ACS Sustainable Chemistry & Engineering

Research Article

pubs.acs.org/journal/ascecg

Leach-Proof Sol–Gel Microcapsules as Curing Agents for One-Pot Thermosetting Resins

Rosaria Ciriminna,[†] Marzia Sciortino,[†,‡] Aster de Schrijver,[§] Delphine Desplantier-Giscard,[∥] François Béland,[∥] and Mario Pagliaro*[,†]

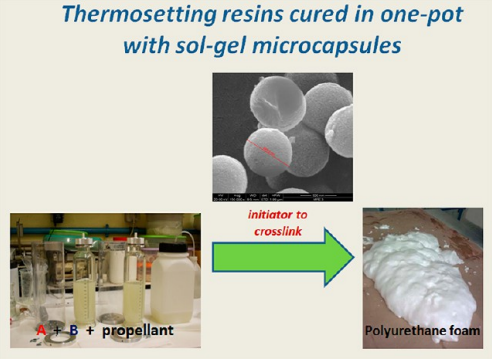
[†]Istituto per lo Studio dei Materiali Nanostrutturati, CNR, via U. La Malfa 153, 90146 Palermo, Italy

[‡]Dipartimento Sistemi Agro-Ambientali, Università degli Studi di Palermo, Viale delle Science, 90128 Palermo, Italy

[§]Greenseal Chemicals NV, Port of Ghent, Haven 2270, Belgicastraat 3, B 9042 Gent, Belgium

[∥]SiliCycle Inc., 2500 Parc-Technologique Blvd., Quebec City, Quebec, Canada G1P 4S6

ABSTRACT: The sol–gel microencapsulation of free-radical initiator benzoyl peroxide in sol–gel methyl-modified silica microcapsules of core/shell geometry allows curing of acrylate-based polyurethane and polyester resin formulations sprayed from a pressurized can without the need to compartmentalize reactants from the initiator to cross-link. These results open the route to widespread application of sol–gel microcapsules to efficiently cure polymer and composite mixtures that are widely used as functional coatings, molding compounds, adhesives, and sealants.



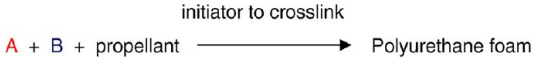
KEYWORDS: *Microencapsulation, Sol–gel, One-pot, Curing agent, Thermosetting resin, Benzoyl peroxide, Free-radical polymerization*

INTRODUCTION

The development of microencapsulated curing agents is a major objective of the thermosetting polymers industry,[1] particularly for applications concerning resins used as adhesives, sealants, molding compounds, and functional coatings.[2,3] The interest is also high toward the development of self-healing polymers based on capsule rupture.[4]

Curing agents are employed as initiators to cross-link the polymer. For example, polyurethane foams are formed by reacting an isocyanate with a polyol thoroughly mixed and permitted to expand and cure in the presence of an initiator (typically an organic peroxide mixed to a tertiary amine as accelerator) and a foaming agent (today simple hydrocarbons) into a cellular polymer. In the so-called "two component" foams (Scheme 1), the foam precursor A and its curing agent B are mixed at the nozzle where they start curing much more quickly than in "one-component" foams where curing is due to atmospheric relative humidity.

Scheme 1. Polyurethane Foam Formation



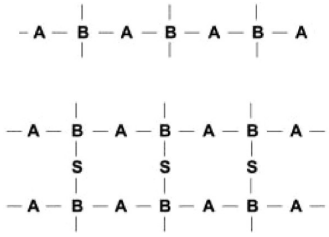
The reaction is exothermic, and the mixed liquid expands many times its original volume in a matter of seconds, forming a rigid foam plastic that chemically bonds to the surface to which it is sprayed. In detail, the isocyanate molecule contains two or more isocyanate groups ($R-(N{=}C{=}O)_{n\geq 2}$ (normally toluene di-isocyanate, TDI; or methyl di-*p*-phenylene isocyanate, MDI), and the polyol contains two or more hydroxy groups per molecule ($R'-(OH)_{n\geq 2}$).

Polyurethane is an excellent insulating material (λ = 0.023 W m^{-1} K^{-1}), particularly useful in keeping buildings warm during winter.[5] Especially as spray foam (SPF) sprayed directly into the gaps, walls, and roofs, thermoset polyurethane both insulates and air seals, offering one of the most effective ways to reduce energy consumption in construction. Accordingly, these foams are widely used at construction sites, and SPF is one of the fastest growing products in the construction marketplace.[6]

Polyester resins, in their turn, are widely used resin systems, particularly as standard laminating systems in the marine industry and composites industry.[7] In Scheme 2, "B" indicates the reactive sites in the molecular chains of the polyester "–A–B–". With the addition of styrene "S" and in the presence of an initiator to cross-link (typically a radical inititiator such as benzoyl peroxide), the styrene cross-links the polymer chains at each of the reactive sites to form, without the evolution of byproducts, a three-dimensional polyester resin that usually is a chemically resistant and hard solid.

