J Mater Sci (2006) 41:5490–5494
DOI 10.1007/s10853-006-0272-8

Inorganic and hybrid hollow spheres by coating of microcapsules as templates

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Received: 4 May 2005 / Accepted: 31 October 2005 / Published online: 17 June 2006

Abstract Microcapsules containing tetradecane as core and an amino resin as wall material were synthesised and used as templates for the production of micro hollow spheres. That way, the prepared microcapsules have been mineralised with titania by thermal hydrolysis of titanyl sulphate and subsequently transformed into inorganic and organic/inorganic hybrid hollow spheres. Laser diffraction studies after the different process steps show that the particle size remains constant. This means that control of the size of the hollow spheres is achieved by controlling the droplet size of the emulsion entering the microencapsulation process.

Introduction

The growing demand for advanced materials and constructional elements with lower costs and higher functionalities gave rise to greater efforts in tailoring product properties on the level of individual particles. Promising examples for this new class of materials are micro hollow spheres consisting of a gaseous core enclosed in a solid shell. The application of such hollow spheres as fillers leads to cost and weight reduction and can considerably improve the mechanical, electrical, thermal and acoustic properties of the materials. Additionally, hollow spheres can be used as micro reactors and catalyst support. For the manufacturing of hollow spheres, beneath the technically used processes like spray drying and spray pyrolysis, syntheses in liquid phase are widely explored.

Direct formation of hollow spheres using emulsions [1–4] and coating of template particles with a wall material have been published. The latter are transformed into hollow spheres by dissolving or burning out the core material. For the coating process, different methods like layer-by-layer techniques [5–13], sol–gel methods [14–19], liquid phase deposition [20], and forced hydrolysis [21–24] are described. Mostly templates of polystyrene or poly(methyl methacrylate) of narrow size distribution in the submicrometer range are used. Not much work has been done until now to synthesise hollow spheres with larger particle sizes through the template driven route. The present paper aims at synthesising microcapsules in the range of 0.1–100 μm as templates for the manufacturing of hollow spheres and subsequent coating of these templates with titania by thermal hydrolysis of titanyl sulphate.

Experimental

Synthesis of microcapsules

The capsules were synthesised by encapsulating tetradecane as the core material using the in-situ polycondensation of precondensates of melamine and formaldehyde as described in the literature [25]. Typically, 2.7 g citric acid (anhydrous for synthesis, Fa. Merck) were dissolved in 120 mL distilled water and the solution divided into 20 mL and 100 mL portions. In the first solution 5.7 g of the

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precondensates (Piamid M70, Fa. Piesteritz), having a solids content of about 70%, and in the second solution 1.2 g poly(ethylene glycol) (PEG 400, Fa. Fluka), as a protective colloid, were dissolved. Afterwards 35 mL tetradecane (Linpar 14, Fa. Stuart) and the solution containing the stabiliser were separately heated up to 60 °C, mixed, and subsequently emulsified using an Ultra Turrax (T25, Fa. Ika-Labortechnik) at 8,000 rpm within 10 min. Under continuous emulsifying the dissolved precondensates were added to the emulsion and further emulsified for 10 min. Afterwards the hardening of the capsule wall took place within 2 h at 60 °C under agitation at 300 rpm. To characterise the microcapsules, the particles were separated from the liquid phase by filtration and washed two times with 80 mL distilled water and another two times with 80 mL ethanol. Drying of the capsules was done under ambient conditions.

