MECHANICAL CHARACTERIZATION OF TiO_2 CERAMICS CONTAINING Al_2O_3 AND SiO_2.

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Abstract. *Recent studies had shown that the TiO_2 powder could be used in water and waste treatment. In order to develop ceramic devices for this purpose, the characterization of the mechanical properties of these ceramics becomes important. We compared mechanical properties of ceramics prepared from two different powder suppliers, with distinct degrees of purity. The first lot presented 98.5% purity (TiO_2^{PA}) and the second one, 91.0% of TiO_2, with 4.3% of Al_2O_3 and 1.4% of SiO_2 (TiO_2*). The powders were analyzed by X-ray diffraction and He picnometry. We prepared samples with these two materials mixed, varying their concentration from 5 to 95% in mass, as well samples containing only TiO_2^{PA} or TiO2*. The samples were prepared in the form of bars under 40MPa pressure and sinterized at 1450^oC. The mechanical characterization involved three point flexural tests, analyzed by Weibull statistics, measurements of apparent density by Archimedes principle, determination of Young's modulus, verification of surface roughness and wettability. The powder analyses indicated that theirs density are equivalent and the diffractometry did not detected any significant difference between them. In conclusion, the mechanical analyses suggested that both TiO_2 present similar mechanical properties, suggesting the technological use of the cheaper one, that is, TiO_2*.*

Keywords*: ceramics, titanium dioxide, mechanical properties, bactericidal action*

1. Introduction

In the last decades, ceramic materials have become an important option in the metallic and wood component substitution, as well as biomaterial. During and after to Second World War, the research in materials, especially the ceramics, took a larger impulse due to the cost-quality relation allied to good mechanical performance, as well as in the improvement of the human being's quality of living.

In the case of porous ceramic, they present a wide application variety and can be used as permoselectives membranes and filters or in catalysts. In many of those applications it is necessary a considerable control of the porosity geometry to assure the working of the used product.

Titanium dioxide has a lot of interesting and useful features and hence is widely utilized in technological applications. It has been used as white pigment, photocatalyst, biocompatible material and, as a semiconductor material, used in solar battery. Recently, titanium dioxide has been used in sterilization process of several environment types. For instance, powder TiO_2 has been used in polluted waters by *Escherichia coli* [Wei, 1994] or in soils polluted by phenols or derivatives [Hamerski, 1999]. Such properties appear when the ceramic material is exposed to the near ultraviolet radiation, typically emitted by the Sun, producing and adsorbing OH radicals in the TiO_2 surface and that are responsible for the photo-catalytic degradation process. The bactericidal action, can also be observed in ceramic form of TiO_2 as reported by Santos, 2001.

The aim of the work presented here was characterize mechanically a sample of raw and cheaper material constituted by impure TiO_2, before evaluating it in technological applications.

Many industrial plants use TiO_2 powders with purity of 91,0%, possessing silica (SiO_2) and alumina (Al_2O_3) as main impurity. This titanium dioxide (named hereafter as TiO_2*) presents a smaller commercial cost and good availability in the international market. On the other hand, TiO_2 of analytic purity (98.5% purity) has been used in researches in several scientific and technological areas. However, this TiO_2 (named hereafter as TiO_2^{PA}) is more expensive and little available in the market.

In previous works [Wei, 1994, Hamerski, 1999, Santos, 2001,Dagan, 1993] it has been discussed the application of the titanium dioxide (TiO_2) as biomaterial in medical and dental implants and as bactericidal agent. In the implant cases, the porosity level can allow the bone cells growing and developing with larger easiness inside or over the implanted organ. Further, the bactericidal action can be influenced strongly due to the alteration in the contact area with the environment to be sterilized.

However, the value of the mechanical strength is influenced strongly by the porosity level that this material possesses, what turns the control of the level and form of the pores in the feature determination extremely important. The study of porous ceramic, according to Salvini, 2000, shows that the main criteria of ceramic filter evaluation are the permeability, the efficiency of the impurity retention and the mechanical strength. In the case of filters, these should remove the maximum of impurity according to low resistance to the drag fluid. This characteristic can be obtained by the void volume increase in the structure (porosity). However, this strategy usually reduces the mechanical strength of the material structure.

