TiO_2 CERAMIC CONFORMATION USING STARCH AND COMMERCIAL PROTEIN

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Abstract: The use of the conformation method for consolidation with commercial starches in the production of ceramic pieces is relatively recent, being an alternative of low production cost and reduced pollutant potential to the human habitat. This method uses the starch property of forming gel when warm, in aqueous environment, between 55ºC and 80ºC in temperature. This fact allows to its use as binder and pore former element. In order to enlarge the possibilities of application of titanium dioxide ceramics (TiO_2), this work worried in producing samples using this method of direct conformation what makes possible the production of complex geometry pieces. It was used two different compositions: the former, with the addition of commercial starch, that in this case it was the corn starch - density equal to 1.54 g/cm^3 - and the last, with powdered commercial jelly - density equal to 1.62 g/cm^3. The used corn starch was the commercial corn starch that is current human use and it has not any alteration physical or chemical. In order to characterize the ceramics, three-point flexural test was made in TiO_2 samples, according to the ASTM C1161/94 norm, and the results were analyzed by Weibull statistical method. Furthermore, mercury porosimetry and apparent density tests, according to the ASTM C20/87 norm, were made in these ceramics. The samples were also analyzed by measures of specific area and superficial roughness, besides microstructure analysis by light microscopy. The alternative of the commercial jelly use in substitution of the starch showed to be viable, producing ceramics with quite similar mechanical properties to the ceramics made with commercial corn starch.

Keywords: *consolidation, commercial starches, titanium dioxide, Weibull*

1. Introduction

The conformation by commercial starch consolidation process has been become, in the last decade, a way of ceramic production with vast application due to its reduced cost and low environmental impact. Besides those advantages, the use of the commercial starch without chemical or physical modifications is of easy obtaining and it provides the making of objects with complex geometry (Campos, 2001a; Campos, 2001b).

Another factor to be considered in the starch consolidation process is the double usefulness of this element, that acts as binder and as pore former when puts into aqueous solution and warms to the temperature in that gelling process occurs (Lyckfeldt, 1998). In that way, it is possible to control the porosity level of the material and, indirectly, some mechanical characteristics of this by the amount of added starch.

In order to use the advantages of the starch properties and to increase the largest capacity of proportionate gel formation for the commercial jelly, this work intended to produce, by conformation with consolidation process, and to characterize titanium dioxide ceramic (TiO_2) using two compositions: the former, only containing commercial starch and the last, using commercial jelly. The intention of the work was of comparing the properties of the ceramic produced by the two compositions, supposing that, possibly, the commercial jelly could provide a more effective connection among the particles of the ceramic due to the presence, even in small amount, of proteins. This effectiveness, possibly, would be responsible for the completion of the spaces among the particles for the proteins. This fact doesn't occur fully in the process with starch, as Fig. (1) shows. The use of the jelly/protein in the ceramic production was shown in the works of Santos (2002) and Ortega et al. (2003). In this last one a derivation of the process gel casting was used.

In that way, samples were produced by commercial corn starch and commercial jelly consolidation and mechanical tests were made for the characterization of these ceramics. The microstructure verification was made by light microscopy and the results of the two compositions were compared. The choice of the titanium dioxide was due to the bactericidal properties of TiO_2, under the powder form, observed in sterilization processes of polluted waters by

Escherichia coli (Wei et al., 1994) or soils polluted by phenols or derived of this (Hamerski et al., 1999). Such properties occurred when the ceramic material was exposed to the ultraviolet radiation, with close wavelength to the Sun, producing and adsorbing OH radicals in the TiO_2 surface and that are responsible for the photocatalytic degradation process (Gerischer & Heller, 1992; Dagan & Tomkiewicz, 1993). Santos (2002) confirmed this characteristic of bactericidal action, now applied to a ceramic solid of TiO_2.

