Journal of Colloid and Interface Science 464 (2016) 183–190

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Influence of surface modification on structure formation and micromechanical properties of spray-dried silica aggregates

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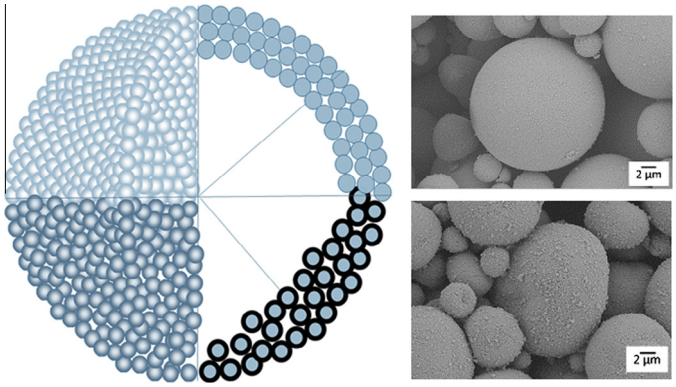
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 July 2015
Revised 12 November 2015
Accepted 13 November 2015
Available online 14 November 2015

Keywords:
Nanoindentation
Silica
Surface modification
Micromechanical properties
Spray drying
Aggregates
Structure formation

ABSTRACT

Spray drying processes were utilized for the production of hierarchical materials with defined structures. The structure formation during the spray drying process and the micromechanical properties of the obtained aggregates depend on the particle–particle interactions, the primary particle size and morphology as well as the process parameters of the spray drying process. Hence, the effect of different primary particle systems prepared as stable dispersions with various surface modifications were investigated on the colloidal structure formation and the micromechanical properties of silica particles as model aggregates and compared to theoretical considerations. The obtained results show that the structure formation of aggregates during the spray drying process for stable suspensions is almost independent on the functional groups present at the particle surface. Further, the mechanical properties of these aggregates differ considerably with the content of the bound ligand. This allows the defined adjustment of the aggregate properties, such as the strength and surface properties, as well as the formation of defined hierarchical aggregate structures.

1. Introduction

Nanoparticles are attributed as important raw material for new or enhanced high quality products in a broad range of the analytical, chemical, pharmaceutical, food and dye industries [1,2]. Obviously, the product quality depends on the properties of the nanoparticles as well as on further processing steps, e.g. the formation of complex nanostructures via spray-drying. Spray-drying is an important process to produce aggregates for different applications. The structure formation before and during the spray-drying process can be controlled by varying the process (air and temperature pattern

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http://dx.doi.org/10.1016/j.jcis.2015.11.028
0021-9797/

inside the column, atomizer type and geometry, product separation geometry, etc.) and formulation parameters (solids content, additives, degree of agglomeration, particle interaction forces, solvents). Based on these parameters complex secondary particles can be designed with various aggregate sizes, morphologies, porosities, surface areas, compositions and internal structures which determine the required application and processing properties [3,4]. More or less complex nanoparticulate structures are in demand for a huge number of industrial products [5,6].

Beside the aggregate structure, the size, the binding mechanism between the primary particles, and thus, the mechanical properties of the secondary particles determine further processing and application. These binding mechanisms are responsible for the micromechanical deformation and fracture behaviour of the structures, especially in spray dried aggregates. The resultant micromechanical properties of the secondary particles depend on the aggregate size and internal structure as well as on the particle–particle interaction forces [7,8]. Especially the density, strength and deformation behaviour of solid bonds within nanostructured aggregates is important to affect the micromechanical aggregate properties [9]. Besides these solid bonds, liquid bonds and capillary forces as well as attractive particle–particle interaction forces (e.g. Van der Waals forces, attractive electrostatic forces) can also have an effect on the mechanical properties [10–13]. Basic research on this plastic and elastic deformation behaviour as well as on the aggregate fracture nanoindentation were done by Kendall and Weihs [14] and Raichman et al. [9]. Furthermore, Rumpf described the fracture behaviour of aggregates [10,15,16]. In order to obtain the desired product features, e.g. mechanical aggregate properties, considerable research of the chemical and physical processes which take place during surface modification and the formulation as well as their effect on the aggregate structure formation are required. Additionally, the aggregate structure, the properties and the rearrangement of the particles during the indentation process influence the mechanical properties [17,18]. These micromechanical properties of secondary particles in the micrometer size range were typically measured via a compression test using nanoindentation devices.