Formation of inorganic and organic/inorganic hybrid hollow spheres

For the mineralisation of the capsules 1.5 g $TiOSO_4 \cdot H_2O$ (Ti as $TiO_2 > 29\%$, Fa. Merck) with a TiO_2 content of 34.9% were dissolved at room temperature in 80 mL distilled water and directly, after hardening of the capsule wall, mixed with the capsule suspension. Thereby agglomeration of the particles due to filtration and washing steps was avoided. Precipitation of the inorganic material occurred within 4 h at 60 °C under mild stirring at 300 rpm. The overall reaction equation can be written in the following form:

$$TiOSO_4 + 2H_2O \leftrightarrow TiO(OH)_2 + H_2SO_4$$

After completing the reaction, the product was filtrated and washed twice with 100 mL distilled water and dried under ambient conditions. To form the organic/inorganic hollow spheres, the tetradecane was removed by extraction with chloroform. Therefore 2 g of coated capsules were suspended in 50 mL chloroform (>99%, Fa Merck) and separated by filtration. The extraction procedure was repeated two times to make sure all of the tetradecane was removed from the capsules.

Inorganic hollow spheres were produced by burning out the organic capsule at 1,000 °C for 1 h in air. A flow chart of the single steps is given in Fig. 1.

Microcapsules, coated capsules, and hollow spheres were characterised by laser diffraction (Mastersizer 2000, Fa. Malvern Instruments), DSC/TG analyses (STA 409C, Fa. Netzsch) and scanning electron microscopy (SEM) (Gemini 1530, Fa. Leo). Prior to SEM investigations the samples have been coated with a thin (~14 nm) conducting layer of gold (SCD 040, Fa. Balzer).

For lack of information about the refractive index of the complex multi-shell system, the Fraunhofer model instead of the complex Mie theory was made standard practice calculating the particle size distribution (PSD). All given results are based on the measured volume distribution.

Results and discussion

Microencapsulation

The first characterisation of the microcapsules was done by laser diffraction. Due to the low stability of the emulsion, the particle size distribution of the emulsion could not be directly determined. Thus the PSD was measured after adding the wall material and further emulsifying for a period of 10 min. Within this second emulsification step a thin wall around the droplets is formed leading to suitable stability of the droplets for PSD measurements. A second determination of the particle size was done after 2 h of hardening the capsule wall to ascertain distribution changes during the hardening process. In Fig. 2 the PSD and in Table 1 the characteristic values of the emulsion and the capsules are shown.

Two peaks, the first in the range of 0–10 μm and the second in the range of 10–90 μm, can be seen. Interpretation of the second peak, with respect to the pictures taken by light and SEM, leads to the conclusion that the second peak indicates the emulsion droplets or the microcapsules, respectively. It follows that the volume-weighted mean diameter is 29.2 μm for the emulsion droplets and 33.5 μm for the microcapsules after the hardening step. The additional peak occurring in both distributions can be explained by homogeneously precipitated particles of the resin, which are formed directly after addition of the precondensates to the emulsion. Due to precipitation of small particles on the tetradecane/water interface during the hardening process, the amount of these particles decreases and the d_{10} value increases from 9.9 μm for the emulsion to 17.5 μm for the capsules. Besides, the hardening process causes a reduced specific surface and a narrow size distribution, while the d_{50} and d_{90} values almost stay constant.

For the characterisation of the capsule surface and the shell thickness SEM investigations have been done. The prepared microcapsules show a dense polymeric layer of amino resin (Fig. 3a). The shell thereby shows a smooth particular structure with larger particles incorporated into the wall or aggregated to the surface. This indicates that in the first stage of the encapsulation process a large amount of small particles are formed which are precipitating on the droplet surface forming a dense layer. This process is paralleled by the molecular growth and coagulation of particles in solution. Depending on the time of deposition

