both air sealing and insulating, are marketed in pressurized containers fitted with a dispensing device. In 2012, the global OCF market was estimated at 400 million aerosol cans, with an annual 6% rate of growth mainly taking place in the emerging markets.<sup>4</sup>

In general, polyurethane (PU) foams are formed by reacting an isocyanate containing two or more isocyanate groups ( $R-(N=C=O)_{n \geq 2}$ ) with a polyol comprising two or more hydroxy groups ( $R'-(OH)_{n \geq 2}$ ). These are then thoroughly mixed and permitted to expand and cure in the presence of an initiator and a foaming agent into a cellular polymer. In detail, the OCF chemical process involves four consecutive stages (Scheme 1).<sup>5</sup>

In the first step, a mixture of polyol blend, isocyanate, and blowing agent is added to the aerosol can where prepolymerization takes place with formation of urethane bonds (the reaction is exothermic and releases 24 kcal/mol).<sup>6</sup> Upon dispensing the froth, the liquid prepolymer rapidly expands into a low-density froth due to fast evaporation of the blowing agent. The froth exposed to air cures by reaction with ambient

## Scheme 1. Four-Stage Process Affording Cured Polyurethane Foam<sup>a</sup>



<sup>a</sup>Adapted from ref 5, with kind permission.

moisture, resulting in conversion of the remaining  $-NCO$  groups into (linked) amino groups and concomitant  $CO_2$  production that causes a second expansion of the froth and heat release (the reaction between water and isocyanate groups is strongly exothermic and releases 47 kcal/mol water). The initially discharged foam thus expands and achieves a tack-free (non-viscous) state, sealing hollow spaces with a low-density fully cured foam.

In practice, the OCF producers blend the polyol (component A), polymeric methylene diphenyl diisocyanate (PMDI, component B), and the blowing agent (component C).

Free MDI is toxic and since late 2010, all cans commercialized in the European Union containing levels above 1% free MDI monomer (of the total amount of chemicals in the aerosol can) require a harmful warning together with the “R40”

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risk phrase (“Limited evidence of carcinogenic effect”). Furthermore, the use of chlorinated paraffins as the blowing agent is under pressure for causing harm to the environment. In the European Union, the introduction of the “dead tree” and “dead fish” labeling on the aerosol cans or pressure vessels is under review. In the United States, federal agencies such as the Occupational Safety and Health Administration, U.S. Environmental Protection Agency, and National Institute for Occupational Safety and Health in 2009 formed a Federal SPF Workgroup along with the Consumer Products Safety Council.<sup>7</sup>

Clearly, there is a need to green the chemistry of polyurethane foams. This, among other things, requires the use of glycerol today obtained in large and increasing surpluses from the biodiesel and oleochemicals industry<sup>8</sup> in place of traditionally employed monoethylene and diethylene glycols (MEG and DEG) obtained from oil-derived ethylene. Furthermore, the higher amount of OH groups in glycerol compared to both MEG and DEG results both in considerably lower percentage of free monomeric MDI and higher cross-linking density of the cured foam.

In general, a number of effective methods of reducing the NCO:OH ratio at the prepolymer stage exist. However, most of them impair performance because these prepolymers have a high degree of oligomerization affording distinctly different molecular weight distributions and physical properties when cured. One exception, for example, is the newly developed formulation *Greenadduct*,<sup>9</sup> giving less than 1% monomeric MDI on the total chemicals along with froth/foam with acceptable physical and fire properties.

Because both glycerol and water are needed for optimal curing up to the state in which no free –NCO groups are present in the thermoset final polymer, we reasoned that the sol–gel microencapsulation and controlled release of aqueous glycerol might improve the curing process. Similar sol–gel microspheres and microcapsules indeed are emerging as a most promising alternative to traditional microencapsulation technologies.<sup>10</sup> Their facile and mild synthesis in liquid phase affords spherical free-flowing and floating glassy particles of high load (up to 80–90% in weight) that makes them ideally suited for several industrial applications.<sup>10</sup>

In the following, we report that aqueous glycerol microencapsulated in silica-based microspheres affords the formation of better and more sustainable one-component foams due to controlled release of glycerol and water from the microspheres.

