



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

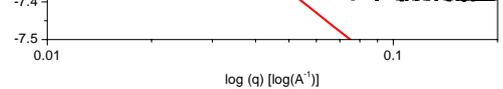
Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



Experiment title: Synthesis and coarsening kinetics of rutile nano-particles

Experiment number:
ME-505

Beamline: BM26	Date of experiment: from: 15-11-2002 to: 18-11-2002	Date of report: 1-3-2003
Shifts: 9	Local contact(s): Dr. Igor Dolbnya	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

Dr.ir. J.G.P. Goossens*, Eindhoven University of Technology, The Netherlands
 Dr.ir. T.A. Tervoort*, Dipl. Ing. R. Nussbaumer*, Dipl. Ing. M. Kristiansen*, ETH Zürich, Switzerland

Report:

Introduction

Rutile, a crystal modification of TiO₂, possesses attractive optical properties, such as a very high refractive index (~2.75), high UV absorption up to the proximity of the visible wavelength range, and transparency in the visible wavelength range. Primary or secondary rutile particles with dimensions above 100 nm (resulting in opaque composites) are already widely used to protect polymers from UV radiation. However, nanocomposites of polymers and rutile are of special interest in optical applications that require transparency, such as transparent UV-protecting materials or lenses. However, rutile nanoparticles have not been readily available so far. We have now been able to prepare such colloids with average diameters around 5 nm by hydrolysis of TiCl₄ in strongly acidic aqueous solutions at relatively low temperatures. The particle dimension must be accurately controlled. Due to their high specific surface energies, inorganic nanoparticles typically aggregate, which must be prevented. In this study, time-resolved observations of the rutile synthesis were performed by simultaneous SAXS and WAXS to elucidate the structure development.

Synthesis of nanoparticles

TiCl₄ was distilled at ca. 55 mbar into a dropping funnel with pressure balance. Thereafter, the dropping funnel was flushed with argon and connected to a round bottom flask containing 700 ml water and 28 ml concentrated hydrochloric acid (37% w/w) which had previously been cooled to 1-2 °C with an ice bath, also flushed with argon. 28 ml of TiCl₄ were slowly dropped into the aqueous phase, still cooled with ice. After addition of TiCl₄, the round bottom flask with the transparent reaction solution was disconnected from the dropping funnel and equipped under ambient atmosphere [1]. From each fresh solution, aliquots were taken and transferred into the rotating sample cell and placed in the beam.

Sample cell and experimental procedure

To perform in situ experiments, an electrically heated brass holder containing a rotating round sample cell was kindly provided by C. Houssin [2]. Slow rotation was necessary to keep the synthesis mixture homogeneous, as only a small spot near the center of the cell was exposed to the X-ray beam. Two clear mica sheets with a thickness of 25 µm were used as windows. Space was provided by a 0.5 mm thick Teflon ring on which was put a very small amount of grease. Heating of the sample holder from RT to the reaction temperature of 90°C (60°C) took about 90 s (60 s). During the sample preparation any contact was avoided between the colloid and the brass. Experiments were performed at 30, 60 and 90°C with 15 min old colloids. Other Experiments were performed in glass capillaries with a diameter of 0.7 mm. For this reason, the colloid has been heated up in an oil bath under reflux to 60°C and was hold at this temperature. Three capillaries were filled up to about 1.5 cm and immediately closed with a flame. This was completed 15 min after the synthesis and then every 7 min until the dispersion turned opaque after 90 min. The left-over of this synthesis was taken from the oil bath and stored at room temperature for 24 h. All TiO₂ was precipitated in this time. This flask was connected to a vacuum (~ 100 mbar) and with stirring heated to 80°C. After 48 h, another capillary was filled.

SAXS and WAXS

The combined SAXS and WAXS experiments were performed at Beamline ID 26 (DUBBLE) at the ESRF (Grenoble, F) [3], using a camera length of 4 m (10⁻³ < q < 2.5*10⁻²) with a wavelength of 1 Å. A linear detector (1D quadrant gas-filled) had been used for the experiments. WAXS data were collected with a microstrip gas chamber detector. In the table the frame-rates and some experimental conditions are shown. The scattering from a water/HCl mixture (25:1) at the reaction temperature was used as a background pattern. The data were normalized for the intensity of the X-ray beam and corrected for detector response prior to background correction. The basic data correction, the analysis of the time resolved data, and the interactive fitting of a calculated scattering pattern to measured data were performed using in-house-developed IgorPro procedures and Origin.

Results

The dispersion shows another behavior in the rotating cell with respect to the point of becoming opaque in comparison to the one liter round flask, which was used in the earlier reported syntheses. This may be due to faster heating rates with less volume for the dispersion heated to 90°C. In the next figure, intensity contour plots are shown vs q and time and show the particle growth in dependency of temperature and time. The experiment performed at 30°C did not show any increase in intensity compared to the ones at 60°C and 90°C.