Received: July 3, 2013
Revised: September 3, 2013
Published: September 9, 2013

Scheme 2. Representation of Polyester Resin Uncured (top) and Cured (bottom)



Prolonged research efforts have been devoted in the last two decades to identifying environmentally and economically viable alternatives to routes based on petrochemicals for both polyurethanes and polyester resins. Biologically derived building blocks such as soybean oil or glycerol can be used, such as in the case of soy-based polyurethanes by a nonisocyanate route[8] or like in the case of the insulation foam based on α-silanes where the prepolymer isocyanate group is bonded firmly to a silyl group.[9]

In this context, the effective compartmentalization of the curing agent (the initiator to cross-link) in leach-proof microcapsules would be highly desirable because in this case no reciprocal isolation of the A and B reagents from the initiator to cross-link would be needed, and much more precise polymerization would occur due to fast release of the curing agent where and when it is needed with all reactants mixed in one pot.

Traditional polymer-based microcapsules, however, generally suffer from poor chemical and physical stability and are not suited as leach-proof materials. For example, benzoyl peroxide (BPO), a peroxide initiator widely employed for radical polymerization of PU acrylate foams, was recently micro-encapsulated in urea-formaldehyde microcapsules that were then evaluated in terms of self-healing efficiency in bone cement formulations where such relative fragility is a boon.[10]

Similarly, when an organic peroxide curing agent is microencapsulated in a phenol-formaldehyde resin shell to cure unsaturated polyester resins, rapid and unwanted leaching of the curing agent occurs in response to the rising temperature encountered during the molding process.[11]

The sol−gel microencapsulation of functional molecules in porous silica-based glasses is emerging as a promising alternative among numerous microencapsulation technologies.[12] Accordingly, in a recent preliminary study aimed at investigating the structural properties of sol−gel microcapsules doped with the BPO cure initiator, we were concluding that encapsulation of this peroxide in micrometer-sized core/shell silica particles would stabilize the core material and allow the use of said microcapsules in place of dissolved BPO to cross-link polymers in industrially relevant applications.[13]

In the following, we describe the first synthesis of such leach-proof curing microcapsules, where a mesoporous shell is made of organically modified silica (ORMOSIL), and their use as curing agents of both polyester resins and acrylate-based polyurethane foams.

EXPERIMENTAL SECTION

Materials and Methods. We first remind that the free-radical initiator, curing agent, and cross-linking agent (di)benzoyl peroxide (BPO) in the pure state is a highly flammable explosive compound classified as toxic because of high acquatic toxicity.[14] However, BPO dispersed in water can be safely handled.

Microcapsules Synthesized with Ethanol and Toluene as Co-Solvents (MEB). A solution of deionized water (125 mL), ethanol (75 mL), cetyltrimethylammonium bromide (CTAB, 1.5 mL, 25 wt %), and aqueous ammonia (2.5 mL, 25 wt %) was stirred at room temperature at 5000 rpm using an Ultra-Turrax T-25 basic with S 25 KR-18 G dispersing tool from IKA until a clear solution was obtained. The resulting solution was mixed with a solution of tetraethylorthosilicate (TEOS, 8.2 mL), methyltrimethoxysilane (MTMS, 1.2 mL), and Luperox A70S (BPO dispersed in water, 70% w/w, 667 mg) dissolved in toluene (3.7 mL) under magnetic stirring.

The resulting mixture was left under agitation at 500 rpm for 24 h, after which the white precipitate formed was separated from the process liquor by filtration, washed extensively with deionized water, and mildly dried in an oven (40 °C) for three days. To further increase the amount of benzoyl peroxide entrapped in the microcapsule core, the MEB capsule synthetic protocol uses toluene as co-solvent.

The resulting capsules, whose average size was around 1 μm, were uniformly dispersed in the USPER backbone in the presence of the accelerator dimethyl aniline, flame retardant TCPP (tris(chloroisopropyl)phosphate), and foam stabilizer Tegostab B8870 (a silicone surfactant, Evonik) without aggregation or swelling of the mixture for three consecutive days, after which the can was ermetically sealed and added with the propellant LPG bringing the pressure up to 5 bar. Table 1 lists the detailed composition tested in the presence of the MEB capsules prepared according to this modified synthetic protocol.

Table 1. USPER Backbone Compositions Tested with MEB Microcapsules of Enhanced BPO Content

component	Resipur 9106
resin	134 g
dimethyl aniline	0.79 g
MEB	8.0 g
entrapped BPO	2.0 g
Tegostab B8870[a]	5.3 g
TCPP[b]	10.7 g
LPG	111 mL

[a]Tegostab B8870: foam stabilizer. [b]TCPP: flame retardant.