In this work it will be compared the mechanical properties of ceramic produced with two lots of powder TiO_2, with different degrees of purity and, consequently, different production costs. The control of the porosity level can be made by the production method. A method widely used in the ceramic material production is the uniaxial pressing. This process may be defined as the simultaneous uniaxial compaction and shaping of a granular powder with small amounts of water and/or organic binders during confined compression [Wang, 1976].

2. Materials and Methods

2.1 Materials

Two commercial TiO_2 powders with different composition and cost were used. The first material samples were a titanium dioxide TiO_2^{PA} – rutile (*LABSYNTH SA)* with a high purity (98.5 wt.%). The second one, was constituted by an impure titanium dioxide TiO_2* (Dupont S.A.- R-902 – furnisher BASF S.A.) with TiO_2 (91.0 wt. %), Al_2O_3 (4.3 wt. %) and SiO_2 (1.4 wt. %).

The purpose of the present work was to study the capacity to produce ceramic with TiO_2*, as well characterize its mechanical properties. Thus the powders were mixed (ball mill) according to the table 1.

Table 1 – Powders mixing

Sample	A	B	C	D	E	F	G
TiO_2* (wt%)	0	5	25	50	75	95	100
TiO_2^{PA}(wt%)	100	95	75	50	25	5	0

The selection and application of organic or inorganic binders can be classified as critical factor in the uniaxial pressing process. The polyvinylic alcohol solution PVal (4.0 wt. %) was used as binder.

2.2 Preparation and sintering

TiO_2* and TiO_2^{PA} samples were prepared from powders with addition of 0.5 wt% PVal and 10.0 wt% distilled water. The mixtures were then ball milled for 30 min to homogenize them completely, sifted through a 10-mesh sieve, placed in a non-porous metallic mold. The powders were pressed in a unixial press at 40 MPa using stearic acid as a lubricant for the walls of the steel die. After pressing, the samples were pre-sintered for one hour at 1100ºC in an electric furnace (EDG - 1800), using a heating rate of 5ºC/min and sintered one hour at 1450ºC in an electric furnace (EDG - 1700), using a heating rate of 3ºC/min

2.3 Characterization of Ceramic Powders

The production of advanced ceramic materials generally begins with powders, which are transformed into useful objects or components by a variety of thermal, mechanical and chemical processing methods. The resulting properties and performance characteristics of these materials are known to depend significantly on the chemical and physical properties of the starting powders. Consequently, accurate characterization of the starting powders is essential to achieving high quality, reproducible production of current materials and the development of new materials with optimized or designed properties [Munro, 1988, Roosen, 1988, Tarì, 1998].

In this work, the identification of the powder crystalline phases was accomplished through X-rays diffractometry (Siemens kristalloflex - Cu anode – angular range (2θ): 4º to 70º). In well-controlled conditions, X-ray diffraction is a non-destructive characterization technique, keeping the material properties unchanged.

In any controlled ceramic process, the control and understanding of powder density is essential, because the physical and chemical characteristics that affect powder density will influence the manner in which the powder reacts and behaves during subsequent processing steps.

In this work, the specific mass of the powders was determined by helium picnometry using a Micromeritics picnometer model 1305. This technique allows the differential determination of the specific mass by the expansion in a cell with the sample, in relation to calibrated cell.

2.4 Characterization of Ceramic Pieces

The ceramic's mechanical strength was evaluated by three-point flexural testing, following the ASTM C1161/94 standard [ASTM, 1994], using an EMIC testing machine at a speed of 0.5 mm/min. The standard formula for the strength of a beam in three-point flexure [ASTM, 1994, Callister Jr., 1999, Piorino, 1990] is as follows:

$$\sigma = \frac{3\,QL}{2\,bd^2} \tag{1}$$

where:

Q = breakload;
L = outer (support) span;
b = specimen width;
d = specimen thickness.

