COMPARATIVE STUDY OF TITANIUM DIOXIDE'S RHEOLOGICAL PROPERTIES

Lucie JEZERSKA[1,*], Jakub HLOSTA[1], Martin ZIDEK[1], Jiri ZEGZULKA[1], Jan NECAS[1], Katerina MAMULOVÁ KUTLAKOVA[2]

[1]VSB – Technical University of Ostrava, ENET, 17. listopadu 15, 708 33 Ostrava, Czech Republic

[2]VSB – TU of Ostrava, Nanotechnology Centre, 17. listopadu 15, 708 33 Ostrava, Czech Republic

** Corresponding author: lucie.jezerska@vsb.cz*

Abstract

Titanium dioxide is widely used material. Although it was described some 210 years ago, it still represents a topic of intense scientific research and also many publications were written. The rapidly growing interest in this material has been recently initiated by its special utilization. Titanium dioxide is used primarily as a component of paints and plastics, paper, leather, the treatment of ceramics, but also as an additive in food or as an ingredient in cosmetics and pharmaceutics. The aim of the presented paper is characterization of TiO_2 samples which show different rheological properties due to different volume of fine particles. Experimental work was performed by the Freeman Technology FT4 Powder Rheometer and CPS DC24000 Disk Centrifuge. The devices allow to obtain a considerable amount of information about powder properties and behavior like a bulk density, granulometry, friction, compressibility, aeration, permeability or mechanical interlocking. All of these parameters give information about behavior of bulk solids in wide scale of industrial applications because many flow failures can happen (e.g. arches, chimneys, etc.). Two commercial samples which differed in size fine particles fraction were used. The results of laboratory experiments show that difference in fine fraction has an influence on the rheological properties of the samples and their further processing. The changes were observed mainly in compression factors and permeability powders.

Keywords:

Rheological properties, flowability, titanium dioxide, comparative measurements

1. INTRODUCTION

Titanium dioxide is an inorganic material that might crystallize to different modifications [1]. As often described, there are three main types of TiO_2 structures: rutile, anatase and brookite. The size dependence of the stability of various TiO_2 phases has recently been reported [2]. Rutile is the most stable phase for particles above 35 nm in size. Structure of all three modifications can be described by octahedrons. The difference is in distortion of octahedrons and their connection into spatial nets. In anatase the octahedrons touch upon vertexes, in rutile upon edges (**Fig. 1**), and in brookite both upon vertexes and edges [3]. Crystallized structures anatase and rutile are the most known and used ones in industry. The largest commercial usage of TiO_2 is its usage as a white pigment in colouring industry. About 25 % is used for production of plastic packaging materials. The fibres without pigment are clear and they have "greasy" look. Titanium dioxide adds matt shine to the fibres. In paper mill TiO_2 is added to white papers and to thin papers that are supposed to be non-transparent [4]. Titanium dioxide is also added to enamel, pottery, cement and white rubber [5, 6].

The aim of the presented paper is characterization of TiO_2 samples which show different process behaviour during the transport and discharge of the samples from bulk bags. Other studies show that removing of air significantly affects features of bulk solids and always impairs the flowability [7]. This might appear as a result of storage, transport or as a side effect in process of manufacturing, e.g. because of vibrations [8].

Results indicate that the less air the powder contains, the more energy is required to putting it into motion [9, 10]. Titanium dioxide shows reduced total energy with increasing air velocity. This behaviour is typical for most of the powders that are average sensitive to aeration [11]. The effort to find the dominant parameter (aeration, compressibility, angle of internal friction, permeability etc.) and the cause of different behaviour of two at first site identical samples led to their detailed characterisation in the field of mechanical-physical features. Samples were tested in terms of flow properties in powder rotational rheometer. Analysis of selected measured data is the content of individual chapters.

2. MATERIALS AND METHODS

Materials

Two samples of TiO_2 were used in this work. There are two industrial samples, which are called TiO_2 (A) and TiO_2 (B) in this article. X-ray powder diffraction was done to determine differences in crystallographic structure. The shape of particles was captured by a SEM (Scanning Electron Microscopy). SEM photos are illustrated below in **Fig. 1**. The samples look identically at the first sight.