The scale-up of this synthesis was carried out as follows. Luperox A75 (1.866 g, 75 wt % BPO in water) was predissolved in 13 mL toluene. This solution was added to a solution made of TEOS and MTMS (24.6 and 3.6 mL, respectively) affording solution "A". A second solution (solution "B") was prepared by mixing deionized water (375 mL), ethanol (225 mL), CTAB (4.5 mL, 25 wt %), and aqueous ammonia (7.5 mL, 25 wt %) kept under fast stirring (7000 rpm) at 50 °C using a Ross HSM-100LC high shear mixer. Solution "B" was then added to solution "A" under stirring at 5000 rpm. After about 1 min, the particles condensed, after which the high shear mixing was replaced by smooth mechanical stirring for 24 h. The resulting product was separated from the process liquor by centrifugation, washed extensively with deionized water, and dried at 40 °C for three days.

Microcapsules Synthesized without Organic Solvent (MMB). A solution of deionized water (150 mL) and 3-aminopropyltrimethoxysilane (APTMS, 3 mL) was mixed under magnetic stirring (1000 rpm) with a solution of MTMS (9 mL) and BPO (Luperox 70, 300 mg). The resulting mixture was left under agitation for 24 h. The white precipitate was filtered, washed extensively with deionized water, and dried in oven at 40 °C for three days.

Materials Analysis. The capsules were analyzed using a JEOL microscope JSM-840A, while the particle size distribution was measured with a Malvern Mastersizer Hydro 2000S.

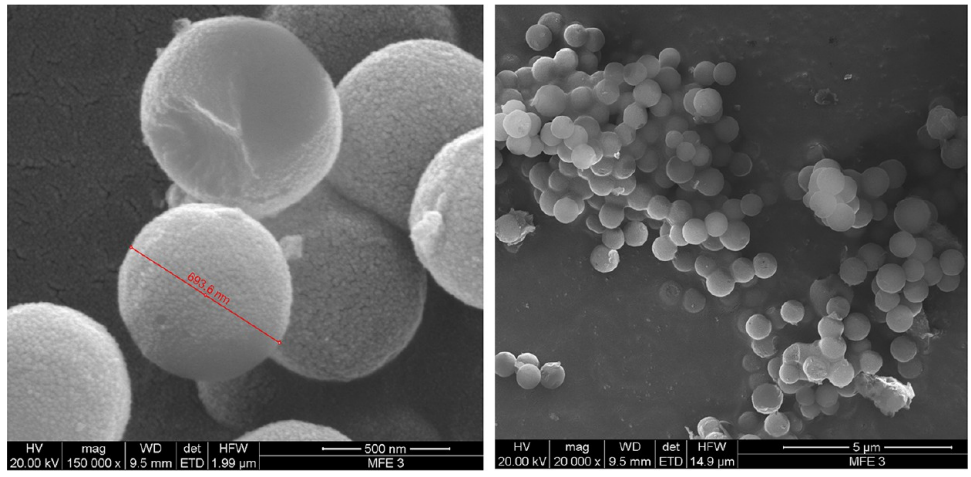


Figure 1. SEM photographs of MEB microcapsules.

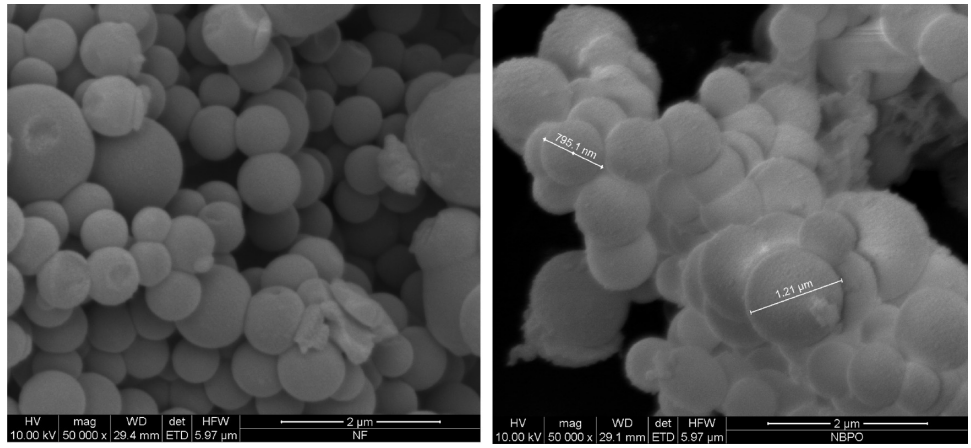


Figure 2. SEM photographs of MMB microcapsules.

