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Sol-Gel Microspheres Doped with Glycerol: A Structural Insight in Light of Forthcoming Applications in the Polyurethane Foam Industry

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Porous silica-based microspheres encapsulating aqueous glycerol can be potential curing agents for one-component foams (OCFs). Such agents have the advantage of an enhanced sustainability profile on top of being environmentally friendly materials. A synthetically convenient and scalable sol-gel process was used to make silica and organosilica microspheres doped with aqueous glycerol. These methyl-modified silica microspheres, named "GreenCaps", exhibit remarkable physical and chemical stability. The microspheres were characterized by scanning electron microscopy, transmission electron microscopy at reduced pressure, and cryogenic nitrogen adsorption—desorption analysis. The structure of the materials was also analyzed at the molecular level by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. As expected, the degree of methylation affects the degree of encapsulation and pore structure. Microspheres similarly methylated, however, can differ considerably in surface area and pore size due to the templating effect of glycerol on the organosilica structure. The results of the structure analysis reveal that glycerol is efficiently encapsulated, acts as a template, barely leaches over time, but is released by depressurization. A proper application of these microspheres can later on enhance both the environmental and health profile, as well as the technical performance (curing speed, foam quality, and froth thixotropy) of spray polyurethane foams.

Introduction

Spray polyurethane foams (SPF) cured by atmospheric moisture are widely and increasingly used in the construction industry as versatile sealants and adhesives to fix polystyrene and polyurethane panels to walls and insulate buildings. Such foams are formed by reacting a di- or polyisocyanate with a polyol containing on average two or more hydroxyl groups.[1]

In detail, the self-expanding, adhesive gap filler cured by moisture is a one-component foam (OCF) derived by methylene diphenyl diisocyanate (MDI) and comonomer polyols such as mono- and di-ethylene glycols.[2] The precursor polyol blend (component A) and oligomeric MDI (component B) are mixed with a blowing agent (component C) and pressurized within a can. This is stable for at least 12 months at ambient temperature. Once sprayed, the mixture reacts with moisture and cures up to the state in which no free isocyanate (–NCO) groups are present in the final thermoset polymer, which is the most important safety problem of the polyurethane (PU) industry.[3] When it is fully reacted or "cured", the foam is stable and does not present a health hazard. However, the foam continues to react for some hours after application, during which uncured isocyanates can cause skin, eye, and lung irritation and chemical sensitization when absorbed through the skin.[4]

We have recently described the use of porous silica-based microspheres encapsulating aqueous glycerol as potential new curing agents, affording the formation of OCFs with an enhanced sustainability profile.[5] The worldwide production of pressurized OCF cans has grown from 474 million in 2011 to over 500 million in 2013, with annual growth forecasted to continue at 4.9%—up to 600 million cans by 2016.[6] Accordingly, research aimed to improve the environmental and health aspects of spray PU foams is of significant relevance.

Silica and organically modified silica (ORMOSIL) microparticles doped with active organic species are emerging as high-performance materials with application in widely different domains.[7] With a rigid ceramic porous structure, glassy silica particles do not swell and can be mixed with the polyurethane prepolymer mixture without extra handling, without breaking, and with no leaching of the entrapped curing agent during prolonged storage of the cans. For example, when added at a concentration of up to 2 wt% of the isocyanate component, the 5%-methyl-modified microspheres leach a minimum

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amount of the entrapped glycerol and are stable for several months both at ambient pressure and under pressurized conditions typical of OCF cans.[8]

We now report the results of a thorough molecular and morphological investigation of these materials carried out using scanning electron microscopy (SEM), transmission electron microscopy (TEM), diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, and cryogenic N_2 adsorption measurements coupled to degassing cycles. The results are of general validity and provide new insights that will be useful for the development of silica-based "GreenCaps" solid curing agents for the polyurethane OCF industry.

Results and Discussion

A typical SEM photomicrograph of the 5%-methyl modified silica (**CG8**) microparticles shows isolated and partly aggregated microspheres polydispersed in size, with a predominant diameter of 50–60 μm (Figure 1, top). Limited aggregation adds to the benefits of these materials in light of possible practical applications (e.g. they do not clog the valve during spraying from a commercial OCF can).

The SEM pictures at a higher degree of magnification (Figure 1, bottom) show that the microspheres are comprised of organosilica grains of less than 100 nm size, namely the typical morphology of micro- or mesoporous sol-gel materials.