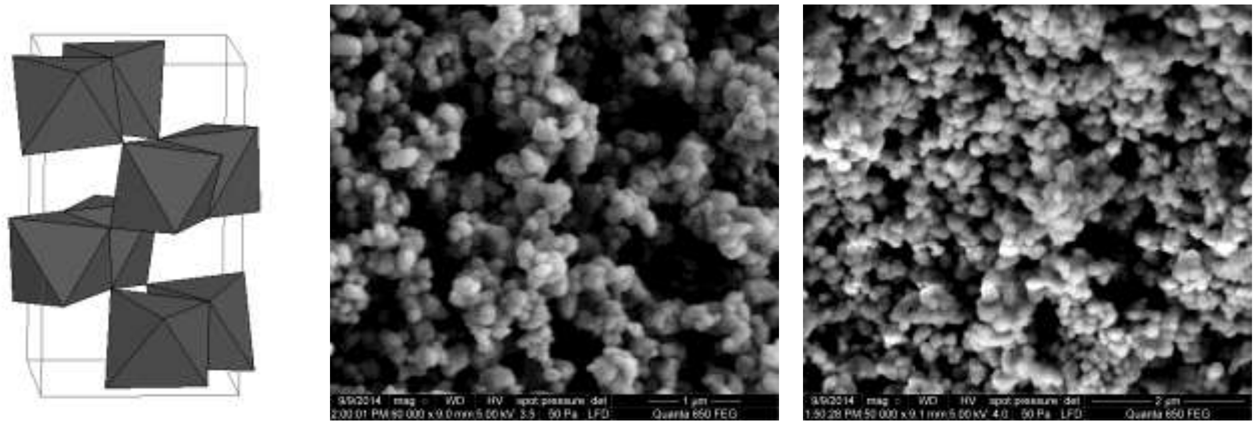

Fig. 1 Rutile crystal structure [3] and TiO_2 SEM photos. Left photo – sample TiO_2 (A), right photo – sample TiO_2 (B).

X-ray powder diffraction

The XRPD patterns were recorded under CoKα irradiation (λ = 1.789 Å) using the Bruker D8 Advance diffractometer (Bruker AXS) equipped with a fast position sensitive detector VÅNTEC 1. Measurements were carried out in the reflection mode, powder samples were pressed in a rotational holder, goniometer with the Bragg-Brentano geometry in 2 θ range from 5 to 80°, step size 0.03°. Phase composition was evaluated using database PDF 2 Release 2004 (International Centre for Diffraction Data).

Bulk properties

The device used for bulk properties measurement was an FT4 Powder Rheometer. FT4 is a universal powder tester, combining patented blade methodology for measuring flow energy with range of shear cells, wall friction modules and other accessories for measuring bulk properties. The methodologies allow measurement of flow energy in relation to many variables and all packing states, shear properties of consolidated or unconsolidated powders, bulk properties – bulk density, compressibility and permeability. The above properties allow to powder samples to be comprehensively characterized for the extreme of packing and environmental conditions that occur in everyday processing.

Particle size distribution

A particle size analyzer The CPS Disc Centrifuge DC24000 was used for measuring particles size in the range of 0.01 micron to 40 microns. The system is most effective with particles between 0.02 and 30 microns. The analyzer measures particle size distributions using centrifugal sedimentation within an optically clear spinning disc that is filled with fluid. Sedimentation is stabilized by a density gradient within the fluid, and accuracy of measured sizes is insured through the use of a known size calibration standard before each test. The concentration of particles at each size is determined by continuously measuring the turbidity of the fluid near the outside edge of the rotating disc.

3. PARTICLE AND BULK PROPERTIES

The motion and behavior of bulk solids and powders depend on many factors and properties of particulate matter. Flowability or jamming of bulk solids inside hoppers and silos is influenced by wall friction, cohesive forces between particles and inner resistance of powder. Due this fact is widely used aeration of material inside the hoppers. Aeration is one of the important bulk properties tests of this article. Also shear cell, bulk density, compressibility and permeability assessments were done.