Figure 3. Glass cans used throughout this work before (left) and after addition of backbone + MEB and backbone + MMB microcapsules (right).

RESULTS AND DISCUSSION

The SEM images show that the MEB capsules are spherical rather monodispersed and with sizes beween 700 and 900 nm (Figure 1).

Similarly, the SEM images in Figure 2 show that the MMB particles, too, are microspheres with sizes between 800 and 1200 nm (0.8 and 1.2 μm).

Test of Microcapsules in Polyester Resin Formation. The microparticle samples were tested in transparent glass cans in order to observe visible changes. Hence, we first studied the curing of an orthophthalic unsaturated polyester resin made of 66% polymer diluted in styrene (Resipur 9106)[15] using either the MEB and MMB capsular materials added to a 395 mL glass can (Figure 3).

Table 2 lists the mixture compositions tested. In unsaturated polyester resin (USPER) formulations, the initiator to cross-link is added to the resin shortly before use. Accelerators such as an amine are usually added to the resin by the polyester manufacturer to create a "pre-accelerated" resin capable to cure at lower temperatures and at a greater rate.

Each can was filled, closed and left for three days at ambient temperature observing the behavior of the added micro-capsules.

dx.doi.org/10.1021/sc4002092 | ACS Sustainable Chem. Eng. 2013, 1, 1572−1579

Table 2. USPER Backbone Compositions Tested with MEB and MMB Microcapsules

component	MEB	MMB
resin	160 g	160 g
dimethyl aniline	3.3 g	3.3 g
microcapsules	6.96 g	17.8 g
entrapped BPO	1.050 g	0.9 g
Tegostab B8870[a]	3.3 g	3.3 g
TCPP[b]	29.5 g	29.5 g
LPG	111 mL	111 mL

[a]Tegostab B8870: foam stabilizer. [b]TCPP: flame retardant.

After 1 h, the MEB particles were evenly dispersed in the backbone, showing no evidence of particle aggregation and no curing. Particles of sample MMB, on the other hand, rapidly aggregated, showing also the effective curing of the resin. Indeed, after three days, the mixture turned into a well-cured solid polyester resin, despite the fact that the amount of entrapped peroxide increases in the order of MMB≪MEB,[13] namely, the amount of entrapped peroxide is much higher for the partly methyl-modified MEB silica capsules compared to fully methylated MMB particles obtained from polycondensation of MTMS alone catalyzed by amino-propyltrimethoxysilane.

Further investigation was therefore carried out using only the MEB capsules. First, the can was added with the MEB microcapsules prepared with ethanol only as co-solvent. The can was hermetically sealed and added with LPG (a mixture made by propane, dimethyl ester, and butane) used as propellant in 60% volume ratio with respect to the liquid volume. The resulting mixture was left for four more days at ambient temperature during which no evidence of curing was observed.

After this extra time, the mixture was pressurized at 5 bar using an optimized LPG mixture (Altachem gas: 46.5% propane, 33.5% butane, and 20% isobutene) as both solvent and propellant for the polyurethane foam. The mixture was left for a further three days at ambient temperature and then sprayed. Slow curing was observed, with visibile gelification of the foam. After 2 h, all the foam had turned into a gel due to action of the entrapped BPO slowly released from the broken capsules. The reason for the delayed spraying is to allow pressure equilibration between the capsule inner and outer environment through the porous organosilica shell acting as a molecular sol−gel membrane.[16]

Figure 4. Images of the sprayed USPER foam added with MEB microcapsules: (a) immediately after erogation, (b) and (c) 30 min after erogation, (d) 60 min after erogation, (e) 90 min after erogation, and (f) 180 min after spraying.

dx.doi.org/10.1021/sc4002092 | ACS Sustainable Chem. Eng. 2013, 1, 1572−1579

Aiming to increase the amount of entrapped (and released) BPO, we modified the original MEB capsule synthetic protocol using toluene along with ethanol as co-solvent. The new MEB capsules containing a larger amount of peroxide in their core were then added to the same prepolymer mixture described above. Again, no swelling occurred, and no curing was observed for a subsequent four days. The mixture was thus pressurized at 5 bar using the optimized LPG mixture and leaving the pressurized mixture to rest for four days. A valve was thus inserted, and the mixture sprayed.

Figure 4 shows the foam formed after spraying the USPER foam added with MEB microcapsules immediately after erogation and at regular time interval up to 3 h after spraying. Curing, partly screened by styrene evaporation, clearly took place. The pressure sensed by the encapsulated BPO compartmentalized within the mesoporous capsule walls suddenly drops from 5 bar to atmospheric pressure. Hence, the pressurized content in the capsule core bursts, and the capsules break releasing the initiator. Unlike polymer capsules, the shell is made of harder lipophilic organosilica,[13] where its high chemical affinity for the entrapped BPO prevents its leaching in the reactant mixture, despite the mesoporosity of the shell.