In general, spray drying research can be classified into atomization studies, studies on gas flow patterns, single droplet drying studies and theoretical modelling of the drying behaviour [19]. The effects of different atomizer systems and geometries as well as various materials and process conditions on the morphology of the secondary particles are presented in the literature (e.g. Walzel [20], Walton and Mumford [19]). Another possibility to control the structure during the spray drying process is the usage of nanoparticle suspensions of various materials, particle sizes, particle size distributions, morphologies or surface modifications as building units [21]. In this study, the effect of silica nanoparticles with various particle sizes and surface modifications on the structure formation during the spray drying process was investigated. As the product properties relevant for application and further processing, the micromechanical properties of the aggregates (secondary particles) were characterized using nanoindentation. For the micromechanical properties the aggregate strength as well as the elastic and plastic deformation energies were selected as the characteristic parameters.

2. Materials and methods

2.1. Synthesis, modification and spray drying of silica nanoparticles

For the preparation of silica nanoparticles according to Stöber et al. [22], tetraethyl orthosilicate (TEOS) as precursor, ammonium hydroxide and distilled water as catalyst and ethanol as solvent were used to synthesize nanoparticles in a size range of 60–650 nm. The different particle sizes were achieved by varying the ammonium hydroxide concentration while keeping constant the amounts of water, ethanol and tetraethyl orthosilicate as described by the works of Stöber and Jaeger [22,23]. The particle size increased with the amount of the ammonium hydroxide concentration. The synthesis was performed in a 1 L reactor under stirring for 24 h at 7 °C. Subsequently, the particles were separated by centrifugation for 15 min at 7500 rpm and washed twice with distilled water to remove the unreacted precursor and by-products from the suspension.

For the surface modification of the silica nanoparticles, different additives, such as (3-glycidyloxypropyl)trimethoxysilane (GLYMO), ethoxytrimethylsilane (E3MS), 6-amino-1-hexanol and 2-[2-(2-methoxyethoxy)ethoxy]acetic acid (trioxadecanoic acid, TODA), were selected in dependency of their different binding mechanisms to the particle surface and the expected interparticulate interactions during the formation of aggregates during spray drying. The relations are specified in Table 1.

Subsequently, the additives were added after the washing process with water as solvent, then agitated for 24 h on a magnetic stirrer and afterwards washed to remove the unbound additives. With the renewed addition of water as solvent, nanoparticle dispersions with 5 wt.% were prepared and then spray-dried at a drying temperature of 100 °C and separated with a cyclone (spray dryer 2M8-Trix, Inc. ProCepT). Depending on the selected process parameters (air speed of 0.3 m^3/min; pump speed of 15%), aggregates with a median aggregate size of 8–15 μm were produced.

2.2. Analysis methods

Dynamic light scattering (DLS, Malvern, Zetasizer Nano ZS) was utilized to characterize the particle sizes x of the synthesized silica nanoparticles before and after surface modification. Elemental analysis (FlashEA 1112, ThermoQuest Italia S.p.A) and thermogravimetric analysis (Mettler Toledo TGA/DSC, under oxygen flow in the range of 25–900 °C) were used to investigate the amount of the bound additive at the particle surface. Furthermore, FT-IR spectra were recorded on an ATR Vertex V70 by Bruker. To measure the aggregate size x_A after spray drying, laser diffraction (Helos, Sympatec) was used; the structure of the aggregates was characterized *via* scanning electron microscopy (SEM, LEO 1550, Zeiss). The micromechanical properties of the aggregates were measured *via* nanoindentation (TriboIndenter® TI 900, Inc. Hysitron) using a "Flat Punch" indenter tip with a diameter of 50 μm. For the measurements a loading function with a maximum indentation displacement of 500 nm and a constant indentation rate of 100 nm/s for the loading and unloading sections was adjusted. By stressing the aggregates at small aggregate deformations und using a substrate with a comparatively high hardness, a negligible

Table 1
Binding mechanisms of the selected additives and expected particle interactions after the surface modification.

Additives	Binding mechanism	Interparticulate interactions	Terminal group
Without additive	–	Solid or hydrogen bond	–OH
GLYMO	Chemisorption	Cross-linking via epoxy ring	
E3MS	Chemisorption	Van-der-Waals interactions	$-CH_3$
6-Amino-1-hexanol	Chemisorption [24]	Dipole–dipole-interactions	$-H_2N$
TODA	Chemisorption	Van-der-Waals interactions	$-CH_3$