## EXPERIMENTAL SECTION

**Materials.** Glycerol, tetraethylorthosilicate (TEOS), methyltriethoxysilane (MTES), *n*-hexane, decalin (decahydronaphthalene mixture of *cis* + *trans* isomers), 37 wt % hydrochloric acid (HCl), and sorbitane monooleate (Span 80) were purchased from Sigma Aldrich. All chemicals were used as received without further purification.

**Synthesis of Microspheres.** Adapting the procedure of Galgali and co-workers,<sup>11</sup> the micrometer-sized silica and organosilica microspheres were synthesized via sol–gel hydrolytic polycondensation of TEOS and MTES carried out in the droplets of a water-in-oil (W/O) microemulsion containing emulsified aqueous glycerol. Solvent *n*-hexane or decalin were employed as continuous organic phase and non-ionic Span 80 (sorbitane monooleate) as surfactant.

In detail, the sample CG6 of silica microspheres was synthesized starting from a W/O microemulsion comprising a 30 wt % aqueous solution of glycerol dispersed in a mixture of Span 80 and decalin previously stirred at 9500 rpm using the Ultra-Turrax T-25 with S 25 KR-18G dispersing tool (IKA). A prehydrolyzed TEOS solution at pH 3 obtained via addition of aqueous HCl (0.05 N) was added dropwise to this emulsion under constant stirring (overhead rotor at 600 rpm).

The resulting mixture was stirred at ambient temperature for 1 h. The temperature was then increased stepwise, first at 75 °C and then at 100 °C, keeping the mixture each time at the newly set temperature for 1 h. The microspheres thereby obtained were filtered through a glass filter and washed with decalin. The microparticles were stored under decalin until use.

Using a similar approach, a sample of silica microspheres (CG7) was synthesized starting from a W/O microemulsion comprising a 30 wt % solution of glycerol in water dispersed in a mixture of Span 80 and *n*-hexane previously stirred at 9500 rpm with the same Ultra-Turrax T-25 dispersing tool mentioned above. The prehydrolyzed TEOS solution at pH 3 was added dropwise to the latter emulsion, and the resulting mixture was kept at 25 °C for 1 h under constant stirring with an overhead rotor at 600 rpm. The temperature was increased up to 50 °C, and the mixture was kept under stirring at 600 rpm for 48 h. The white-yellowish material thereby obtained was filtered through a glass filter, washed extensively with *n*-hexane, and stored under *n*-hexane until use.

The sample of 5% methyl-modified silica microspheres CG8 was synthesized following the procedure previously employed for the CG6 sample, starting instead from TEOS alone, from a mixture of MTES (5% in molar terms) and TEOS (95% in molar terms). For all samples, the molar ratio  $r = \text{H}_2\text{O}:\text{Si}$  (i.e., between water and the hydrolyzable –OEt groups in the Si alkoxides) was set at  $r = 12$ . Table 1 lists the overall microemulsion composition used to synthesize the CG8 sample.

**Table 1. Overall Microemulsion Composition Used To Synthesize the CG8 Sample**

component	amount (mL)	amount (mol)
glycerol	11.92	0.163
water	30	1.67
Span 80	4.06	0.0093
decalin	128.37	1.16
TEOS	45.82	0.205
MTES	2.50	0.012
HCl (0.05 N)	17.02	$8.51 \times 10^{-4}$ (HCl)

**Test of Microspheres in Curing OCF Formulations.** The sol–gel microspheres were dispersed in reference OCF formulation 7720 to screen their behavior in curing one-component foams. In detail, formulation 7720 comprises of 2,2'-dimorpholinodiethylether as catalyst/accelerator, tris(1-chloro-2-propyl)phosphate (TCPP) as flame retardant, and B8871 (Evonik) as foam stabilizer. No aggregation or swelling of the mixture was observed for three consecutive days. Table 2 lists the formulations tested in the presence of the CG

**Table 2. OCF Backbone Compositions Tested with CG Microspheres**

formulation	microcapsule amount	tack-free time
7720	0	10 min
8234	2 pbw of GC7	8 min
8235	5 pbw of GC7	8 min
8288	2 pbw of GC8	not determined
8289	5 pbw of GC8	not determined

spheres, whereas Table 3 lists a typical formulation tested with the CG8 microspheres. The foam was each time sprayed on paper and in a mold. An output test was also conducted for each material's sample.