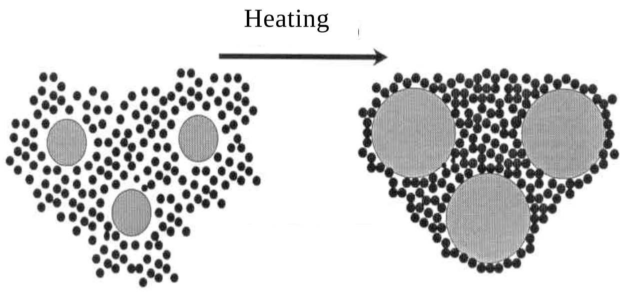

Figure 1 - Growing of the starch grains (larger circumferences) by water absorption, evidencing the spaces among the particles during the gelling process (Lyckfeldt, 1998).

This process can allow enlarging the use of such ceramic in the production of filters and membranes, for instance, to hemodialysis equipment when joint the bactericidal characteristic of TiO_2 and the improvement of the ceramic properties by commercial jelly use. Besides, as the ceramic materials are present in the medical and odontological area in great amount, mainly as material of dental restorations and bone reconstruction (Cahn, 1992), the TiO_2 ceramic would be a good use option as biomaterials due to the characteristics described previously (Santos, 2002).

2. Materials and methods

The titanium dioxide powder, density equal to 4.38 g/cm^3 (Santos, 2002), was inserted in a ball mill and, soon afterwards, in a sieve with the purpose of regularizing the particle sizes. Later, slips were prepared containing TiO_2, distilled water, Disperlam LA defloculant and 15%, in mass, of corn starch, density equal to 1.54 g/cm^3 (Campos, 2001a), and of commercial jelly, separately. The jelly possessed density equal to 1.62 g/cm^3, obtained by helium picnometry, and for each 100 g, as informed for the manufacturer of this, about 9.0 g in proteins, 87.7 g in carbohydrates and 0.2 g in alimentary fiber.

Then the slips were put into a mechanical agitator and a ball mill with the purpose of homogenizing the mixture. After, the slips were poured into no porous molds. The gelling and drying stages were made, respectively, at 60ºC and 120ºC of temperature, in oven.

Later, the samples were sintered at 1450ºC of temperature in electric furnace with a heating ratio of 5ºC/min and holding at for one hour. Samples were produced under the form of bars according to the dimensions proposed by the Astm C1161/94 norm - configuration B / length 45 mm, width 4.0 mm and thickness 3.0 mm.

Sintered samples were exposed to the three-point flexural test, in agreement with the Astm C1161/94 norm and their results were analyzed by the Weibull statistical method. Besides, density and apparent porosity, as well as level of absorption of water, values were obtained by semi-analytical scale of precision 0.001 g use, based on the Archimedes' principle and Astm C20/87 norm.

The verification of the superficial roughness was made by Mitutoyo Surftest 301 rugosimeter and roughness parameters Ra (medium roughness), Rt (total roughness) and R_3z (medium roughness of the third peak and depression) were obtained.

Microstructure features were available by light microscopy, being used an Epiphot/Nikon microscope with a digital camera connected to this. The captured images were analyzed by specific software denominated *Image-Pro*. It was obtained characteristics as *porosity level*, *aspect ratio* and *medium area* of the pores.

3. Results and discussion

Fig. (2) and Tab. (1) present the results of the three-point flexural test, after analysis by Weibull statistical method. A sensitive increase is verified in the rupture strength of the material consolidated with commercial jelly, whose probable cause is due to the effective improvement of the connections among the particles of TiO_2. The process of including gelling of the jelly, filling out with larger efficiency the intergranular spaces, might have provided this fact. However, there was a decrease in the homogeneity of the material, fact that possibly indicates that the material flow during the heating and sintering stages was a little prejudiced, in relation to the starch consolidation process. However, this fact didn't produce a reducing in the mechanical strength of the TiO_2 ceramic consolidated with commercial jelly.