Obviously, the quality of the foam obtained necessitates optimization in light of application requirements. Yet the leach-proof nature of the capsules, their remarkable stability under pressure, and their rupture after spraying could be clearly demonstrated.

Test with Urethane Acrylates. We then evaluated the performance of the MEB microcapsules in a polyurethane foam formation. The formulation tested herein (LIS 11, made by Greenseal Chem) makes use of a blend of a NCO-terminated prepolymer of glycerin, MDI, and a NCO-terminated prepolymer of 2-ethyl hexanol, further acrylized by hydroxy-propyl acrylate. All available NCO groups react with the OH groups of the hydroxy-acrylate to form acrylic groups, while to avoid high viscosity, the resulting acrylate is blended with nonpolyurethane acrylates isobornyl acrylate (monofunctional) and 1,6 hexane diol diacrylate (bifunctional). This formulation usually produces soft free-radically cured flexible films and foams. Urethane acrylates are the most valued polyurethane precursors produced by reacting polyisocyanates with hydroxyl alkyl acrylates chosen from a broad class to produce foams capable of meeting performance requirements of different end uses.[17]

First, we checked the availability of entrapped BPO on the microparticle external surface with a gel time test. A small MEB microparticle sample (0.5 g, 2.42% w/w) was mixed with the resin (20 g, 96.77% w/w), and dimethylaniline (0.17 g, 0.82% w/w) was used as activator for organic peroxide initiation. No curing was observed even after 45 h, proving a lack of BPO accessible to reactants in the outer surface of the microcapsules.

Hence, a much larger resin sample was mixed with dimethylaniline, flame retardant TCPP, and foam stabilizer Tegostab B8870. This mixture was eventually added with the microencapsulated BPO particles (MEB, Table 3).

Upon addition of the capsules, the viscosity of the mixture rapidly increased. Figure 5 shows also the temporal behavior of the mixture allowed to rest for five days next to a control mixture (i.e., backbone with no added microcapsules observed under the same conditions). Urethane acrylates resins are less dense than USPER resins, and the particles, if not stirred, settled to the bottom of the flask (Figure 5b). However, the capsules were easily redispersed by magnetic or mechanical stirring. Left without agitation, after five days, most of microcapsules were found again settled at the bottom of the flask (Figure 5d).

Table 3. Urethane Acrylate Compositions Tested with MEB Microcapsules of Enhanced BPO Content

component	urethane acrylates
resin	170 g
dimethyl aniline	0.79 g
MEB	10.2 g
entrapped BPO	2.50 g
Tegostab B8870[a]	6.8 g
TCPP[b]	13.6 g
LPG	111 mL

[a]Tegostab B8870: foam stabilizer. [b]TCPP: flame retardant.

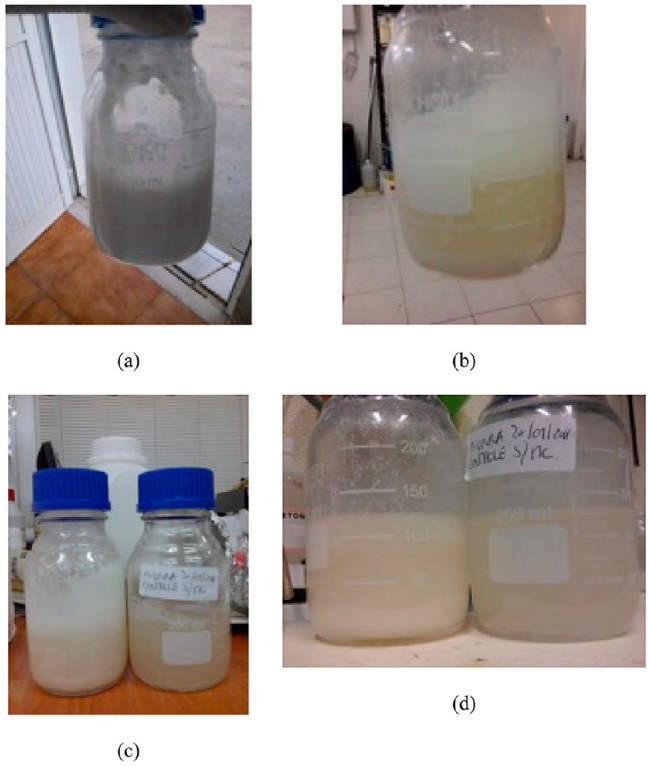


Figure 5. Images of the urethane acrylates mixture with MEB microcapsules: (a) after one day, (b) after two days, (c) after two days with control mixture (right), and (d) after five days with control mixture (right).