The TEM microphotographs of the same sample reveal another relevant characteristic of these microspheres: they burst upon depressurization. In fact, the TEM images are obtained under vacuum (pressure below 10^{-5} mbar) and clearly show fragments of broken microparticles of ~40 μm diameter (Figure 2, left) and splashes of the dopant blurring an image of even smaller fragments (Figure 2, right). The fact that the walls of the microspheres cannot withstand sudden depressurization may be advantageous for their foreseen application, which involves spraying from pressurized cans.

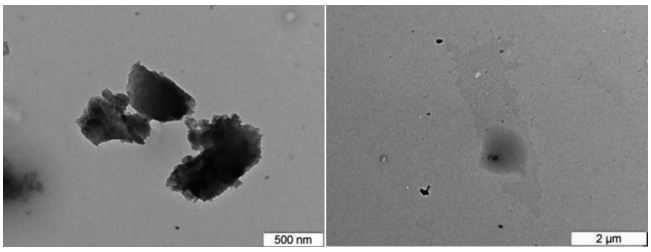

Figure 2. TEM microphotographs of the **CG8** dried microparticles obtained under vacuum (pressure below 10^{-5} mbar). White scale bars: left = 500 nm, right = 2 μm.

Detailed dynamic thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the microspheres carried out under nitrogen atmosphere show a consistent efficacy in the microencapsulation of the hydrophilic glycerol molecules within the inner porosity of both silica and organosilica microparticles.[9]

The amount of entrapped glycerol varies between 33 wt% for silica (**CG7**) and 35 wt% for 5%-methylsilica (**CG8**), confirming that glycerol is encapsulated within the large inner porosity and not adsorbed on the external surface. The TGA analysis also confirms that the microparticles are made of full silica and organosilica microspheres, and not of core/shell microcapsules, as the residual inorganic content of around 40 wt% is almost twice as large when compared to core/shell microcapsules.[10]

The DRIFT spectra of all the dried samples are compared in Figure 3, and the assignments of the visually detected bands are summarized in Table S1 in the Supporting Information.

Apparently, repeated washing with decalin removes all traces of Span 80, since there is no evidence of its strong νC=O band (expected at ~1740 cm^{-1}) in any of the spectra.

The number of active modes of glycerol and the overlapping of strong ones with the main

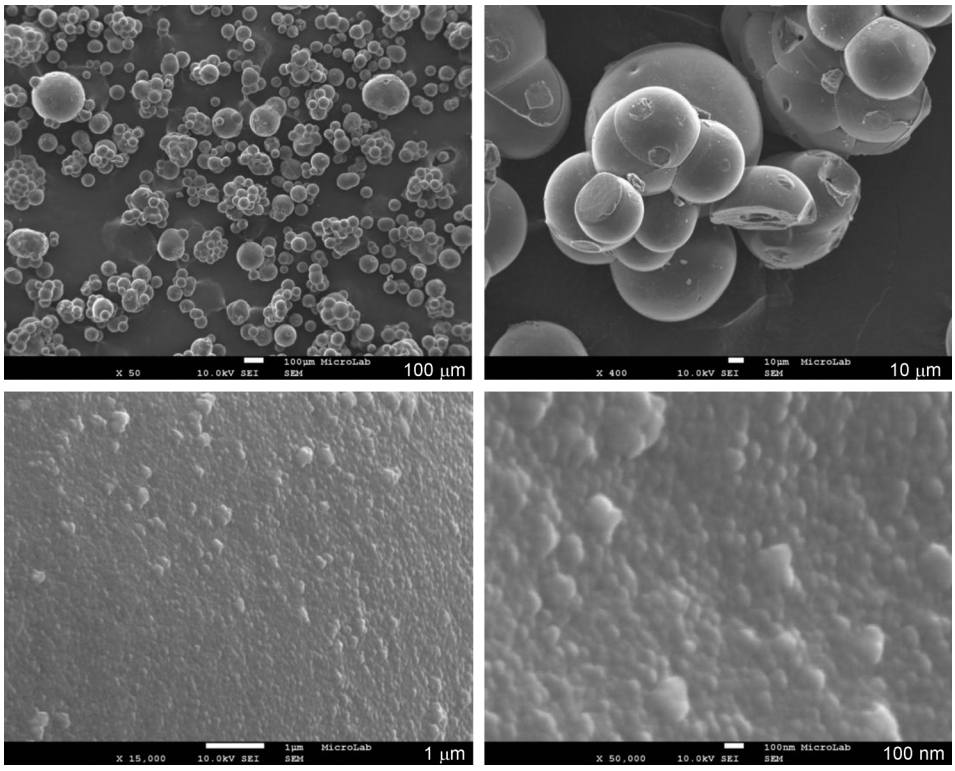

Figure 1. SEM photographs of 5% methyl-modified silica (**CG8**) dried microparticles doped with aqueous glycerol at four different degrees of magnification. Units of white scale bars are indicated in the lower right corner of each panel.