The results were analyzed based on Weibull's statistical method [Wang, 1976, Piorino, 1990, Chiang, 1997], that defines the probability of failure (P) according to the expression

$$\ln\left(\ln\frac{1}{1-P}\right) = m(\ln\sigma) - m(\ln\sigma_0) \tag{2}$$

Where $\underline{\sigma}_0$ is the characteristic strength depending on the distribution function, σ_{50} is the "average" strength value and $\underline{m}$ is a constant related to material homogeneity, named *Weibull modulus*. The larger the value of m, more homogeneous is the strength value. As $\underline{m}$ becomes infinite, fracture occurs only that the characteristic strength σ_0; that is, the strength is absolutely predictable.

Young's modulus may also be determined by resonance tests and ultrasonic techniques. In this work, the modulus elastic (E) was determined by ultrasonic method. This technique generally assumes the body as isotropic. Poisson's ratio can also be obtained through the relationship of the dimensional changes parallel and normal to the applied stress direction.

Apparent density was determined based on the ASTM C20-00 norm [ASTM, 2000] and Archimedes principle. This technique is used to evaluate and to compare materials that are not attacked by water. Apparent porosity also was obtained by this method.

Three parameters were chosen in this work for evaluates the surface roughness: Ra (mean roughness), Rt (total roughness) and R_3z (mean roughness of the third peak and depression) [Guimarães, 1999].

The hydrophilic and hydrophobic characteristics of the titanium dioxide samples were evaluated through contact angle (θ) [Adamson, 1997]. The material's wettability is directly associated with its superficial tension and with behavior of the solid liquid interface, assuming that the material in question is solid. The contact angle is measured by the tangent between a drop of the liquid and solid surface, as shown in Figure 1.

Considering a drop at rest, i. e., with the variation of the surface free energy per unit area tending to zero one has:

$$\gamma_{LV}\cos\theta = \gamma_{SV} - \gamma_{SL}$$
$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \tag{3}$$

Where γ_{LV}, γ_{SV} and γ_{SL} are, respectively, the interfacial tensions between liquid and steam, solid and steam, and solid and liquid.

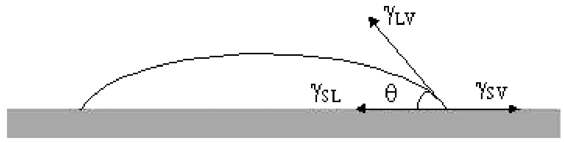

Figure 1 – Contact angle

3. Results and Discussion

3.1 Analysis of ceramic powders

The results obtained by helium picnometry are shown on table 2. It can be seen that both TiO_2 samples are equivalent, in terms of powder specific mass.

Table 2 – Powders density.

TiO_2*	TiO_2^{PA}
4.24 $g.cm^{-3}$	4.23 $g.cm^{-3}$

Figures 2a and 2b show the TiO_2* and TiO_2^{PA} powder X-rays diffractograms. They show a typically rutile sample profile, with the observed diffraction peaks corresponding to a rutile structure. We can observe that the presence of the impurity didn't c hange the peak's position, showing that has not significant structural change with the increase of the Al_2O_3 and SiO_2.