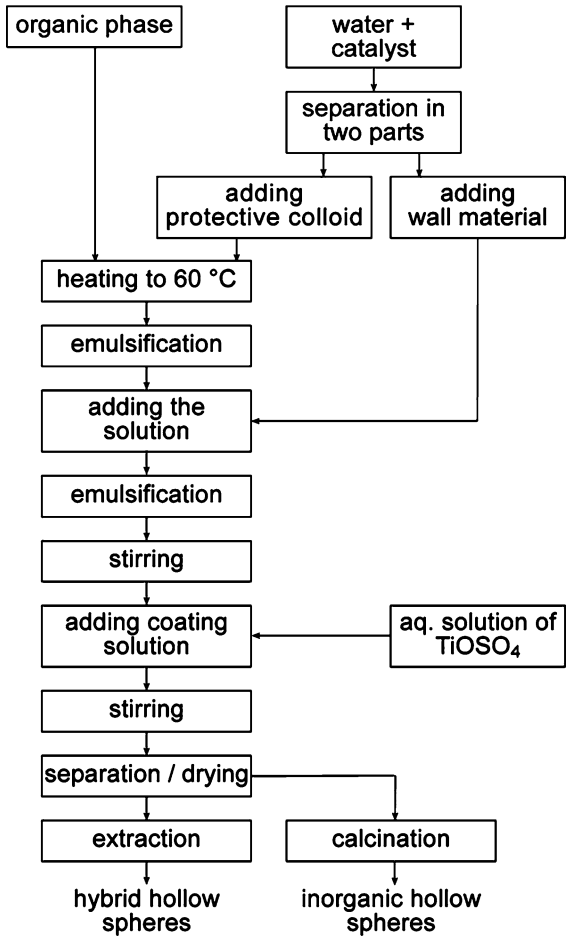

Fig. 1 Flow chart for the template-driven synthesis of hollow spheres

the particles are incorporated, prior to the end of the wall formation, or agglomerated to the surface, after the wall formation. In both cases the surface roughness of the formed capsules is increased. In the prepared samples a number of capsules were broken, which gives the opportunity to determine the layer thickness of the amino resin.

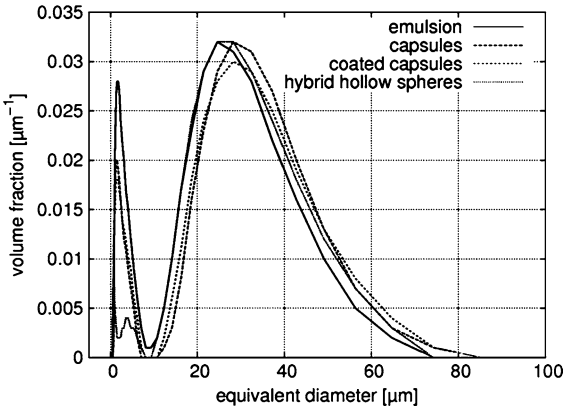

Fig. 2 Particle size distribution of the emulsion, microcapsules, coated and extracted microcapsules

The shell thickness is determined to be 100 nm (Fig. 3b) although thinner layers can be found.

The decomposition of the microcapsules was investigated by thermal analysis (Fig. 4). The samples were heated with a heating rate of 10 °C/min up to 1,000 °C under an N_2/O_2 atmosphere. The capsules show weight losses of about 85% in the temperature range from room temperature to 250 °C. These weight losses are accompanied by an endothermic effect between 20 °C and 100 °C and a second endothermic effect at 190 °C that passes into strong exothermic effect. The first effect can be explained by the evaporation of small amounts of water whereas the second effect seems to be coupled with the evaporation (endothermic) and subsequent combustion (exothermic) of the enclosed tetradecane. In the further temperature range up to 620 °C an additional weight loss of 15% occurs, which can be assigned to the combustion of the organic resin.

Capsule coating

After hardening the capsule wall, the microcapsules were directly coated with the inorganic material. After the mineralisation practically no difference can be seen between the PSD of the capsules and that of the mineralised particles (Table 1, Fig. 2). This gives evidence that almost all of the material is incorporated into the inorganic coating and no homogeneous titania particles have been formed. SEM investigations show that the coated particles have the same shape and surface structure as the uncoated particles (Fig. 3c). EDX investigations underline that titanium oxide was precipitated on the capsules whereas no decision could be made if a continuous coating was achieved or not.

In the thermal analysis the same steps of weight loss (84% between room temperature and 250 °C and 15% between 250 °C and 600 °C) coupled with the same thermal effects could be found (Fig. 4). The residual mass is 1.5%, which is in good agreement with the theoretical mass of precipitated titanium oxide (1.6%).