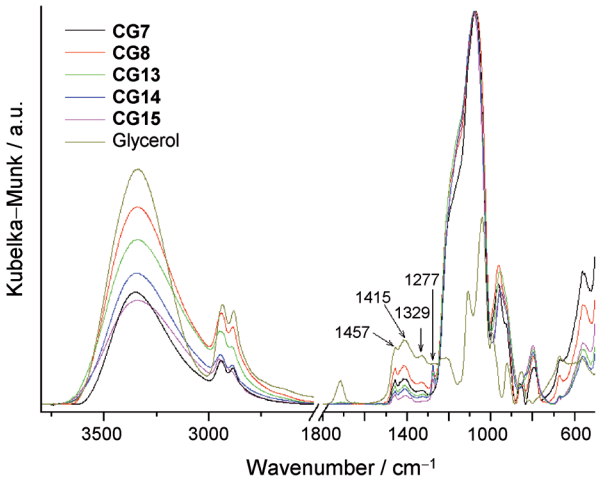

Figure 3. DRIFT spectra of dried silica microspheres doped with glycerol, normalized to the silica ν_{as}Si–O–Si band. The spectrum of pure glycerol is included for comparison, not normalized. For sample compositions, see Table 4 in the Experimental Section.

ORMOSIL bands render the fine analysis of the spectra challenging. The broad νOH band (centred at ~3300 cm^{-1}) results only from the overlapping of uncondensed silanol and glycerol OH groups, since there is no evidence of water in the spectra (absence of the δHOH mode at ~1630 cm^{-1}), probably removed by previous drying.

In the νSi–OH/νSi–O$^-$ region (950–960 cm^{-1}), there is also a partial overlap with two glycerol bands (at 993 and 924 cm^{-1}). Nevertheless, some conclusions may be drawn from these two spectral regions: microspheres **CG7** and **CG8**, which have similar glycerol loads, show different relative intensities of the OH-related bands (lower for **CG7**), which may be explained by a more extensive condensation in the inorganic microspheres. For similarly methylated samples with increasing amounts of glycerol (**CG15**, **CG13**, and **CG8**), the relative intensities of the same bands follow the sequence of the glycerol content in solution, suggesting that the final load in the microspheres follows the same order.

Samples **CG13** and **CG14** have similar initial glycerol content, so the dopant contribution to the intensities of these two OH-related bands should be comparable. As **CG14** is more organically modified than **CG13**, condensation could be more hindered, resulting in an increased relative intensity of the OH-related bands. However, the opposite trend is observed, suggesting that the effective glycerol load in the more organically modified microspheres (**CG14**) is slightly lower. This is confirmed by the spectral region correlated exclusively with glycerol deformation modes (at 1457, 1418, and 1331 cm^{-1}, assigned to the $\delta_{sc}CH_2$, δ_{ip}OH, and τCH_2 coupled with δCH modes, respectively). This suggests that a slight bleaching of glycerol may have occurred in the more organically modified **CG14** structure.

The profile of the ν_{as}Si–O–Si silica band (~1080 cm^{-1}) does not change significantly, in spite of the two superimposed glycerol modes. Apparently, the inorganic silica structure is not modified by methylation up to 10% methyltriethoxysilane (MTES) or by doping with glycerol up to 35 wt%. On the other hand, the glycerol fingerprints identified in the spectra are not shifted from their characteristic frequencies, showing that glycerol is only physically entrapped, and so available to be released.

The proof of methylation is clear from the observation of the (Si)–CH_3 deformation band, at 1277 cm^{-1}: it is most intense for microspheres **CG14** and is absent from the spectrum of microspheres **CG7**. However, the degree of methylation is not straightforward from this band due to its overlap with glycerol and silica bands, and this will be addressed below.