The optimized LPG mixture "Altachem gas" was used also as solvent and propellant for the polyurethane foam. The can was then sealed, and the LPG added to the mixture was hermetically closed bringing the pressure to 5 bar. No visible changes in the pressurized mixture were observed through the glassy can even after seven days. Hence, the pressurized mixture containing the gas was sprayed through a valve.

Figure 6 shows that a foam rapidly formed pointing again to capsule rupture and release of the entrapped BPO with consequent curing. Again, the quality of the foam is far from being optimal, but the concept, namely, that the initiator can be efficiently segregated into organosilica particles and then suddenly released upon spraying the capsules from a pressurized can, was proven also for polyurethane foams.

Figure 6. Images of the sprayed urethane acrylates foam added with MEB microcapsules: (a) immediately after erogation, (b) 5 min after erogation, (c) 15 min after erogation, (d) 60 min after erogation, (e) 120 min after erogation, and (f) 240 min after erogation.

Scale-Up of Capsule Synthesis. Willing to check the reproducibility of the synthetic method and aiming to upscale the synthesis of the leach-proof capsules, we repeated their preparation in another laboratory and then scaled up the synthetic protocol at industrial premises equipped with larger batch reactors.

The microcapsule synthesis was found to be largely reproducible, as shown by the SEM images in Figure 7 and

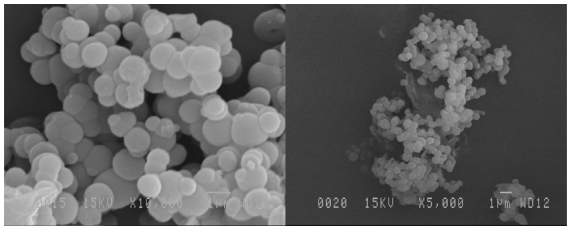


Figure 7. SEM images of MEB samples made on a lab scale in Canada (left) and in Italy (right).

by the bimodal particle size distribution analysis in Figure 8, in which the capsules made in a laboratory scale in Italy (MEB 6) are compared to those made under a similar laboratory scale in Canada (DDG2-174).

The bimodal tendency reoccurring toward the larger size ranges is due to partial aggregation of the capsules upon drying (also evident in Figure 7), as all measurements were taken using dried powder samples.

The size of the capsules is of crucial importance to ensure formation of leach-proof and compact particles. This was shown by another experiment by which, willing to synthesize 500 g of capsules, we attempted the synthesis of five 100 g microcapsule samples per batch in a 10 L reactor.

Figure 9 shows the SEM images of the five capsule samples obtained under the same stirring rate of the lab scale protocol (5000 rpm). The 10-fold scale-up of the synthesis now affords larger particles, and their more fragile nature is shown by the numerous particles broken during the synthesis.

This problem that is common in scaling up the synthesis of sol–gel microcapsules can be simply solved by rising the stirring rate (from 5000 to 7000 rpm) to ensure homogeneity of the microemulsion wherein the sol–gel polycondensation and microencapsulation actually takes place.

Figure 10 clearly shows that now the particle size decreases to the original 1 μm average diameter, with almost no capsules found broken.

In conclusion, we have developed a series of leach-proof sol–gel microcapsules doped with the free-radical initiator benzoyl peroxide that can be employed for curing polyurethane foams and polyester resin coatings without the need to separate the initiator to cross-link from the reagents.

In our case, rupture and release of the entrapped initiator takes place upon spraying the capsules from cans that are typically pressurized at 4–6 bar under hydrocarbon atmosphere in the presence of the polymer precursors without leaching of the encapsulated curing agent in the reactant mixture.

The core/shell organosilica-based microcapsules are prepared from O/W emulsions via ammonia-catalyzed condensa-

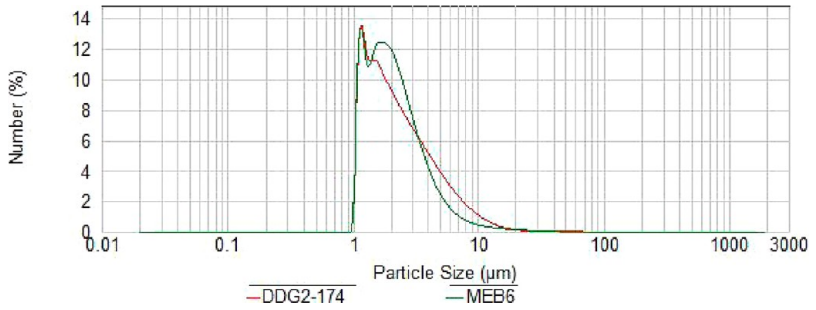


Figure 8. Particle size distribution (number of individual particles) in MEB samples made on a lab scale in Canada (red) and in Italy (green).

