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Storing water in powder form by self-assembling hydrophobic silica nanoparticles

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Abstract

Water-rich powder containing up to 98% (by weight) of water and characterized by the same flow properties as dry powder was prepared by a simple mixing process. Each particulate consists of a microscopic water droplet surrounded by a network of self-associated hydrophobic fumed silica particles. The cohesion of the silica network, attributed to the van der Waals interactions, is reinforced by particle entanglements and is probably further enhanced by the fractal structure of the network. Once the network is created, the formed shells are strong enough to withstand gravity forces and external stresses. High hydrophobicity and micrometer-sized thickness of the shells ensure that the water phase is kept within the boundaries of the particulates, thus preventing water droplet coalescence. The conditions leading to the formation of water-rich powders strongly depend on the silica particle hydrophobicity.

Keywords: Fumed silica; Water-rich powder; Powder flow; Environmental scanning electronic microscopy; Freeze fracture

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1. Introduction

There is a strong need nowadays for consumer-friendly products in powder form. They include unit-dose products or rapid dissolution formula which are easy to handle and display a good stability upon storage. In particular, powder forms carrying liquid active substances have attracted a lot of attention in the past decade, especially in food, pharmaceutical and cosmetics industry [1]. The elaboration of a “physical” barrier between a sensitive ingredient and the environment has many advantages, such as the preservation of the active against degradation (protection from water, UV, oxygen...) or the prevention of loss of volatile material in the case of perfumes and fragrances. The formulations are safe, because they prevent all contact with the encapsulated material before use and allow a controlled release of the active ingredient. Most liquids encapsulated in powder forms are oils used to incorporate lipophilic substances as flavours, essential oils, anti-oxidant or poorly water soluble drugs [1,2]. Encapsulation techniques are often based on the preparation of an oil in water emulsion followed by the evaporation of water and solidification of film-forming polymers originally present in the aqueous phase. Spray drying, involving the drying of the emulsion droplets in hot air, is the most widely used technique. Further agglomeration of the particles can be achieved in a fluidised bed [1]. In most cases, the oil content is below 50% (w/w) of the total dry material. These systems, also called “dry emulsions”, are self-emulsifying systems, i.e. they are able to spontaneously reform the original emulsion upon dispersion in water [3]. Another technique allowing the incorporation of both oil and aqueous phases in powder form is based on the Concentrated Powder Form (CPF) technology [4], a high pressure spraying process. It consists in mixing the liquid with a supercritical gas, such as carbon dioxide, under high pressure. The solution is then expanded through a nozzle generating fine liquid droplets which are intensively mixed with the powder. The liquid is either adsorbed on the solid surface or absorbed in the cavities of porous carriers. Liquid absorption capacity in most cases reaches up to 70% by weight, depending on the carrier and liquid characteristics. This

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technology is already used in the spice industry and in the production of animal feed [4].

The present work deals with innovative powder forms which can encapsulate up to 98% (by weight) of an aqueous phase. In its simplest formulation, the solid phase is made of hydrophobic silica nanoparticles and water incorporation is achieved using simple mixing processes. This type of powder form was first described in a patent published in 1969 by Degussa [5]. However, despite promising applications, this innovation did not find a real success in industrial applications until recently [6]. This may be due to the quite important cost of fumed silica and some problems related to the product storage, as for example the uncontrolled release of water in the presence of a glass container or when large quantities are involved. Due to the development of new technologies to convert liquids into solid forms, renewed interest has emerged for this process in the last few years. High level of water encapsulation predicts promising applications in food, pharmaceuticals and cosmetics industry [7–9].

The water-rich product obtained is a free flowing fluffy powder. Water can be easily released by mechanical stress, e.g. by rubbing it onto the skin. The encapsulation process allows protection and vectorization of water-soluble active agents and can be easily developed at an industrial scale. However, it is crucial to control the different stages of particulate processing and to understand the mechanism of particle association at a microscopic level in order to optimize the performance of the products.