The spectra of the dried samples were deconvoluted in different regions into Gaussian and Lorentzian components, as detailed in Figures S1–S2 and Table S2 in the Supporting Information. In the CH stretching region (2500–3000 cm^{-1}), it was possible to identify the different contributions from the νCH_2 modes of glycerol and the ν_{as}(Si)CH_3 mode of MTES, as summarized in Table 1.

Table 1. Positions of the components obtained by deconvolution of the νCH spectral region.

Wavenumber [cm^{-1}]						Assignment
Glycerol	**CG7**	**CG8**	**CG13**	**CG14**	**CG15**	
—	—	2959	2956	2963	2956	ν_{as}(Si)CH_3
2941	2942	2937	2932	2938	2928	ν_{as}(C)CH_2
2881	2885	2886	2887	2889	2888	ν_s(C)CH_2

It is interesting to note that the microspheres with significant glycerol content (**CG7** and **CG8**) present minor band shifts of their νCH_2 modes, whereas for samples with lower glycerol content, one or both components appear shifted beyond the spectral resolution.

On the other hand, the ν_{as}(Si)CH_3 component appears at the characteristic wavenumber for ORMOSILs with an equivalent methylation degree.[11] The weak ν_s(Si)CH_3 component could not be retrieved,[12] which is acceptable, taking into account the low methylation degree of the samples and also the low symmetry expected for the methyl groups in these hybrid networks.

The glycerol content could also be withdrawn from the quantitative analysis of the spectra in the glycerol exclusive range (1300–1500 cm^{-1}). The results are displayed in Table 2. The relative glycerol contents in the dried samples (second row of Table 2) confirm the spectral observation and are in general agreement with the known values determined by TGA.[9] Comparison between samples **CG13** and **CG14** confirms that methylation has an influence on the final dopant quantity, with less organically modified structures favoring the glycerol stability within the microspheres.

The relative degree of methylation was also assessed using the integrated areas of the (Si)CH_3-related components [ν_{as}(Si)CH_3 at ~2960 cm^{-1}, δ_s(Si)CH_3, at 1277 cm^{-1}, and νSi–C at 830 cm^{-1}). Taking as reference the initial 5 molar% for sample **CG8**, the degree of methylation (third row of Table 2) compares reasonably well with the MTES content in the initial solu-

Table 2. Relative glycerol content and degree of methylation of the microspheres, as assessed from the DRIFT spectra.

	CG7	CG8	CG13	CG14	CG15
% Glycerol[a]	3.1	3.0	1.5	1.3	0.7
Relative % glycerol[b]	33	32	16	14	7.5
% Methylation[c]	—	5	5.4	6.8	4.2

[a] Obtained from the ratio 100×[Integrated area of the glycerol bands (1500–1300 cm^{-1})/total integrated spectral area]. [b] Experimental value obtained for **CG7** by TGA (33 wt%) taken as reference.[9] [c] Obtained from the ratio 100×[Integrated area of the $Si(CH_3)$ related components/total integrated spectral area], and referred to the initial methylation (in molar%).

tions: it is quite similar for samples **CG8** and **CG13** and higher for **CG14**. Only for **CG15** is the methylation degree lower than expected from the initial composition, as already suggested from the observation of the spectrum. As referred to above, this sample differs from the others, having been obtained from a sol with a considerably higher amount of silicon alkoxides.

The DRIFT spectra of the **CG7** (silica) and **CG14** (5% methyl-modified silica) microspheres only dried and after the second degassing program (see Experimental Section) are compared in Figure 4 for the typical glycerol regions.

For sample **CG14**, the main silica band becomes somewhat narrower, and the relative intensity of the νSi–OH/νSi–O^- band reduces significantly, due to the decrease of the glycerol νC–O modes at 1110, 1042, 993, and 924 cm^{-1}. The decrease is