3.1 Granulometry and XRPD

Particle size distribution and XRPD spectra of both TiO_2 samples are shown in **Fig. 2**. Particle size distribution indicates about 40 % higher volume of nanoparticles in range from 0 to 170 nm in TiO_2 (B) sample. X-ray powder diffraction confirms an occurrence of rutile in a both cases. Spectrum shows the same kind of the tetragonal system (space group P42 / mnm (136)) of the samples in a chemical point of view.

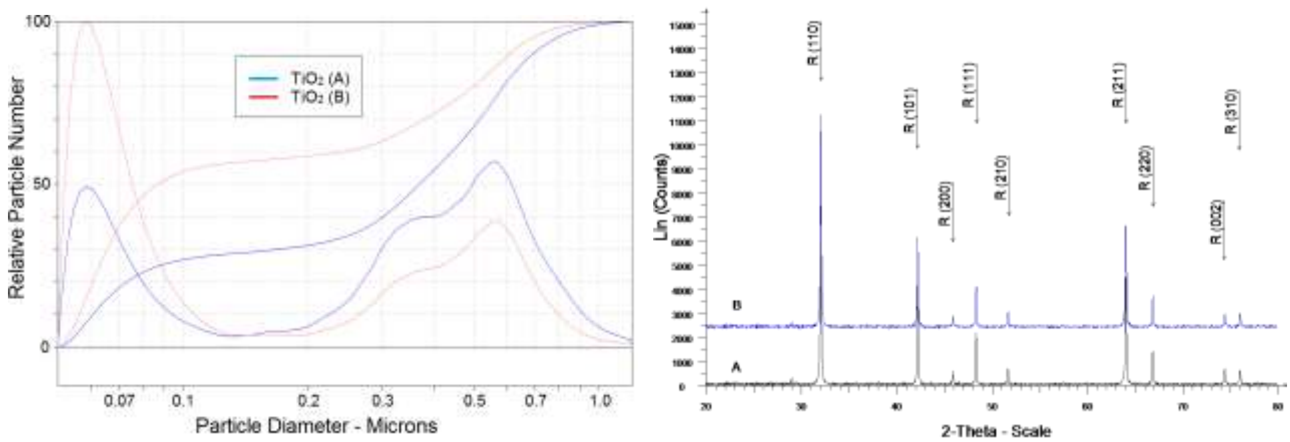

Fig. 2 Granulometry and XRPD spectrum results.

3.2 Shear cell test

Shear properties are important for understanding how easily the consolidated powder, which was previously at rest, will begin to flow. In every process and storage environment, powders will be subjected to consolidation stresses causing changes in density and mechanical interparticle forces. For flow to occur, it is necessary that yield point of the powder is overcome. Physical properties such as size, shape and surface characteristics of the particles will greatly influence the yield point, as will variables like moisture content or level of flow additive.

For consolidation load was used 15 kPa pre-shear stress in this test. Corresponding values of all important friction parameters (σ_1, σ_c, ff_c, T, φ) are listed in **Table 1**. To characterize flowability, Jenike proposed to use the ratio of the major principal stress σ_1 to the unconfined yield strength σ_c, called the flowability index [12].

His classification of flow behavior according ff_c is presented in **Table 1**. Both samples are in the same cohesive group, but the sample B with a large amount of fine particles exhibit slightly worse flowability and higher angle of internal friction *φ.* Shear test results indicate no significant impact of different granulometry to shear properties of the TiO_2 samples.

Table 1
Shear test results

Sample	σ_1 (kPa)	σ_c (kPa)	ff_c (-)	T (kPa)	φ (°)	*Flowability classification*
TiO_2 (A)	35.4	14.5	2.44	2.87	46.7	Cohesive material
TiO_2 (B)	38.9	17.2	2.26	3.00	51.5	Cohesive material

3.3 Aeration and permeability

The bulk properties of all powders are affected by air to some extent since the space between the particles is filled with air. The amount of air influences how the particles interact with each other and this impact directly upon the flow properties. Some powders are readily aeratable and only require a small amount of air to transform the powder bulk into a fluidized bed, in which the powder behaves as a fluid and requires only a small amount of energy to produce flow.

