SUPERCRITICAL FLUID AIDED MICRO-ENCAPSULATION OF TITANIUM DIOXIDE

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Abstract

TiO_2 particles of less hat 0.2 μm diameter were coated with a thermal swing in a fluidized bed with DMSO-$SCCO_2$ as the solvent system, and Chitosan as the biopolymer coating. The encapsulation experiments were performed in a pressure range of 110-120 bars and a temperature range of 41-50°C (314-323 °K). TEM results confirmed average coating thickness of 27-40 nm, while AFM showed particle roughness of 2-4 nm for the encapsulated samples.

Introduction

Chitosan has proven to be an excellent partner in tissue engineering, and TiO_2 is present in almost all the cosmetic products, so this combination could be promising on skin treatment and regeneration.

Titanium dioxide is a white, opaque and naturally occurring mineral. It has a variety of uses, as it is odorless and absorbent. From medicine to make-up, plastics and. In powder form titanium dioxide (TiO_2) is widely used as an intensely white pigment to brighten everyday products such as paint, paper, plastics, food, medicines, ceramics, cosmetics - and even toothpaste. Its excellent UV ray absorption qualities make it perfect for sunscreen lotions too. It is also inert and biocompatible, making it suitable for medical devices and artificial implants. Titanium dioxide is what allows osseo-integration between an artificial medical implant and bone.

Titanium dioxide is one of the tops fifty chemicals produced worldwide, widely available and well characterized. It is low cost, non soluble in DMSO or $SCCO_2$, and the particle size used is less than one micron and is porous, this last characteristic will allow to evaluate if the porosity has any effect on the encapsulation process; all this properties made reasonable to use it as part of a new encapsulation method in development.

Encapsulation of TiO_2

The encapsulation experiments were performed in a pressure range of 110-120 bars and a temperature range of 41-50°C (314-323 °K), using different contact periods (Table 1). When the encapsulating mix is covering the particles, all the conditions were kept constant in order to achieve a better coverage, followed by a temperature increase, which causes chitosan precipitation. The temperature is not reduced to avoid re-dissolution of the chitosan and subsequently the DMSO is extracted.

The encapsulation cell was preloaded with the solid sample to be encapsulated and sealed. Then the heating bath was activated six hours before the experiment will be running to guarantee stable temperature inside and outside the cell. The carbon dioxide was charged to the system using a continuous pump which kept it at 0 °C, liquid phase, while pumped into the system, at continuous flow rate, the system pressure was controlled with a backpressure regulator. After leaving the pump, the CO_2 was pre-heated in order to reach supercritical conditions inside the encapsulation vessel.

Once the system reached the required operation conditions (T and P) and the particles were fluidized, the coating solution, a DMSO-Chitosan mix, was pumped into the system by the HPLC pump, and the supercritical ternary system (Chitosan-DMSO-CO_2) stays in contact with the solid particles for at least 30 minutes. The system is considered stable when the temperature difference registered at the inlet and outlet of the encapsulation cell in no more than 1 °C. After this adsorption period the cell temperature was increased at constant pressure, causing the coating material to precipitate over the solid particles. The temperature was kept invariable to avoid re-dissolution of the polymer, and the carbon dioxide flow is increased for the DMSO to leave the encapsulation vessel with the carbon dioxide.

Table 1. Coating Experiments Chitosan-DMSO-TiO_2

Core Material	**P (bar)**	**T(C)**	**Contact Time (min)**	**Thickness* (μm)**
TiO_2	110.0	44.0	73	0.0265
TiO_2	120.0	45.0	60	0.0368

*This is an average value, since for each experiment 8-24 samples were collected.

One of the analyses performed in order to estimate the particles size before and after the encapsulation process and the coating thickness for a representative number of particles was a Scanning Electron Microscopy (SEM). This SEM system (Hitachi 800) has features that takes pictures of a group of particles, count the number of particles in the picture and estimated the diameter for each of them. Therefore pictures of the samples were taken before and after the coating, with particle populations in the order of hundreds, establishing a particle size distribution for coated and uncoated TiO_2. The average result is presented on Table 2, and Figures 1 and 2 show the particle size distribution.

Table 2. Average Particle Size from SEM Analysis.

Particle	**# Measurements**	**$Do_{Average}$ (μm)**
Uncoated TiO_2	957	0.39
Coated TiO_2	543	0.40

The results obtained from the particle size distribution do not show too much difference on the particle before and after processing, this could indicate that the coating thickness is on the nanometer order. Another factor that have to be considered is that the SEM picture of the processed samples can involve encapsulated, non-encapsulated and polymer particles, meaning that these analysis give us broad results, but a precise particle size and coating thickness will be obtained through a TEM picture of the particles.

