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Preparation of TiO_2-polymer hybrid microcapsules

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Polyamide microcapsules were coated with TiO_2 by liquid phase deposition (LPD), yielding hybrid capsules of polymer and partially crystalline TiO_2 at 50°C. Characterization was carried out by scanning electron microscopy and X-ray diffraction. By oxidative decomposition of the polymer purely ceramic spheres with diameters of 10 μm and a wall thickness of 200 nm were obtained, the structural integrity of the capsules was maintained throughout the burnout.

1. Introduction

Most procedures for the preparation of microcapsules utilize organic polymers as wall material [1] for the protection of sensitive compounds or drug delivery [2, 3]. For low weight or low dielectric constant fillers [4] and applications, where the encapsulated material needs stronger protection or is to be released at higher mechanical load, inorganic or hybrid materials may be required. Inorganic microcapsules prepared via sol-gel processes are used to encapsulate functional molecules in inert matrices, e.g., to isolate sunscreen substances from contact with human tissues for cosmetic applications [5]. For the preparation of inorganic microspheres, solid polymer cores are frequently used as templates for the deposition of the inorganic phase by precipitation from solution [6, 7], sol-gel techniques [8] or layer-by-layer adsorption of nanoparticles [9, 10]. During the removal of the organic "sacrificial" core at high temperatures the inorganic wall material is densified and purely inorganic hollow spheres remain.

In nature, many products of biomineralization such as nacre, enamel and bone gain their exceptional strength and toughness from the combination of inorganic material with an organic matrix [11]. In this paper we report the bio-inspired synthesis of hybrid microspheres by combination of liquid phase deposition, which allows the preparation of partially crystalline TiO_2 at moderate temperatures, with polymer microcapsules. Hybrid ceramic-polymer spheres are obtained with an intense interpenetration of the inorganic material with the porous polymer network.

2. Experimental

The microcapsules were synthesized by typical interfacial polycondensation as described in the literature [3]. Therefore, an emulsion comprising an aqueous core phase and a continuous phase of a non aqueous liquid was formed. For the microencapsulation process, polyamide produced by the reaction of terephthaloylchloride with diethylenetriamine was used. 3.2×10^{-6} m^3 of diethylenetriamine was dissolved in 20×10^{-6} m^3 of distilled water and 3.2 g NaOH was added to neutralize the HCl which is formed during the polymerization process. Subsequently, the core material was mixed with 10^{-4} m^3 of vegetable oil and emulsified using an ultrasonic tube Ø 19 mm (Labsonic U, B. Braun) with an output power of 160 W for one minute. The vegetable oil is characterized by a viscosity sufficient to prevent the breaking of the emulsion during the reaction time without using surfactants that may negatively affect the coating of the capsules. 3.74 g terephthaloylchloride dissolved in 50×10^{-6} m^3 of vegetable oil was added to the emulsion and the mixture was agitated with a propeller stirrer for 90 minutes at a temperature of 70°C. The capsules were twice filtered and washed with approx. 50 mL ethanol (99.8%, Roth) and dried under ambient conditions.

Microcapsules were redispersed (0.5 g/10^{-4} m^3) in demineralized water (conductivity 0.055 μS cm^{-1}) by sonification for 15 min. Subsequently, the dispersion was separated from sedimented polymer agglomerates. After triple centrifugation and washing with 10^{-4} m^3 of water the microcapsules were finally dispersed in

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60^{-6} m^3 of water and were exposed to a liquid phase deposition (LPD) solution [12–14] of 0.05 M $(NH_4)_2[TiF_6]$ (Aldrich, 99.99%) and 0.15 M H_3BO_3 (Fluka, purum p.a.) by adding 10^{-5} m^3 and 30×10^{-6} m^3 of 0.5 M stock solutions of $(NH_4)_2[TiF_6]$ and H_3BO_3, respectively. Deposition of TiO_2 was achieved by stirring the sample solutions in sealed polypropylene containers at 50°C for 3 to 7 hours. The mineralized microcapsules were subsequently separated from the LPD-solution by suction through 1.2 μm membrane filters (cellulose acetate, Schleicher & Schuell) and washed three times with 10^{-4} m^3 of water.

TiO_2-Particles from homogeneous precipitation were obtained by stirring of LPD-solutions for 3 h without dispersed polymer template under identical conditions. Isolation and washing of these precipitates was carried out by three cycles of centrifugation and washing with 10^{-4} m^3 of water each. All samples were dried in a desiccator over silica gel prior to characterization.