Synthesis of hybrid and inorganic hollow spheres

For the formation of hybrid hollow spheres tetradecane was removed from the core by repeated extraction with chloroform. After drying the capsules under ambient conditions to evaporate the organic solvent, the particles show the same PSD (Fig. 2) as the coated capsules. This indicates that the capsules are not destroyed during the extraction steps. Only the first peak in the range between 0 and 10 µm was decreased due to the removal of small particles during the repeated washing steps. It can be seen from the SEM micrograph (Fig. 3d, e) that the hollow sphere remains its structure after the extraction process and thus stable

Table 1 Specific values and standard deviations of the particle size distributions after the different process steps

	Emulsion[a]	Capsules[a]	Coated capsules[b]	Hybrid hollow spheres[b]
d_{10} (μm)	9.9 (2.7)	17.5 (3.4)	17.0 (0.5)	17.9 (0.0)
d_{50} (μm)	28.8 (0.8)	32.7 (1.5)	32.5 (0.4)	31.3 (0.6)
d_{90} (μm)	47.6 (2.0)	51.7 (2.5)	53.5 (0.2)	51.5 (0.3)
D[4.3] (μm)	29.2 (1.0)	33.5 (1.6)	33.6 (0.3)	33.0 (0.2)
Spec. surface (m^2/g)	0.443 (0.014)	0.354 (0.016)	0.362 (0.007)	0.266 (0.052)
Width = $(d_{90}–d_{10})/d_{50}$ (–)	1.30 (0.15)	1.02 (0.05)	1.12 (0.02)	1.10 (0.0)
Coefficient of variation (–)	0.48 (0.02)	0.42 (0.02)	0.45 (0.01)	0.40 (0.01)

[a]Mean values calculated on the base of ten measurements

[b]Mean values calculated on the base of two measurements

organic/inorganic hybrid hollow spheres are formed. Thermal characterisation of the hybrid structure (Fig. 4) shows a continuous loss of weight up to 92% in the temperature range between room temperature and 600 °C. This endothermic effect proves that the decomposition of the resin occurs within a broad temperature range without characteristic steps. The theoretical amount of titanium oxide (11%) is slightly higher than the residual mass of 8% found by thermal analysis. This is reasonable taken into account that some of the precipitated material is removed during the washing steps.

For the synthesis of the inorganic hollow spheres the coated capsules were calcinated under elevated temperatures in N_2/O_2 atmosphere. Thereby the capsules have formed strong agglomerates that cannot be broken without destroying the capsule structure. Due to the large size of the agglomerates and the lack of possibilities to disintegrate these structures, it is not possible to compare the PSD to the PSD of the other products.

The SEM investigations show (Fig. 3f) that a complete coating of the templates could be achieved. The inorganic shell shows pores in the range of 10–50 nm, which are