The purpose of this work was to study the operating conditions required to obtain such powder forms while varying the characteristics of the solid phase. The obtained powders were characterized by their water content, particle size distribution and flowability. The microscopic structure was studied by different complementary techniques. Langmuir–Blodgett film deposition and observation of the films by Scanning Electron Microscopy were first performed in order to study the self association of hydrophobic silica particles on planar water surface. Due to water evaporation in vacuum, direct observation of the water-rich powder is not possible by classical Electron Microscopy techniques. Therefore, a freeze fracture method was used. This technique was successfully employed to observe the structure of simple or multiple emulsions [10]. This method appears to be the most suitable way to observe the system as close as possible to its original configuration. In addition, the structure of the particulates after water sublimation was examined by Environmental Scanning Electron Microscopy. Strong interactions between silica particles made the shell strong enough to keep its original configuration even after water has been evacuated. This study gave a better insight into the mechanism of water encapsulation in powder form and may offer new development for these products.

2. Materials and methods

2.1. Hydrophobic fumed silica characteristics

Fumed silica of the *Aerosil*® range, supplied by Degussa (Germany), is composed of pure amorphous silicon dioxide (>99,8%) manufactured using a combustion process [11–13]. It consists of sintered branched networks, called aggregates, obtained at high temperature by the collision and fusion of primary silica spheres of typical size 10–20 nm. An aggregate is the smallest particulate in which fumed silica can be dispersed. Further collisions between particulates during the cooling stage result in the formation of micron sized agglomerates (typically 20–30 μm) held together by weak interaction forces such as mechanical entanglements or van der Waals forces. Large agglomerates can be easily broken by sonication. Fumed silica used in this study, *Aerosil*® *R972* and *Aerosil*® *R812S*, are hydrophobic powders made of chemically treated silica aggregates in which most surface silanol groups (Si–OH) are respectively substituted by dimethyl–dichlorosilane and hexamethyl–disilazane groups. The typical structure of *R972* and *R812S* aggregates is shown on Fig. 1. These images were obtained using a Transmission Electronic Microscope (JEM 1200EX, JEOL, Japan). Fumed silica was dispersed in ethanol (~16 g L^{-1}), deposited on Cu-grid and observed after ethanol evaporation. Size determination was achieved by Photon Correlation Spectroscopy using a Zetasiser 3000 (Malvern, United Kingdom). For this purpose, dispersions of *R812S* and *R972* in pure ethanol (>99.8%, Prolabo), at a concentration of 0.8 g L^{-1}, were sonicated for 10 min in an ultrasonic bath (Sonoclean® Digital, Bandelin, Germany), and measurements were performed within the next 5 min. Average values of 270 nm and 350 nm were respectively obtained for *R812S* and *R972* aggregates.

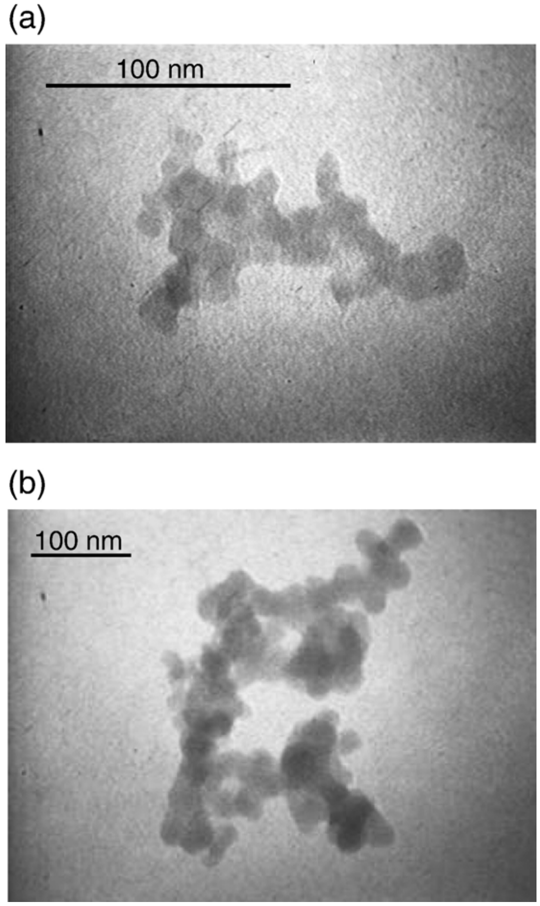

Fig. 1. *R812S* (a) and *R972* (b) aggregates observed by TEM after 10 min of ultrasonic dispersion in ethanol.