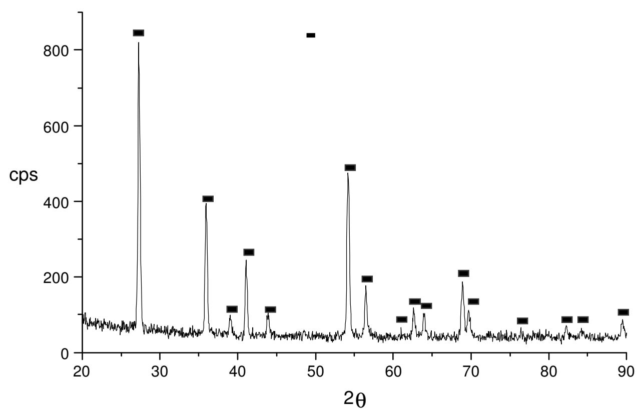

Figure 2a – TiO_2* powder X ray diffractogram

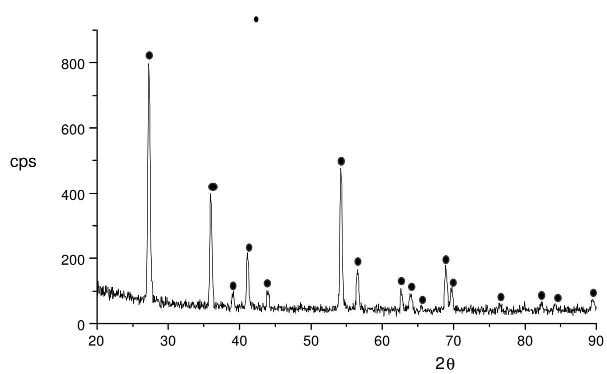

Figure 2b – TiO_2^{PA} powder X ray diffractogram

These results show that the powders have similar characteristics, indicating that the degrees of purity of these don' t alter your fundamental characteristics.

3.2 Ceramics Characterization

Table 3 resume the results of the three-point flexure test, analyzed according to the Weibull statistical method. It contains the values for σ_0 (characteristic strength), σ_{50} (mean strength) and m (Weibull module).

Table 3 – Values of theσ_{50}, σ_0 e m

TiO_2* [wt%]	σ_{50} [MPa]	σ_0 [MPa]	m
0	133	140	10.3
5	128	134	11.6
25	127	133	9.9
50	142	150	8.7
75	141	149	9.4
95	130	135	12.2
100	176	188	6.7

The results for the TiO_2* sample (100%) presented larger value of mechanical strength and smaller module Weibull (smaller homogeneity), when compared with those for TiO_2^{PA} (0%). These first results might indicate that the TiO_2* powders would produce ceramic with resistance values larger than those for TiO_2^{PA} powders.

Apparent density and porosity, based on Archimedes' principle are shown on table 4.

Table 4 – Results using the Archimedes' principle, according to ASTM C 20-00. (V_{pa} – volume of open pores; A_a – water absorption; P_a – apparent porosity; d_a – apparent density; and d_r – relative density)

TiO_2*[wt%]	V_{pa} [10^{-3} cm^3]	A_a [%]	P_a [%]	d_a [g/cm^3]	d_r [%]
0	7.07	0.63	2.48	3.94	93.19 ± 0.92
5	9.00	0.56	2.19	3.93	92.83 ± 0.53
25	7.21	0.44	1.74	3.97	93.70 ± 1.10
50	7.14	0.49	.94	3.95	93.34 ± 0.56
75	5.71	0.41	1.61	3.97	93.67 ± 0.70
95	5.29	0.37	1.46	3.97	93.77 ± 0.59
100	9.64	0.82	3.14	3.88	91.50 ± 1.40

We can notice that the apparent porosity (P_a) don' t vary significantly, with the inclusion of TiO_2*, in spite of the presence of SiO_2 and Al_2O_3. The sample 100% TiO2 presented an unexpected value of water absorption (Aa) affecting the calculations of the apparent density.

Table 5 shows the elasticity modulus and Poisson's ratio for the samples with TiO_2* e TiO_2^{PA}. The values of the elastic modulus are close, confirming the tendencies observed in the flexural test and porosity analyses.

Table 5 – Young's modulus and Poisson's ratio

TiO_2*[wt%]	Young's modulus (GPa)	Poisson's ratio
0	252	0.24
5	232	0.28
25	230	0.28
50	232	0.21
75	251	0.24
95	242	0.23
100	250	0.23

The values obtained for the roughness are shown in the table 6. Again it can be noticed that the roughness is not affected significantly by the presence of SiO_2 and Al_2O_3.