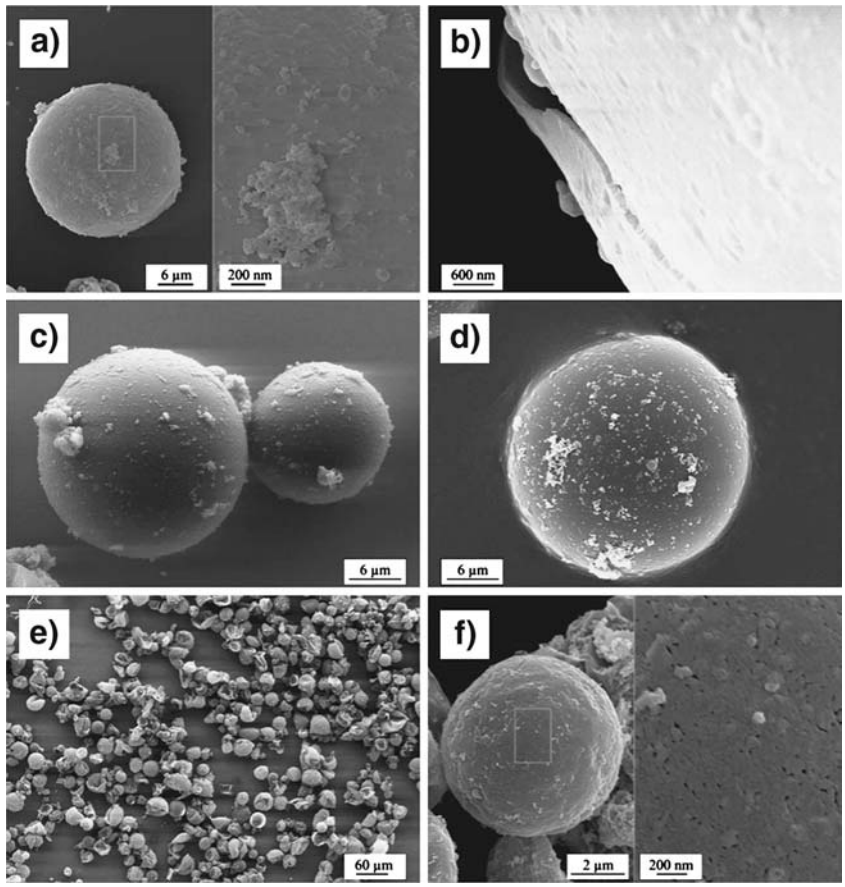

Fig. 3 SEM micrographs of a prepared microcapsule (**a**), a broken capsule where the shell thickness can be determined to be about 100 nm (**b**), a capsule coated with TiO_2 (**c**), organic/inorganic hollow spheres consisting of a shell of amino resin and titania in high (**d**) and low magnification (**e**), and an inorganic hollow sphere (**f**). Right parts of figure (**a**) and (**f**) show the surface of the sphere in higher magnification

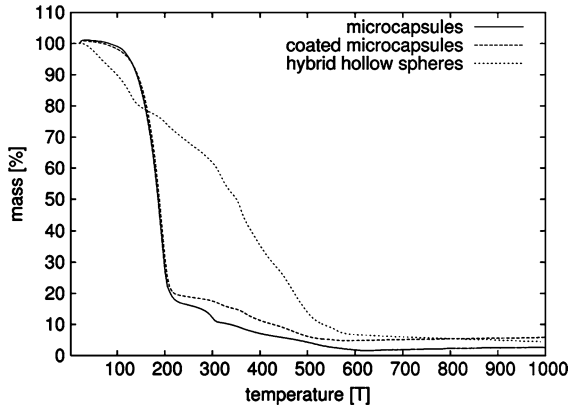

Fig. 4 Thermogravimetric analysis (TGA) of microacapsules, microcapsules coated by thermal hydrolysis and extracted microcapsules forming an organic/inorganic hybrid structure

formed as gaps between small titanium oxide particles. Thereby the shell, having a thickness of about 20 nm, is formed by one layer of these particles only. It seems that during the coating process the primary particles formed are growing or agglomerating and subsequently forming the TiO_2 layer.

Conclusion

It has been shown that liquid hydrocarbons like tetradecane can be microencapsulated by in-situ polycondensation using an amino resin as the wall material. These microcapsules, having a volume-weighted mean diameter of 34 μm, can be used as templates for a subsequent coating process with a thin titania layer. It could be observed that the particle size distribution after distinct process steps like mineralisation and extraction of the liquid core remains constant. This means that control of the size of the hybrid particles is possible by controlling the emulsion droplet size for the microencapsulation process. After removal of the inner tetradecane core stable organic/inorganic hybrid spheres can be formed. Even after calcination the hollow structure is still stable and shows a continuous wall with pores in the range of 10–50 nm and a shell thickness of about 20 nm. In the future more detailed investigations concerning the process of the wall formation will be necessary in order to gain control not only about the size but also about thickness and structure of the coating layer.

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