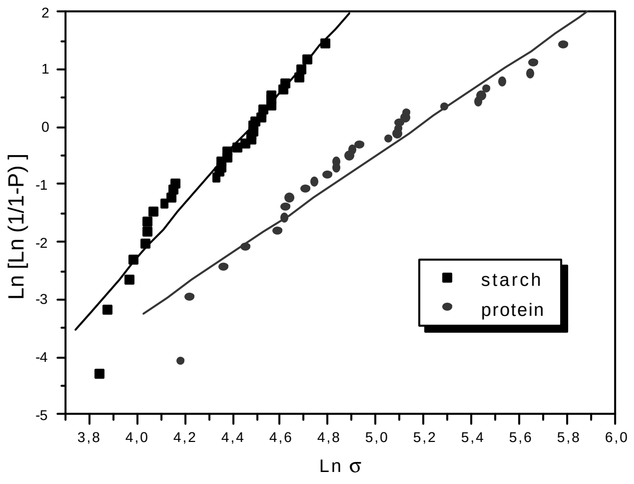

Figure 2 – Weibull's diagrams for TiO_2 samples conformed by starch and protein/jelly consolidation. In this plot, σ is the rupture strain and *P* is the probability of fracture occurring.

Table 1. Results of Weibull statistic method, showing values for TiO_2 ceramics produced by starch and protein consolidation. In this table, σ_0 is the characteristic rupture strain, σ_{50} is the medium rupture strain and *m* is the Weibull module.

Property	Only starch	With protein
σ_0 (MPa)	88.00	135.00
σ_{50} (MPa)	80.60	129.00
m	4.80	3.15

In terms of superficial roughness, as Tab. (2) presents, the increase in the medium and total values of jelly/protein samples in relation to the samples conformed by corn starch consolidation. This property shows, at first, that the process with commercial jelly cannot be indicated in the biomaterial production for bone reconstruction, once the formation of bacteria colonies is extremely affected for the superficial roughness. Since the roughness increases, the probability of growth of these colonies is larger (Santos, 2002). However, in relation to the sterilization capacity of aqueous environments, this material becomes more efficient due to the increase of the contact area. It is important to observe this capacity depends on the activation for ultraviolet radiation of the titanium dioxide bulk.

The reduction of the apparent porosity level in the ceramics consolidated by commercial jelly reinforces the increase of the mechanical strength, possibly caused by the completion of the spaces among particles for the proteins, that ramified with the presence of water and increase of the temperature. This causes a little alteration in the value of the ceramic piece densification.

Table 2. Mechanical properties of the TiO_2 samples produced by starch and protein consolidation.

Property	Only starch	With protein
Contration after burning (%)	12.70	12.40
Apparent density (g/cm^3)	3.57	3.58
Apparent porosity (%)	7.35	2.69
Water absorption (%)	2.05	0.75
Superficial roughness Ra (μm)	2.07	9.80
Superficial roughness R_3z (μm)	1.27	8.48
Superficial roughness Rt (μm)	15.88	19.80
Densification (%)	81.51	81.74

These results allow proposing the use of the conformation by commercial jelly consolidation in elements with specific mechanical properties as, for instance, industrial pieces. In this case values of high rupture strength and low porosity are important factors for the acting of the element.

In Fig. (3) and (4), respectively, light microscopy images of TiO_2 samples conformed by corn starch and commercial jelly consolidation are showed, evidencing their fracture area microstructures of the samples. The results by image analysis are shown in Tab. (3). It is verified that the pores became more circular for the samples consolidated with commercial jelly due to the reduction in the aspect ratio, that is the ratio between the largest and the smallest length of the object. This characteristic reinforces the increase of the ceramic rupture strength because the largest circularity of the pore can serve as homogenizing element of the tension distribution in the material.

The reduction in the porosity level, verified by image analysis method for the samples consolidated with jelly in relation to consolidated with starch, confirms the tendency of the results obtained by test with analytical scale. Since the results of both analysis methods have difference, possibly, the pores cannot be connected.