The CG6 and CG7 SiO<sub>2</sub> microsphere samples were first tested using four basic (B3) OCF formulations in 500 mL cans. We remind the reader that among B1, B2, and B3 acceptable foams (the foam presents no outflow, no curing streaks, no crumbling, and no cell collapse) classified according to flame retardancy, B3 is the cheapest and the most flammable.

The solid microspheres were thus added with the polyol blend containing Voratec SD 301, a polyol with functionality 3 (glycerol),

Table 3. Formulation Tested with CG8 Spheres Added to One 375 mL Can<sup>a</sup>

Formulation			
Voratec SD 301	74,1 g	0,07 kg	75,0 pbw
Voranol P 1010	24,7 g	0,02 kg	25,0 pbw
TCPP	41,5 g	0,04 kg	42,0 pbw
B 8871	6,9 g	0,01 kg	7,0 pbw
DMDEE	1,3 g	0,00 kg	1,3 pbw
Microspheres CG8	4,9 g	0,00 kg	5,0 pbw
Tot polyol	153,4 g	0,15 kg	155,3 pbw
Polyol per can	139,4 g	125,6 ml	
MDI	159,2 g	129,4 ml	
Propane	14,6 g	28,7 ml	LPG mix 30,00%
isobutane	34,0 g	60,4 ml	70,00%
Total LPG (P/B/IB)	48,6 g	89,1 ml	100,00%
DME	20,7 g	30,9 ml	
Tot gas	69,3 g	120,0 ml	
Tot weight chemicals	367,9 g	375,0 ml	

<sup>a</sup>Tegostab B8871: foam stabilizer. TCPP: flame retardant. Voratec SD 301: A low viscosity glycerine-initiated polyether triol. Voranol P 1010: polypropylene glycol, neutralized for use in the production of prepolymers. DMDEE: 2,2'-dimorpholinodiethylether catalyst.

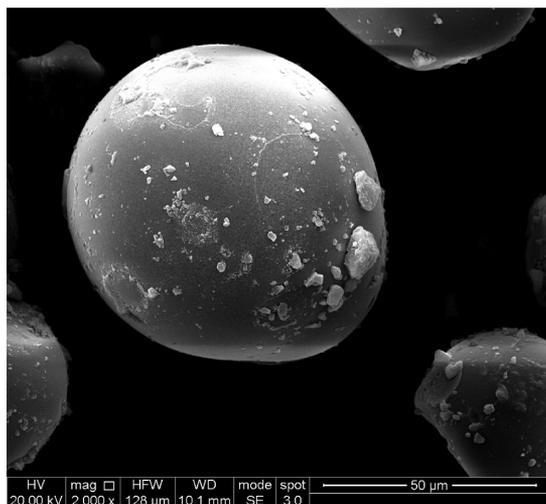


Figure 1. SEM photograph of one CG8 organosilica microcapsule.

and Voranol P 1010, a polyol with functionality 2 (propylene glycol). The optimized ratio in Table 3 balances these two components with the purpose to obtain a foam that is not very rigid and has no problems like shrinkage and outflow. Then, crude MDI was added to the polyol blend in the presence of the doped microspheres. If the mixture remained stable, then the LPG gas in the ratio shown in Table 3 was added to the sealed aerosol can, bringing the inside pressure up to 10 bar.



Figure 2. Reference OCF foam 7720 with no added spheres.



Figure 3. OCF foam 8234 formed with 2 pbw of added CG7 microspheres.

**Materials Analysis.** The microspheres were analyzed using a Philips XL30 ESEM microscope, operating at 25 kV, on samples sprayed on the stab and dried at room temperature, upon which a thin layer of gold had been deposited.