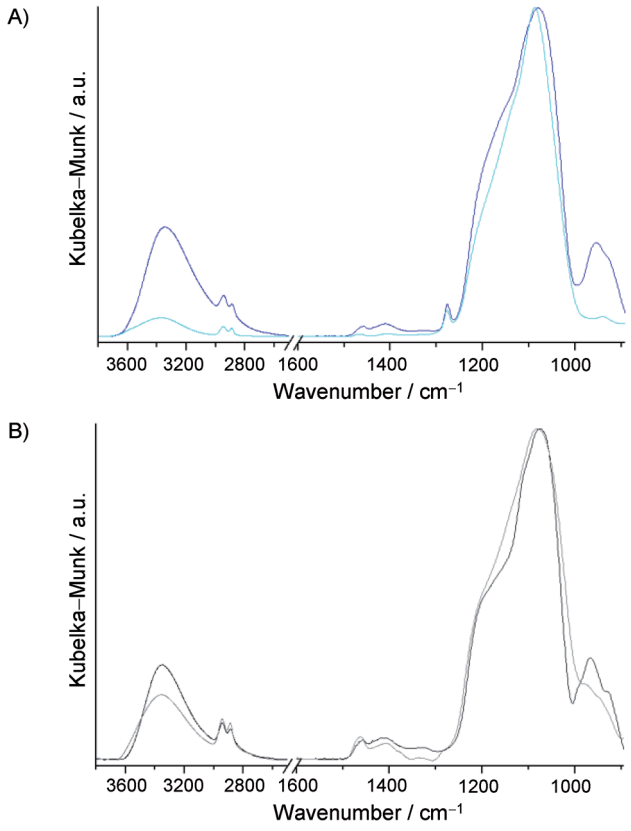

Figure 4. Comparison of the DRIFT spectra of silica microspheres **CG14** (A) and **CG7** (B) doped with glycerol, dried at rt (dark lines) and after degassing at 298/473/298 K (light lines), normalized to the silica ν_{as}Si–O–Si band.

also drastic in the νOH, νCH, and δCH regions. In summary, glycerol is released from the microspheres during the second degassing program, and there are no relevant effects on the structure induced by the degassing temperature.

On the contrary, the inorganic microspheres **CG7** release a negligible fraction of glycerol, indicating that it is more efficiently entrapped. Given the hydrophilic nature of glycerol, the interactions of the hydroxyl functions with the silanol groups of silica are certainly stronger—in full agreement with the well-known retention of alcohols entrapped in silica xerogels.[13]

The nitrogen adsorption isotherms of sample **CG14** after each degassing stage (Figure 5) allow the comparison of pore

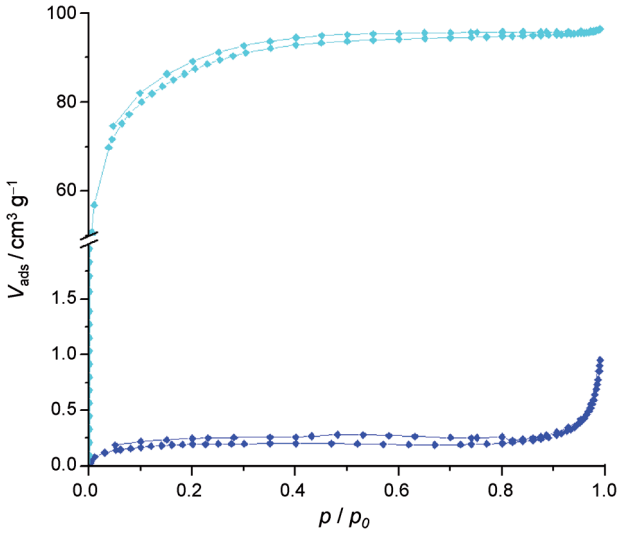

Figure 5. N_2 adsorption–desorption isotherms of microspheres **CG14** after degassing at 298 K (dark blue lines) and after the two-step degassing program (light blue lines).

structure of the same microspheres either filled with glycerol or almost glycerol-free. Both isotherms are type I, described by the Langmuir model and characteristic of microporous materials.[14] The small tail at saturation pressure is associated with interparticle voids, while the slight hysteresis in the desorption branch shows that there is some capillary condensation in small mesopores or in slit-like interstices between microspheres.[15]

However, there is a striking increase in porosity upon the second degassing program; the quantitative analysis of the isotherms showed a tremendous increase in the total pore volume (V_p) from 0.0011 to 0.1487 $cm^3 g^{-1}$ and in the specific surface area ($S_{Langmuir}$) from 0.98 to 406.66 $m^2 g^{-1}$. These effects may be interpreted assuming that there is a large fraction of micropores occupied by glycerol, which is mostly released upon degassing at 473 K.

Additionally, the Dubinin–Astakhov pore analysis, valid for the micro/mesopore frontier,[16] shows that the released glycerol molecules originated mainly from the smaller micropores, since the mean equivalent pore width slightly decreases from 1.82 nm to 1.73 nm as the pores become more available for nitrogen adsorption.