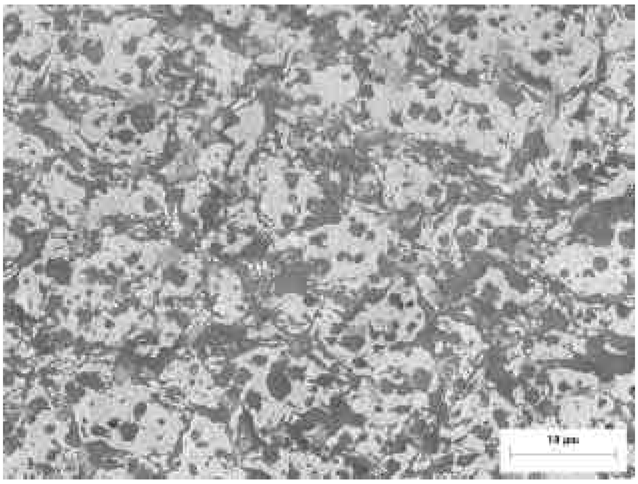

Figure 3. TiO_2 sample microstructure produced by commercial starch consolidation. The sample was sintered at 1450ºC of temperature and its microstructure was verified by light microscopy.

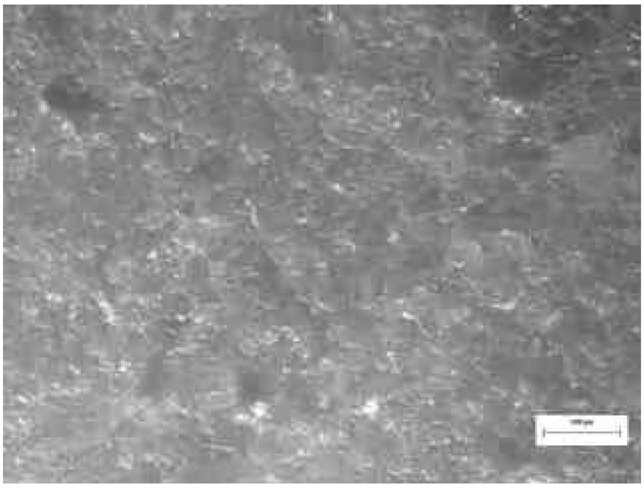

Figure 4. TiO_2 sample microstructure produced by commercial jelly consolidation (protein consolidation). The sample was sintered at 1450ºC of temperature and its microstructure was verified by light microscopy.

Table 3. Results of the light microscopy in TiO_2 samples produced by starch and protein consolidation.

Property	Only starch	With protein
Pore aspect ratio	1.90	1.76
Porosity level (%)	14.93	5.61
Pore medium area (μm^2)	11.81	0.72

Fig. 5 presents a computerized reconstruction of the surface of the samples consolidated with starch and jelly, using a plug-in denominated *Depth from focus*. This plug-in uses as data entrance a group of images denominated stack. Such images are extracted with successive displacements of the graduate ring that controls the microscope focus. After obtained stack, a matrix of odd dimensions covers the images and, for the same coordinates, two outputs are determined: an image in that all areas in focus are present and other image in that the brightness corresponds to the elevations of the surface. At first, this method allows to do a qualitative analysis of the surface of the ceramic material, by comparison of the pieces produced for two consolidation methods. The increase of the superficial roughness of the samples conformed by commercial jelly consolidation can be verified by comparison between Fig. (5-a) and Fig. (5-b), evidencing the roughness enlargement with commercial jelly use. This result confirms the ones obtained in Tab. (2) by rugosimeter measurements and reinforces the greater possibility of environment sterilization for contact area amplification.

4. Conclusions

The production of titanium dioxide ceramic obtained by conformation with commercial jelly consolidation presented a larger mechanical strength value in relation to commercial corn starch consolidation. This fact, associate to the smallest porosity value, can allow its use in elements with specific mechanical properties as industrial pieces. Besides, the increase of the superficial roughness of the TiO_2 ceramic and consequent increase of the contact surface can allow its use as sterilization element of aqueous environments when the material is exposed to the ultraviolet radiation with close wavelength to the produced by the Sun. The use of the conformation by consolidation process allows to be obtained pieces with complex geometry, low production cost and environmental impact. In spite of that, in the case of the consolidation with commercial jelly, the smallest value of the module of Weibull, indicative of smaller homogeneity of the material, suggests that the production procedure should be altered, in way to improve this feature.