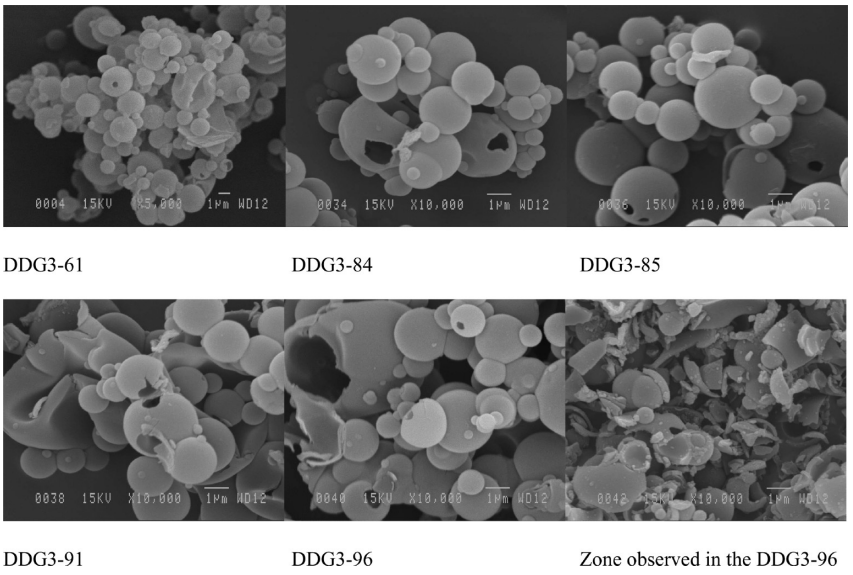


Figure 9. SEM images of five different MEB microcapsules obtained from a 10 L batch reactor stirred at 5000 rpm.

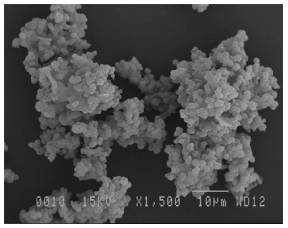


Figure 10. SEM image of MEB microcapsules obtained from a 10 L batch reactor stirred at 7000 rpm.

tion of TEOS and MTMS assisted by a surfactant. The synthesis of the doped organosilica microcapsules is fully reproducible and can be easily scaled up, provided that stirring is adapted to the requirements of larger reaction batch.

It should also be noted that the water phase of the O/W microemulsion can be recovered at the end of the synthesis, thereby closing the materials cycle and reducing the environmental footprint of this mild and clean microencapsulation process.

Combined with the thermosetting resin precursors, the organosilica microcapsules are smoothly dispersed in the resin composition without swelling, while the silica-based capsule wall provides excellent chemical and physical stability that is ideally suited for prolonging the shelf life of these highly reactive formulations.

Silica alone is not the right shell composition, as the SiO_2 microcapsules obtained from TEOS alone (data not shown herein) rapidly leach their content in the polyester or urethane prepolymer mixture curing the reactants. Similarly, entrapment in fully methyl-modified microcapsules obtained from polycondensation of MTMS only results in poor encapsulation of BPO radical initiator.[13]

Fundamental research reported herein demonstrates that these thoroughly developed sol–gel microcapsules are ideally suited for the purpose of one-pot multicomponent polymer formulations to be cured. Remarkably, industrial research recently led to microencapsulated curing agents for industrial molding processes in which the encapsulating shell is composed of a polyurethane resin, which is considerably more resistant to heat compared to traditional polymer capsules.[3] Here, the microencapsulated sol–gel capsules can be used for curing both polyurethane and polyester resin formulations.

Applied research following this report will afford the optimal formulation for these new heterogeneous systems capable of inducing formation of foams and coatings meeting practical application requirements, including reuse of the nozzle used to spray these foams because curing would only occur at the sprayed surface and not within the nozzle as it happens today with consequent clogging and nozzle disposal. A number of forthcoming different uses are expected to emerge from the application of these sol–gel microencapsulated curing agents[18] that will shortly be employed as curing agents for one-pot waste-free thermosetting resins with enhanced sustainability profiles.

AUTHOR INFORMATION

Corresponding Author

*E-mail: mario.pagliaro@cnr.it.