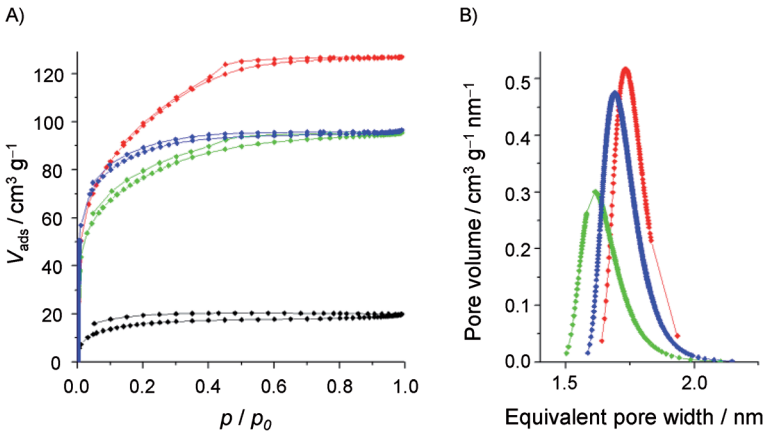

Figure 6. A) N_2 adsorption–desorption isotherms and **B)** Dubinin–Astakhov distribution for microspheres **CG7** (black lines), **CG8** (red lines), **CG13** (green lines), and **CG14** (blue lines), after degassing at 473 K.

Given that the complete degassing program yields a pore structure that is almost glycerol-free, to assess the approximate pore structure of the microspheres without dopant, the nitrogen isotherms and equivalent pore width distributions were compared for all samples after the said degassing program (Figure 6). All the isotherms are type I, with a small hysteresis, so all the samples are microporous. Moreover, all the organically modified samples are much more porous than the inorganic **CG7**, as confirmed by the pore data analysis summarized in Table 3.

Table 3. Specific surface area ($S_{Langmuir}$), total pore volume (V_p), and mean equivalent pore width for selected CG microspheres after degassing at 473 K.

Sample	$S_{Langmuir}$ [m^{2}g^{-1}]	V_p[a] [cm^{3}g^{-1}]	Pore width[b] [nm]
CG7	78.76	0.0305	—
CG8	487.41	0.1962	1.77
CG13	371.80	0.1474	1.65
CG14	406.66	0.1487	1.73

[a] Single point adsorption at $p/p_0 = 0.99$. [b] Mean equivalent (Dubinin–Astakhov).

The extremely low surface area and total pore volume of the inorganic microspheres **CG7** indicate a nonporous structure, to which glycerol has strong affinities (hydrogen bonds and even co-condensation), explaining the difficulty in being released. This is consistent with the extensive condensation suggested by the DRIFT spectra.

The effect of methylation may be evaluated by comparing samples **CG13** and **CG14**. The more modified **CG14** microspheres have a higher surface area and total pore volume and slightly larger micropores, which are consistent with the known effects of the methyl functionalization of the pore walls.

However, the degree of methylation is not the only factor affecting the pore structure. Although microspheres **CG8** and **CG13** are similarly methylated (5% in molar terms), the first are much more porous, with a much higher surface area and larger pores. This is certainly due to an effect of glycerol, as **CG8** has a considerably higher load than **CG13**. Glycerol is present from the first stages of the network formation, and, as glycerol has three lipophobic hydroxyl groups, the methylated micropore surfaces tend to open, yielding a more porous structure than anticipated for a similar organic modification. Therefore, glycerol acts as a template for the ORMOSIL structure.

Conclusions

The investigation of glycerol encapsulation in silica and methylsilica microspheres via SEM, TEM, DRIFT spectroscopy, and cryogenic nitrogen adsorption and desorption cycles shows a number of new results of general validity. First, glycerol is so tightly caged within the microporosity of pure silica spheres that it barely leached even by prolonged degassing at 473 K. Second, there is a consistent efficacy in the encapsulation of the hydrophilic glycerol molecules within the inner structure of silica and ORMOSIL microspheres. When the starting solution content is ~25 wt%, the amount of entrapped glycerol varies between 33 wt% for **CG7** (silica) and 35 wt% for **CG8** (5% methyl-modified silica) samples. Third, glycerol acts as a template for the ORMOSIL structure, with the three lipophobic hydroxyl groups tending to open the as-formed methylated micropore surfaces, eventually yielding a more porous structure than anticipated for similar organic modifications but lower glycerol content. Finally, it is shown that depressurization results in the release of glycerol by collapse of the microspheres.