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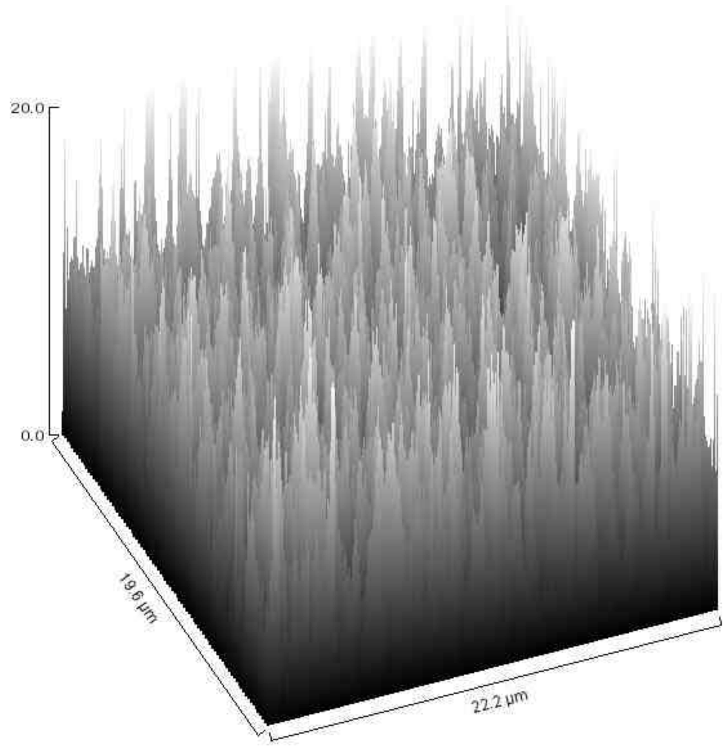
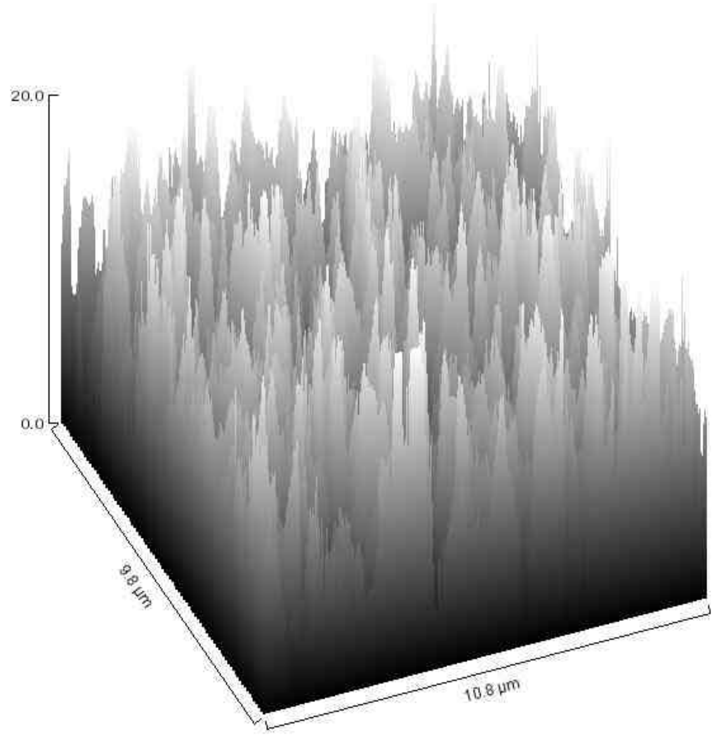


(a)



(b)

Figure 5. Depth from focus of TiO_2 samples produced by (a) starch and (b) jelly consolidation.