Permeability is a measure of how easily material can transmit a fluid (in this case air) through its bulk. For powders, it is influenced by many physical properties such as particle size and distribution, cohesivity, particle stiffness, shape, surface texture and bulk density. External factors such as consolidation stress are also likely to influence permeability by changing the porosity and particle contact surface areas, making it more difficult for the air to pass through the bulk.

Permeability differences may cause problems and fluctuations in air-based technologies. Higher volume of fine particles influences transmission of the air through bulk solids and on basis of this fact TiO_2 (A) showed about 20 % higher (102 mBar against 84.4 mBar) pressure drop across the powder bed at 18 kPa normal load. Aeration test is the basis of the aeration ratio that showed the average sensitivity to aeration regime for both samples. Aeration ratio is for average sensitivity to aeration materials in range from 2 to 20, for sample A is the value 2.04 respectively 2.58 for sample B. Permeability results differences are shown in **Fig. 3** with both of samples behaviour schemes (**Fig. 3** right).

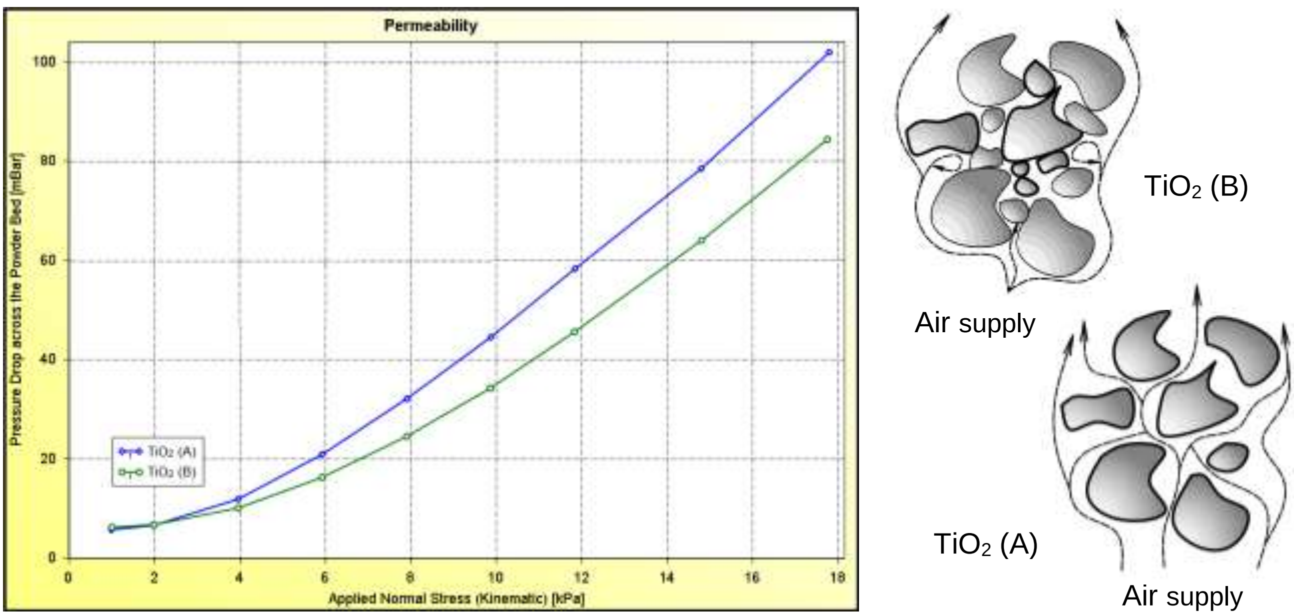

Fig. 3 Permeability test results and different granulometry scheme.

3.4 Compressibility

Compressibility is a measure of how density changes as a function of applied normal stress as shown in **Fig. 4**, right scheme [13]. For powders, this bulk property is influenced by many factors such as particle size distribution, cohesivity, particle stiffness, particles shape and particle surface texture. It is not directly a measurement of flowability, but nevertheless relates to many process environments, such as storage in hoppers or super sacks or behavior during roller compaction. Compressibility test showed obvious differences. Higher content of nanoparticles in TiO_2 (B) sample caused less compression (27.9 %) than TiO_2 (A) sample (36.4 %).