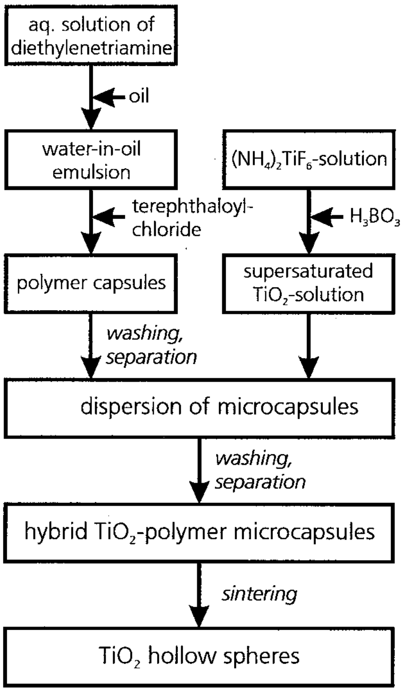

Figure 1 Flow chart for the preparation of inorganic and hybrid microcapsules.

Coated microcapsules, polymer capsules and TiO_2 precipitates were characterized by powder X-ray diffraction (XRD, Stoe Stadi P), scanning electron microscopy (SEM, Hitachi S 800) and differential thermal analysis/thermogravimetric analysis (DTA/TGA, Setaram TAG24).

3. Results and discussion

A flow chart for the preparation of hybrid microcapsules is given in Fig. 1: Polymer microspheres obtained from interfacial polycondensation are dispersed in a liquid phase deposition (LPD) solution, from which partially crystalline TiO_2 can be obtained at 50°C. Under similar experimental conditions film growth rates of approximately 120 nm/h are observed on planar polymer surfaces after induction time of 3 h [15]. Fig. 2b shows the SEM micrograph of a sphere that had been mineralized for 3 h in comparison to an as-prepared polyamide microsphere (Fig. 2a). The pure polymer material has a sharp-edged surface, on which some fragments of smaller, broken capsules adhere. In contrast to this, microspheres mineralized with TiO_2 are covered with globular particles with diameters smaller than 200 nm. The initial surface roughness of the polymer is evened by this coverage.

The thermogravimetric analysis (TGA) of the mineralized capsules is compared with the pure polymer material in Fig. 3. Additionally, the curve for material obtained by homogeneous precipitation from a separate LPD-solution is given as a reference. This precipitate shows a mass loss of approximately 20% below 300°C which can be assigned to the desorption of water. The mass loss reaches a constant level of 22% at temperatures above 600°C. Since the measurements performed on untreated and coated microcapsules show a similar course below 300°C, it is reasonable to assume that in both cases a mass loss of about 20% is caused by the removal of residual water before pyrolysis.

On this basis it can be estimated that the mineralized spheres contain about 34% of inorganic material. Whereas the oxidative decomposition of the pure