The use of glycerol as curing agent for one-component foam (OCF) formulations instead of, for example, oil-derived glycols, is technically and environmentally convenient. The higher amount of hydroxy groups in the glycerol molecule (compared to diol glycols) results in both considerably lower percentage of free monomeric MDI and higher crosslinking density of the cured foam, which results in less curing shrinkage and less outflow of the sprayed material. Furthermore, glycerol is nontoxic and renewable—today being entirely obtained from the biodiesel and oleochemical industries.[17]

From a green chemistry viewpoint, it is also notable that the sorbitan oleate surfactant (Span 80) used to make the silica microspheres is biodegradable, nontoxic, generally recognized as safe (GRAS status from the US Food and Drug Administration), and derived from two natural products: oleic acid and sorbitol.[18]

Named "GreenCaps", these microspheres are currently being tested in Portugal as novel solid curing agents for polyur-

ethane OCF formulations,[19] eventually enhancing both the environmental and health profile and the technical performance (curing speed, foam quality, and froth thixotropy) of spray polyurethane foams.

Experimental Section

Microsphere fabrication

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

Materials synthesis: We have previously described the preparation of the SiO_2 spheres (**CG7**) and of the 5% methyl-modified silica (**CG8**) microparticles,[5] as well as that of the 10% methylated microspheres doped with glycerol (**CG14**).[9] In general, the microspheres were synthesized via sol-gel hydrolytic polycondensation of TEOS or of TEOS and MTES mixtures carried out in a water-in-oil (W/O) microemulsion containing aqueous glycerol dispersed in a mixture of *n*-hexane or decalin, as continuous organic phase, and Span 80, as nonionic surfactant of low hydrophilic-liphophilic balance (HLB) value (4.3) suited for W/O microemulsions.[20] The samples analyzed herein are identified in Table 4.

Table 4. Compositions of the CG samples doped with glycerol.

Sample	Initial solutions		Microspheres
	MTES [molar %][a]	Glycerol [wt %][b]	Glycerol [wt %][c]
CG7	0	25	33
CG8	5	25	35
CG13	5	12.5	—
CG14	10	10	11
CG15	5	8	—

[a] Relative to (TEOS + MTES) solution. [b] Relative to (TEOS + MTES + Glycerol) solution. [c] Determined by TGA.[9]

The samples are very light yellow and granular, with the exception of **CG15**, which is a fine powder (likely due to the fact that this sample was obtained from a sol with a considerably higher Si alkoxide amount).[9] All the samples were dried for seven days at rt, at 20 mbar.

Characterization

The microspheres were analyzed by field-emission scanning electron microscopy (FE-SEM) using a JSM7001F microscope (JEOL, Tokyo, Japan), in secondary electron mode, operated at 10 kV. The TEM micrographs were obtained using an H-8100 electron microscope (Hitachi, Tokyo, Japan), operated at 200 kV, with a LaB_6 filament. The samples were previously dispersed in EtOH and then dropped onto a Formvar-coated Cu grid and left to evaporate. The molecular structure was analyzed by infrared spectroscopy in diffuse reflectance mode (DRIFT), using a Mattson FTIR spectrometer with a Specac Selector (Thermo Fisher Scientific, Waltham, USA), in the range 400–4000 cm^{-1} (wide band mercury cadmium telluride detector), at 4 cm^{-1} resolution. The spectra were the result of ratioing 500 added scans for each sample against the same number of scans for the background (ground KBr).

The pore structure was analyzed by N_2 adsorption–desorption isotherms at 77 K using an ASAP 2020 physisorption analyzer (Micromeritics, Norcross, USA). The equilibration time was 15 s. This characterization was performed twice: after degassing at 298 K for 24 h (at 0.5 mbar) and after a further two-step degassing program: at 473 K for 120 min (at 10^{-2} mbar) followed by an additional cycle at 298 K for 24 h (at 10^{-2} mbar). During the first degassing at 298 K and at 473 K, some glycerol droplets were released to the sampling tube walls. These were removed, and the tube was cleaned. The second degassing program was intended to obtain structural and pore information on the more glycerol-free microspheres.

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Keywords: curing agent · glycerol · microencapsulation · polyurethane foam · silica

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