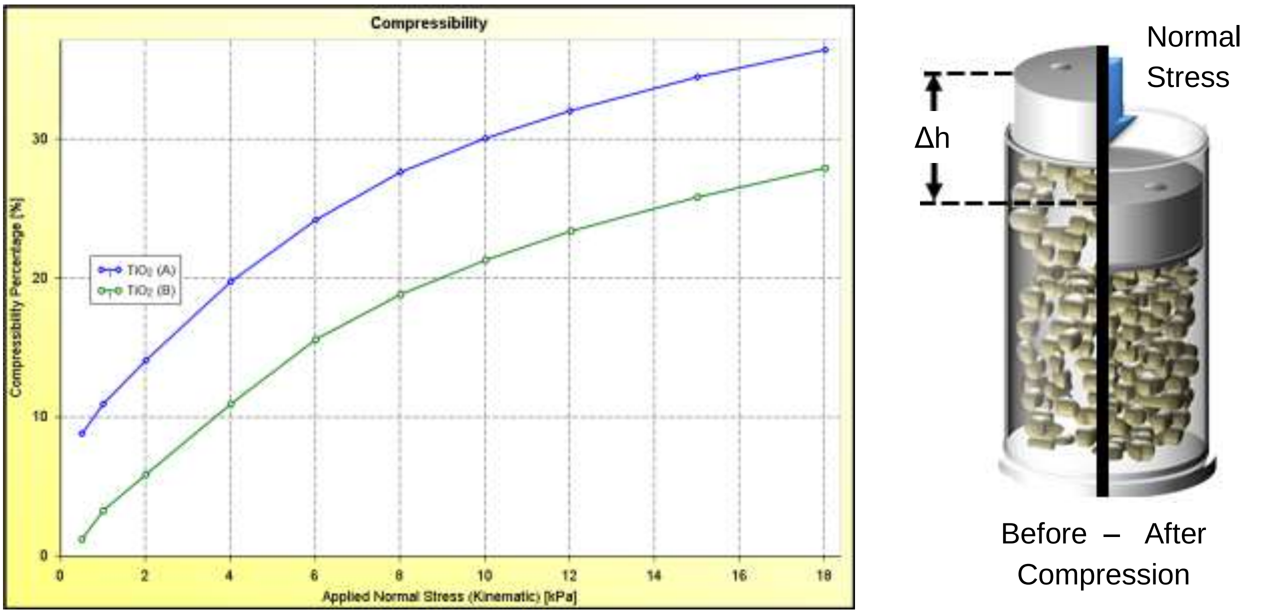

Fig. 4: Compressibility test results and measurement scheme.

4. CONCLUSIONS

The study has shown an influence on the representation of the nanoparticles fraction from 0 to 100 nm of cohesive titanium dioxide to its flow properties, compressibility and permeability. A larger proportion of fine fraction of nanoparticles on the sample B has a slightly negative influence on the flowability. The fine particles don't cover the surface of bigger ones to improve flowability of the powder. On the contrary, this may facilitate arching of the material during processing.

The permeability is about 20 % greater for sample TiO_2 (A) which comprises rather coarse particles. Air has the ability to pass through coarser powder bed easily. For a sample TiO_2 (A) is also greater compressibility (compression factor) which corresponds with the previous results. Easily passing air is pushed out during compression for a sample with a higher proportion of fine particles air-filled spaces are probably filled by fine fraction, thus there is no further compression way of the sample. This slightly increased the proportion of fine nanoparticles fraction caused fluctuations in behavior and in the further processing of TiO_2 powders. The way to avoid this can be a sieving or mixing specific granulometry of particles.

A simple characterization of those parameters - compressibility and aeration should be avoided problematic processing of certain batches of TiO_2. Freeman Technology FT4 appears for this purpose as a suitable tool for use in practice (e.g. for in-process control or standardization) with regard to the simplicity, speed and measurement accuracy.

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