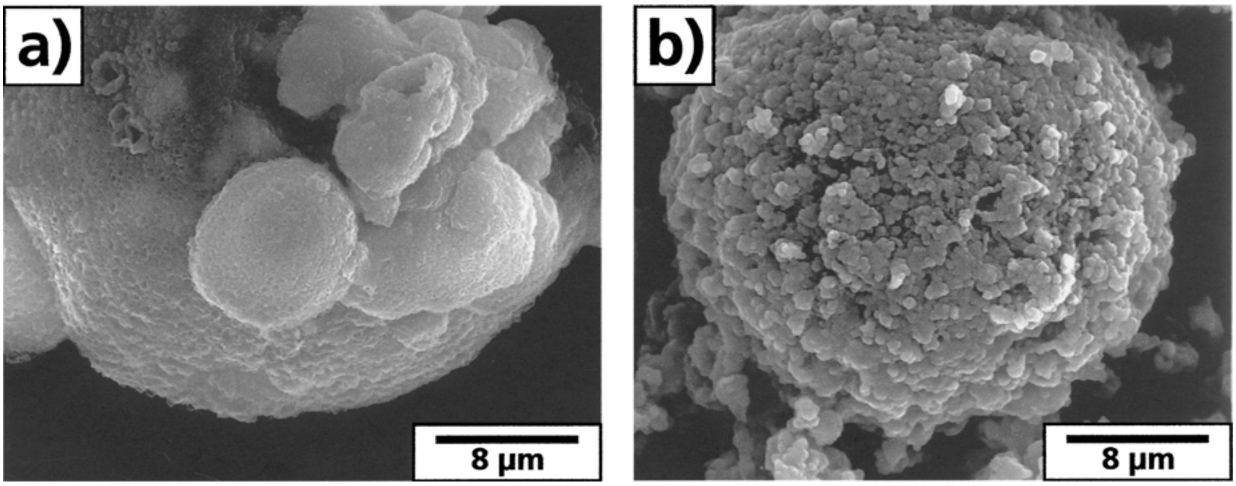

Figure 2 SEM micrograph of an as-prepared polyamide capsule (a) and a capsule that has been mineralized with TiO_2 by liquid phase deposition for 3 h (b).

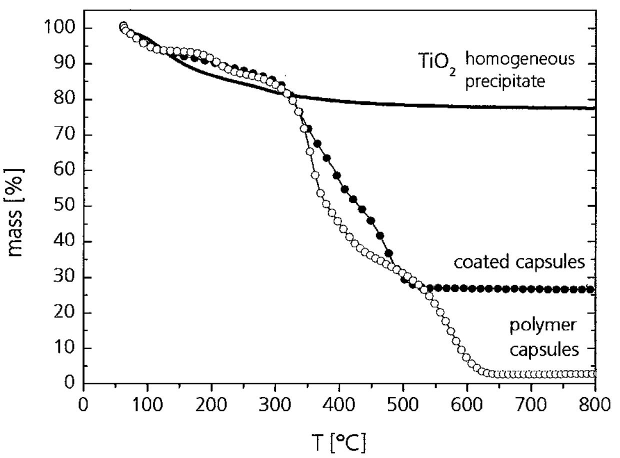

Figure 3 Thermogravimetric analysis (TGA) of polyamide microcapsules, microcapsules mineralized by liquid phase deposition for 3 h and inorganic material homogeneously precipitated by LPD in a separate experiment. All samples were heated at 10 K/min in dry air atmosphere.

polymer is completed at 650°C, the sample mass of mineralized microcapsules already reaches a constant level of 27% at 500°C. Obviously the burnout of the organic material is catalyzed by the presence of the inorganic coating.

The differential thermal analysis (DTA) curves for both coated and uncoated capsules (Fig. 4) shows three distinct exothermal signals in the temperature range between 300°C and 650°C where the mass loss due to pyrolysis of the organic material occurs.

For coated capsules these signals are shifted to lower temperatures in comparison to the pure polymer material whereas the peak pattern is retained. This result indicates that similar decomposition pathways are involved but activation energies are lowered by the presence of the inorganic material.

On the given scale no significant heat flow can be measured with TiO_2-particles from homogeneous precipitation, showing that the exothermic heat flow observed with the coated capsules can be assigned to the decomposition of the organic template.

In order to obtain information about the material deposited on the polymer surface, microcapsules were mineralized for 5 h and investigated by X-ray diffraction (XRD). Fig. 5 shows the diffraction pattern of this material. The anatase modification of TiO_2 clearly can be identified as crystalline phase. Peaks are broadened due to the small size of the crystallites. A crystallite size of about 6 nm could be calculated from the width of the anatase 101 peak using the Scherrer equation [16]. In our previous work on powders homogeneously precipitated by LPD [15], we estimated that the as-prepared inorganic material has a crystalline content of approximately 50% under these conditions compared to commercially available anatase powder (Aldrich, 99.9+%). These results thus indicate that the mineralized microcapsules represent a hybrid structure of a polymer backbone coated with a partially crystalline ceramic material. Upon heat treatment grain growth of the crystals takes place as indicated by the decrease of the respective peak widths.

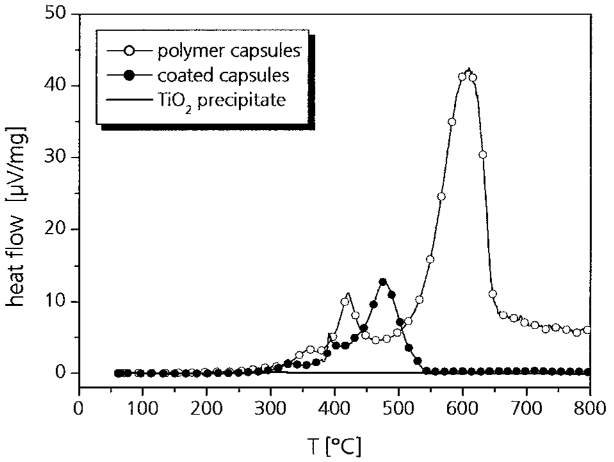

Figure 4 Differential thermal analysis (DTA) of polyamide microcapsules, microcapsules mineralized by liquid phase deposition for 3 h and inorganic material homogeneously precipitated by LPD in a separate experiment. All samples were heated with 10 K/min in dry air atmosphere.