Table 6 – Measurement of superficial roughness (Ra: mean roughness; Rt: total roughness; R_3z: mean superficial roughness of the third peak and depression)

TiO_2*[wt %]	Ra [µm]	R_3z [µm]	Rt [µm]
0	1.94 ± 0.30	2.99 ± 0.98	15.20 ± 3.90
5	1.73 ± 0.51	2.42 ± 0.63	10.90 ± 2.80
25	2.14 ± 0.49	3.20 ± 1.10	14.10± 2.60
50	2.32 ± 0.63	2.13 ± 0.83	12.30 ± 2.10
75	1.76 ± 0.33	1.65 ± 0.56	11.00 ± 2.30
95	2.51 ± 0.55	2.70 ± 1.10	15.20 ± 2.90
100	1.41± 0.35	2.18 ± 0.62	10.40 ± 3.60

The contact angle measurements are shown in Figure 3.

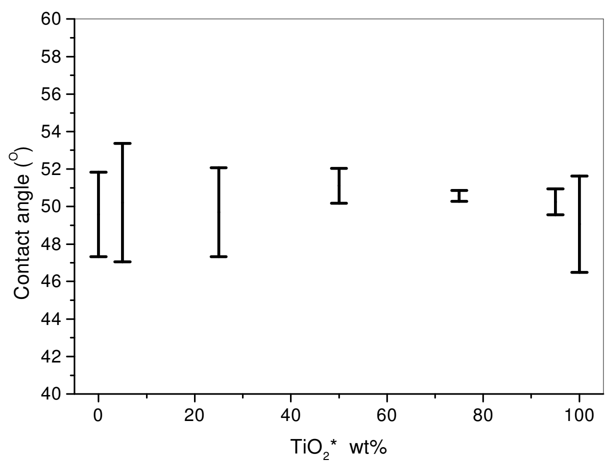

Figure 3: Contact angle values as a function of TiO_2* amounts.

4. Conclusions

This work aimed the determination and comparison of some mechanical properties of two samples of titanium dioxide (rutile). The main objective was evaluate, how the presence of impurity in the powder of TiO_2 would alter its mechanical properties after sintered (ceramic form). The motivation was the possibility of using a cheaper material (TiO_2*) for technological applications involving ceramics.

The initial hypothesis was that the presence of SiO_2 and Al_2O_3 would change the mechanical properties of the porous ceramic. The magnitude of those changes would allow evaluating the use of a raw material of smaller purity, however, smaller cost, in some applications. Considering this initial hypothesis, the proposed methodology was produce samples with an increased amount of TiO_2*, in a matrix TiO_2^{PA}, in order to follow the changing on mechanical properties.

The results of the tests showed that no significant changes exist among the two materials, as well as your mixtures. Those results allowed conclude that the impurities do not make the TiO_2* unable to technological use. On the contrary, the smaller cost of the raw material is a factor that favors your use.

This work showed that the samples prepared with TiO_2* are mechanically equivalent as those prepared with TiO_2^{PA}, what implicates in an economical advantage. Further, the roughness values and mechanical resistance obtained indicate that both ceramics can be used as prostheses in certain body regions that demand smaller effort mechanic. These results are very important because the presented here work is part of a wider project that seeks for the biotechnological use of TiO_2 ceramics. In particular, it is desired using TiO_2 ceramics in the treatment of water, based on its photo-catalytic effect, and in the development of prostheses, to be used in Medicine, Veterinary or Dentistry.

However, in order to explore the biotechnological use, three sets of features must be verified: mechanical properties, physical-chemical stability and toxicity. These features are important to classify a ceramic as a biomaterial or a biocompatible material.

The presence of SiO_2 e Al_2O_3, probably would produce no physical-chemistry changes or toxicity effects, as these substance are reported in Literature as bio-inert substances, to a wide range of application. However, we can never neglects a priori the possibility of aluminum release inside the body. Recent toxicity essays indicated that TiO_2* ceramics can be used in oral cavities, acting as dental prosthetics, with no biological rejection [Santos, 2001].

So, instead of the presented work deals only with mechanical properties, the conclusions indicate that the raw and cheaper impure TiO_2 ceramics can be a good option for technological applications. While the use as prosthetic devices requires toxicity studies, to avoid undesired biological results, there are other applications that one can use the TiO_2 photo-activation properties to kill or at least to control bacterial growing. This range of application includes water and waste treatment even in industrial plants as well domestic installations.

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6. *In memoriam*

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