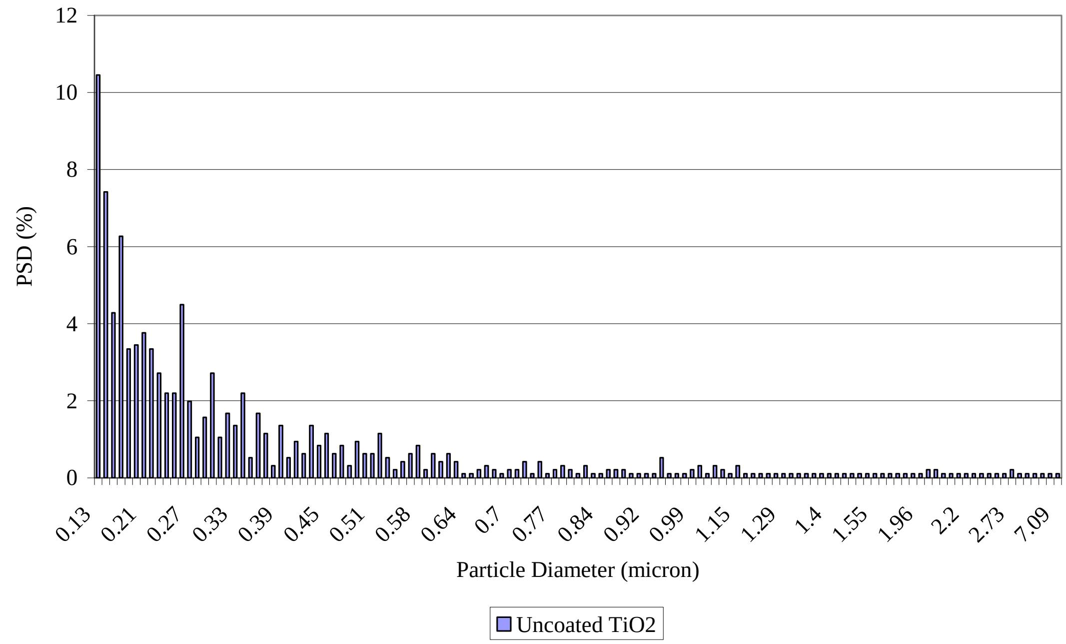

Figure 1. Particle Size Distribution for Uncoated TiO_2 (957 data points).

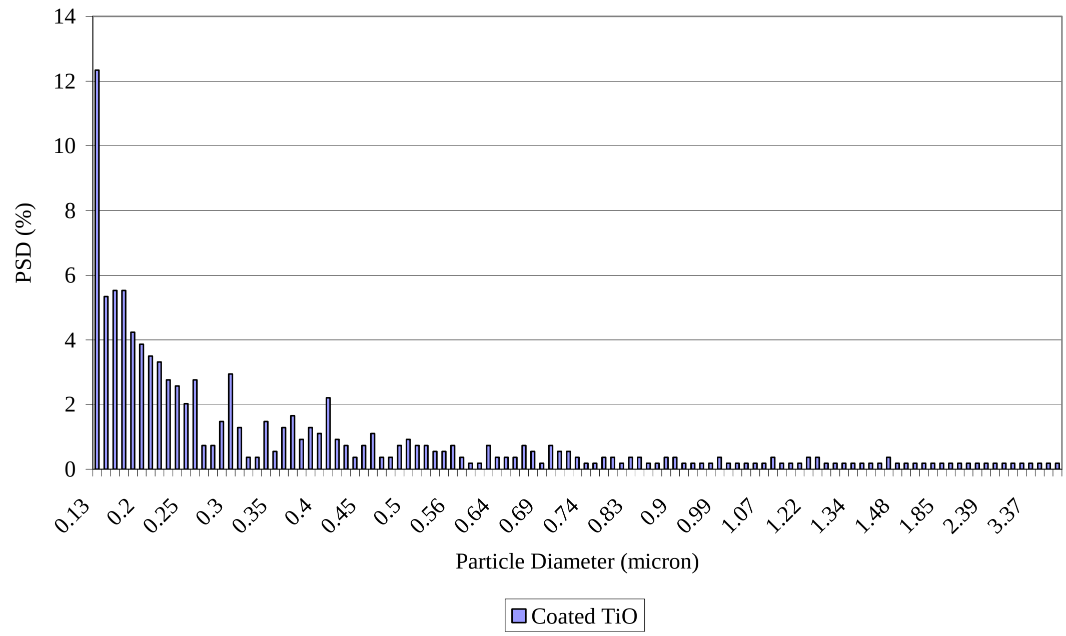

Figure 2. Particle Size Distribution for Encapsulated TiO_2 (543 data points).

TEM analysis of the processed TiO_2 samples confirms the fact that the particles were encapsulated, determining the shape of the encapsulated particles and the coating thickness, as presented in Figure 3.

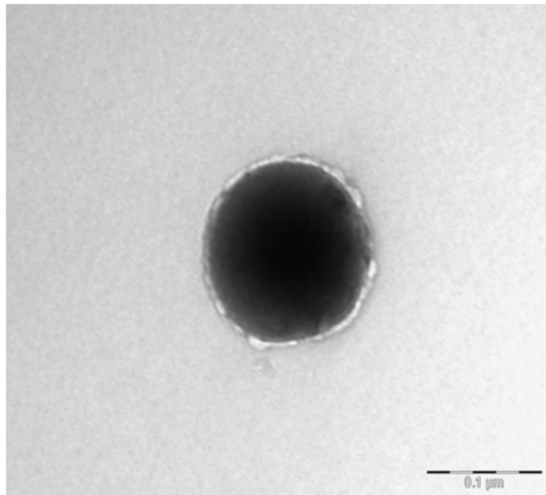

Figure 3. TEM TiO_2 particles coated with chitosan.

Using a set of several pictures taken for each of the samples, the average information about particle size and coating thickness were obtained and presented on Table 3. Where D_o (external diameter), D_i (internal diameter) where calculated from measurements done with the digital TEM.

Table 3. Average TEM thickness measurements for encapsulated TiO_2 particles.

D_o (μm)	**D_i (μm)**	**Thickness (μm)**	**P (bar)**	**T (°C)**	**Contact Time (min)**
0.2575	0.1838	0.0368	120	45	60
0.1840	0.1310	0.0270	110	44	73

Once demonstrated with TEM results that the particles were coated and an average coating thickness was estimated, AFM (atomic force microscope) analysis were performed to study the morphology of the coating. AFM showed particle roughness of 2-4 nm for the encapsulated sample and 46 nm or higher for uncoated ones.

Finally DSC-TGA analysis showed a weight ration of 75% to 25% Chitosan to TiO_2 after the encapsulation process, what could be an indication that the coating material made a way into the porous of the TiO_2 particles.