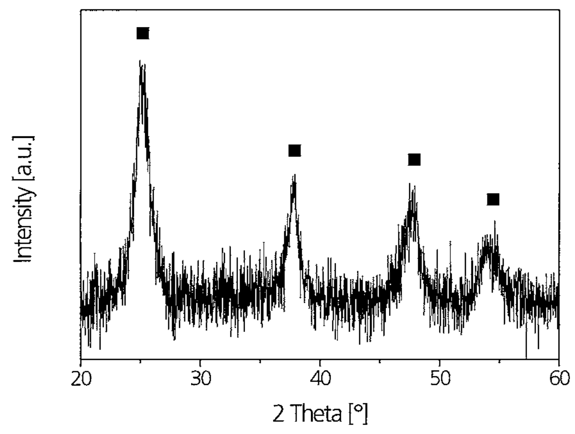

Figure 5 XRD pattern of as-mineralized microcapsules. All peaks (■) can be assigned to the anatase modification of TiO_2 according to PDF-file 47110815.

If the thermal treatment is performed with low heating rates, the inorganic coating of the hybrid material remains intact as can be seen in Fig. 6. This observation is in agreement with reports of other groups, where even the burnout of solid polystyrene latices left the integrity of inorganic shells unaltered [17, 18]. In the case of LPD-coated polyamide microcapsules, only a thin polymer film is oxidized. The volatile decomposition products permeate through the inorganic material without destruction of the overall microstructure. In comparison to the as-mineralized capsules (Fig. 2b), the surface structure of the annealed capsules appears coarsened which is explained by grain growth of the inorganic material as observed by XRD.

Heat treated samples were carefully ground in order to examine the microstructure of the residual inorganic material. In Fig. 7a the SEM image of a fractured inorganic capsule is given, Fig. 7b shows a section of the sphere at a higher magnification. Even though the average wall thickness of 200 nm accounts only for 2% of the total sphere diameter (approx. 10 μm), the structural integrity of the inorganic shell is preserved through sintering. At the inner surface branched morphologies which represent a replica of the porous polyamide template can be seen. In the original ceramic-polymer hybrid microcapsules obviously the inorganic and organic