## RESULTS AND DISCUSSION

The SEM pictures show that the CG microspheres obtained from prehydrolyzed TEOS and TEOS + MTES mixtures are spherical, well isolated, and free floating, with a size around

60  $\mu\text{m}$  (Figure 1). We remind the reader here that sol–gel spheres obtained from emulsified silane precursor mixtures with a common  $\text{H}_2\text{O}:\text{Si} = 12:1$  ratio have about 25 wt % of water content (TGA data not shown). A detailed structural analysis correlating the materials' synthesis procedure with the properties and performance will be the object of a forthcoming study. Herein, we aim the report the performance of these materials in

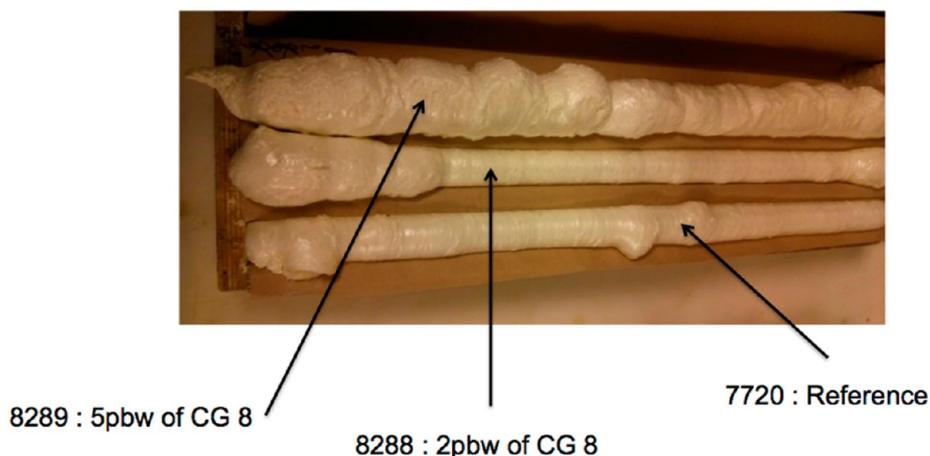


**Figure 4.** OCF foam 8235 formed with 5 pbw of added CG7 microspheres.

curing polymer mixtures of pronounced industrial and environmental relevance.

The cans added with CG6 microspheres heated up quickly, pointing to rapid leaching and reaction between glycerol and water with the prepolymer. When trying to add the LPG gas (after 4 h of preparation), both cans containing the CG6 spheres were already blocked due to curing of the OCF formulation. However, this was not the case for the cans filled with the CG7 sample of  $\text{SiO}_2$  microspheres. After 4 h, the can used for testing was still shakable, despite being more viscous. Hence, LPG was added and the pressure brought to 10 bar, after which a valve was inserted and the mixture sprayed at ambient temperature (23  $^\circ\text{C}$ ) through a dispensing gun.

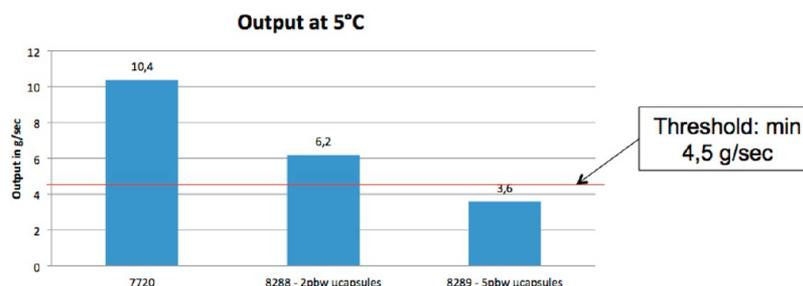
Figures 2–4 show that in each case excellent foams were obtained. However, the shaking rate was much lower for 8234 and 8235 formulations containing the CG7  $\text{SiO}_2$  microspheres compared to reference 7720.



**Figure 5.** CG8 spheres in powder form (top) are added to OCF precursor mixture. The pressurized content in the aerosol cans was thus sprayed on paper (middle) and in a mold (bottom). The 7720 OCF reference foam is also shown.



**Figure 6.** Sections of the OCF foams formed on paper using formulations comprising 2 and 5 pbw of added CG8 microspheres. The 7720 OCF reference foam is also shown.



**Figure 7.** Output for reference and OCF formulations doped with CG8 microspheres.

In other words, the  $\text{SiO}_2$  microspheres start leaching their content (glycerol + water) already in the prepolymer with glycerol acting as cross-linker and water reacting with the terminal -NCO groups. Because of the higher viscosity of the formulation containing the microspheres, the tack-free time is reduced from about 10 to 8 min. Accordingly, the foam output was lower for 8234 and 8235 formulations containing the doped microspheres (see below).