Notes

The authors declare no competing financial interest

ACKNOWLEDGMENTS

This article is dedicated to Professor Donatella Rindone whose unforgettable chemistry teaching in the mid 1980s led one of us (M.P.) to enrol in chemistry university courses. We thank Professor Laura M. Ilharco and Dr. Alexandra Fidalgo, Technical University of Lisboa, for the valued DRIFT IR analysis of the capsular materials. Dr. George Georgiev (Greenseal Chem Portugal) developed the LIS 11 polyurethane resin. His kind assistance to one of us (M.S.) during the tests in Portugal is gratefully acknowledged. Thanks to Professor Joao C. Bordado, Technical University of Lisboa and Greenseal Chem Portugal, for prolonged collaboration on this project. We thank Professor Giuseppe Alonzo, University of Palermo, for co-mentoring M.S. during her doctorate.

REFERENCES

(1) Minami, H.; Kanamori, H.; Hata, Y.; Okubo, M. Preparation of microcapsules containing a curing agent for epoxy resin by polyaddition reaction with the self-assembly of phase-separated polymer method in an aqueous dispersed system. *Langmuir* **2008**, *24*, 9254−9259.

(2) Dougherty, M. J.; McDougal, J. R. Process for the Manufacture of Products from Reinforced Polyester Resins. U.S. Patent 4524043 A, 1984.

(3) Akagawa, M.; Yasuhara; T. Microencapsulated Curing Agent. U.S. Patent 20120248639 A1, 2012.

(4) Blaiszik, B. J.; Kramer, S. L. B.; Olugebefola, S. C.; Moore, J. S.; Sottos, N. R.; White, S. R. Self-healing polymers and composites. *Annu. Rev. Mater. Res.* **2010**, *40*, 179−211.

(5) *The Polyurethanes Book*; Randall, D., Lee, S., Eds.; Wiley: New York, 2003.

(6) *Global Overview of the Spray Polyurethane Foam (SPF) and One Component Foam (OCF) Markets*, 3rd ed.; IAL Consultants: London, April 1, 2012.

(7) Wicks, Z. W.; Jones, F. N.; Pappas, S. P.; Wicks, D. A. Polyester Resins. In *Organic Coatings: Science and Technology*, 3rd ed.; John Wiley & Sons: Hoboken, NJ, 2006.

(8) Javni, I.; Hong, D. P.; Petrović, Z. S. Soy-based polyurethanes by nonisocyanate route. *J. Appl. Polym. Sci.* **2008**, *108*, 3867−3875.

(9) In 2010, Soudal, a construction chemicals manufacturer, started commercialization of Wacker's Geniosil faster bonding foams. www.wacker.com/cms/en/www_archive/www_2008/www_48/48_innovations/48_geniosil/48_geniosil.jsp (accessed September 3, 2013).

(10) Wilson, G. O.; Henderson, J. W.; Caruso, M. M.; Blaiszik, B. J.; McIntire, P. J.; Sottos, N. R.; White, S. R.; Moore, J. S. Evaluation of peroxide initiators for radical polymerization-based self-healing applications. *J. Polym. Sci., Part A-1: Polym. Chem.* **2010**, *48*, 2698−2708.

(11) Dougherty, M. J.; McDougal, J. R. (1984) Process for the Manufacture of Products from Reinforced Polyester Resins. U.S. Patent 4524043 A.

(12) Pagliaro, M.; Sciortino, M.; Ciriminna, R.; Alonzo, G.; De Schrijver, A. From molecules to systems: Sol−gel microencapsulation in silica-based materials. *Chem. Rev.* **2011**, *111*, 765−789.

(13) Fidalgo, A.; Ciriminna, R.; Ilharco, L. M.; Sciortino, M.; Pagliaro, M. Sol-gel microencapsulation of organic molecules: A structural and chemical insight. *ChemPlusChem* **2012**, *77*, 536−540.

(14) SIDnitial Assessment Report For SIAM 15. Korea National Institute of Environmental Research, October 2002. www.inchem.org/documents/sids/sids/BENZOYLPER.pdf (accessed September 3, 2013).

(15) Resipur 9106 from Resiquimica, S.A. is a transparent yellowish liquid orthophtalic unsaturated polyester resin of medium reactivity. It can be cured at room temperature by means of the addition of an accelerator such as a cobalt and an initiator like a methyl ethyl ketone peroxide. http://www.resiquimica.pt/site/EN/pdf/RESIPUR.pdf (accessed September 3, 2013).

(16) The membrane properties of sol-gel porous organosilicas developed by ten Elshof, Castricum, and co-workers in The Netherlands are now well known and form the basis of innovative commercial molecular membranes. www.hybsi.com (accessed September 3, 2013).

(17) *Radiation Curing of Polimeric Materials*; Hoyle, C. E., Kinstle, J. F., Eds.; ACS Symposium Series 417; American Chemical Society: Washington, DC, 1990.

(18) De Schrijver A.; Pagliaro, M.; Ciriminna, R.; Sciortino, M. Leach-proof Microcapsules, The Method for Preparation and Use of Leach-Proof Microcapsules. WO Patent 2011003805 A3, 2011.