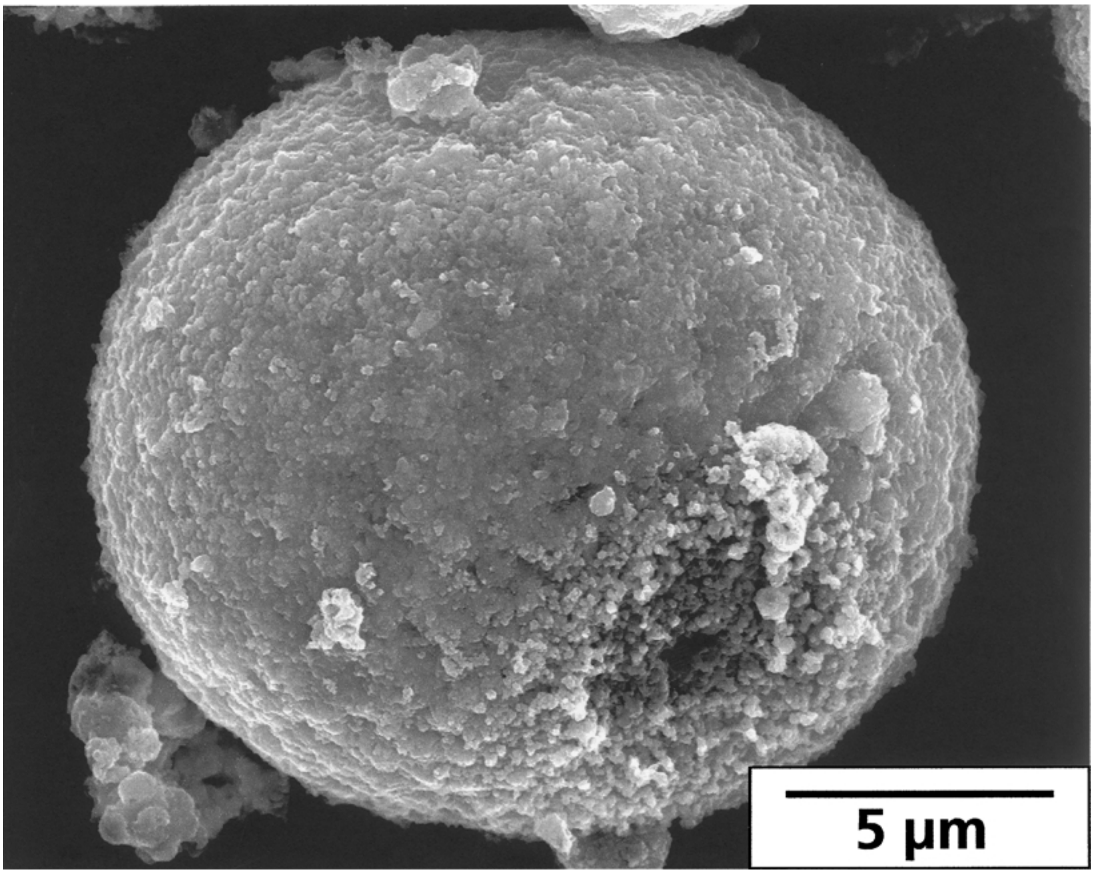

Figure 6 SEM image of polyamide capsule mineralized with TiO_2 by LPD (3 h) after thermal treatment. The material was heated with a rate of 10 K/min in air atmosphere and held at 600°C for 3° h.

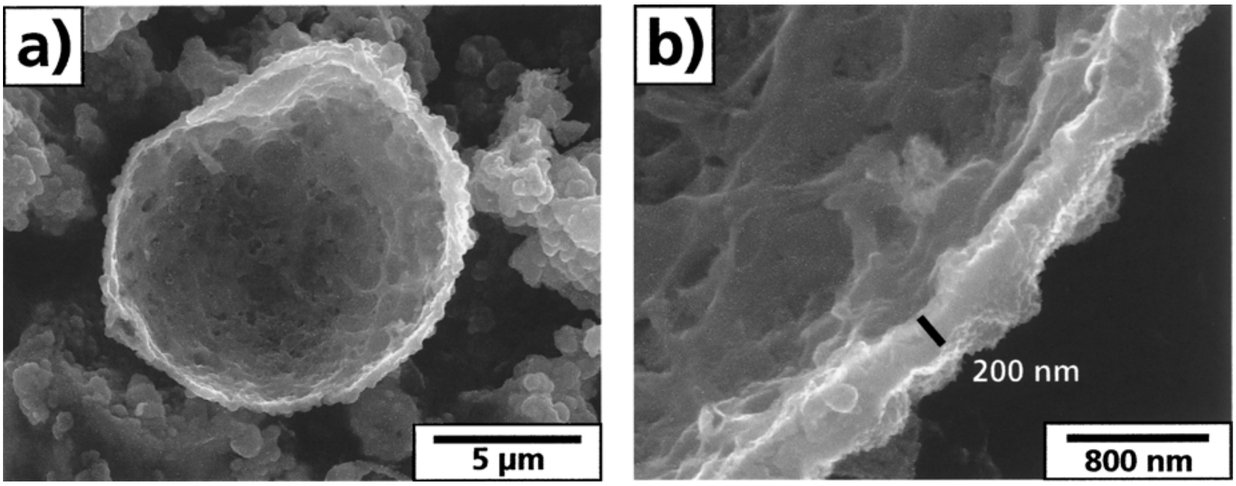

Figure 7 SEM micrograph of fractured microcapsule obtained from mineralization of polyamide spheres, subsequent annealing at 600°C and gentle grinding (a). Section of the sphere at higher magnification (b).

phases had been tightly interwoven. The inorganic material seems to be composed of a coherent film into which particles have been integrated in the course of the mineralization process. This observation is in general agreement with the mechanism of film formation on planar polymer substrates by LPD [15].

4. Conclusions

Hybrid ceramic-polymer microspheres can be prepared by mineralization of polyamide capsules by TiO_2 liquid phase deposition. The inorganic material is interlocked with the porous polymer surface and sustains coherence even through oxidative thermal decomposition of the template. From this observation a high mechanical stability of the hybrid material can be expected, which will be subject of further investigations.

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