Previous insight on the behavior of these microparticles teaches that a slight increase in the capsule shell hydrophobicity significantly reduces the porosity of the shell<sup>12</sup> and significantly increases the material's hydrophobic–lipophilic balance (HLB).<sup>13</sup> Hence, new organosilica microparticles (CG8) were prepared comprising a 5% methyl-modified silica shell. A can was added with the new CG8 microspheres followed by the same polyol blend mentioned above followed by crude MDI.

Remarkably, now the can added with the CG8 microspheres did not heat up as much compared to the reference. Again, after 4 h of stirring, LPG was added to the aerosol can bringing the pressure to 10 bar. The pressurized can was left for 2 days at ambient temperature after which a valve was inserted and the OCF foam sprayed both in a mold and on paper. Also, in this case, like in the case of the GC7 spheres, the foams with the GC8 microspheres were more viscous, but again no problems were encountered spraying the aerosol can content from the pressurized can.

A clear difference among the three foams comprising 2 and 5 pbw (pbw = parts by weight of added CG8 microspheres) sprayed on paper is evident from Figures 5 and 6.

The nature and amount of added microparticles clearly impacts the foam properties. Viscosity increases and the output decreases. Yet, not only are the foam properties still good even in the presence of the GC8 microparticles, but a remarkable increase in the expansion property of the foam is observed; a property which is of obvious interest for a sealing material. It is indeed evident from the foam sprayed in a mold (Figure 5) that an increase in the usual post-expansion of the foam is observed

with comparison to the standard OCF formulation, which is due to extra curing of the foam upon contact with the water released by the doped microspheres.

Finally, it is also relevant that the large output decrease when more microspheres are added (Figure 7) apparently does not impact the properties of the final foams as shown by Figures 5 and 6. This, in turn, might lead to the use of less chemicals for optimal foam formation and thus to materials savings.

Silica and organosilica microparticles have excellent mechanical properties that allow smooth mixing with the prepolymer mixture and then with the LPG propellant. As shown by Galgali and co-workers,<sup>11</sup> sol–gel silica microspheres doped with glycerol have far better mechanical properties than, for example, urea-formaldehyde (UF) polymer microcapsules. Free-floating amorphous silica microspheres bear no static charge, do not swell in organic solvent, have a rigid and porous structure, and retain their high payload during manipulation. Once mixed with the polyurethane prepolymer mixture, the encapsulated water and glycerol molecules are barely released through the well cross-linked spherical shell in GC7 spheres, and even less through the 5% methyl-modified organosilica microparticles (CG8).

We have recently shown elsewhere<sup>14</sup> that sol–gel mesoporous silica spheres act as membranes allowing small hydrocarbon molecules of the LPG propellant to enter the mesopores of the amorphous silica (and organosilica) shell, pressurizing the spheres. Upon spraying the content of the pressurized can from 10 bar to atmospheric pressure, the microspheres release their content (water + glycerol) through the mesoporous membrane thanks to the large 9 bar gradient sensed by the particle shell. This provides the extra water amount needed for fully curing the prepolymer mixture and eliminate all unreacted NCO groups, i.e., as put by an industry's practitioner,<sup>15</sup> the single most important safety problem with polyurethanes.

In conclusion, we have discovered that the sol–gel encapsulation of aqueous glycerol (30% glycerol and 70% water) in silica-based microspheres provides functional materials that can be

used to cure polyurethane foam formulations affording better and greener foam formation. The microspheres partly leach their core content already inside the can. Whereas such leaching is almost instantaneous for SiO<sub>2</sub> spheres of larger mesoporosity obtained from shorter sol–gel polycondensation of the precursor silanes (CG6), this is not the case for the SiO<sub>2</sub> spheres obtained from prolonged sol–gel polycondensation in the hydrophilic emulsion droplets (CG7) and, even more, for the 5% methyl-modified silica microspheres (CG8).

These findings are important<sup>16</sup> and may open the route to advanced and more sustainable foam materials that find wide employment as insulating and air-sealing materials in the construction industry and, in perspective, also for PU, which is widely utilized used as coatings, adhesives, and sealants in many other industrial sectors, including packaging and textiles.

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### Notes

The authors declare no competing financial interest.

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