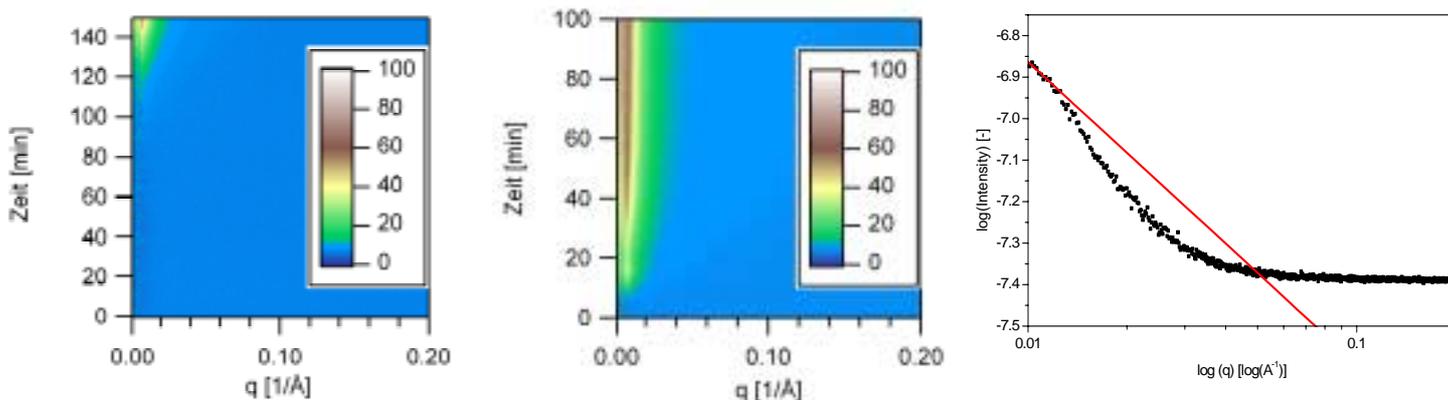


Figure 1: Time-resolved SAXS of the TiO₂ dispersion at 60°C (left side) and at 90°C (middle). Right: Log - log plot of the 60°C data at 150 min. The red line shows the linear fit at small q values used to determine the particle size in the Guinier plot.

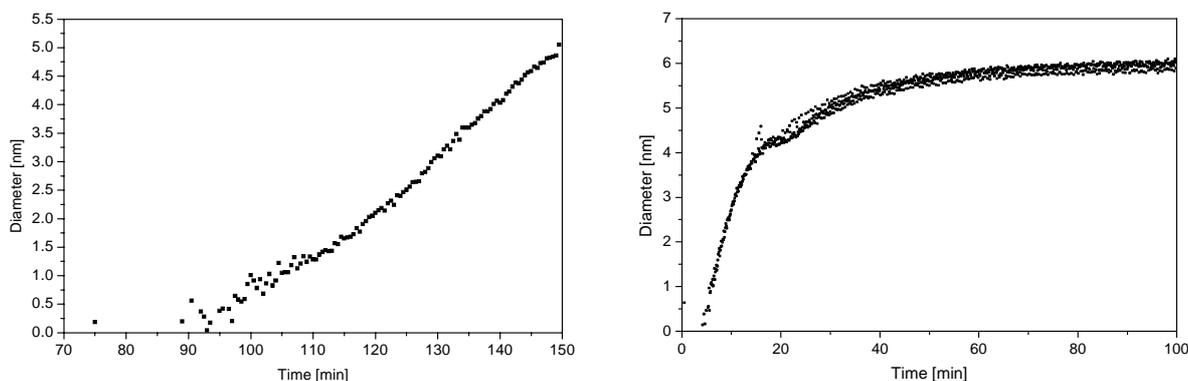


Figure 2: The black dots show the growth of the TiO₂ particles as estimated from the Guinier plot, a) 60°C, b) 90°C.

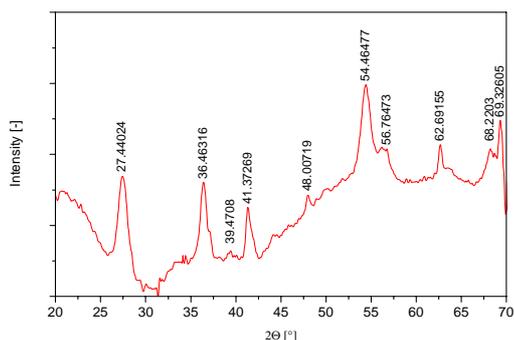


Figure 3: The WAXS pattern obtained from a highly concentrated mixture in a capillary. The average particle diameter was evaluated to be 4.8 nm. It was calculated with the Scherrer equation and the first peak: half high width = 1.24°, theta = 13.72°.

Discussion

A difference in nucleation and crystall growth depending on the temperature and time was observed. The time-resolved capillary experiments showed no new insights. Average Guinier particle diameter in the range of about 5-6 nm were estimated [4]. This is in good agreement with data obtained from XRD and WAXS experiments. TEM experiments show an average particle diameter of about 2.5 - 3 nm [5]. But it is known that the volume average shows higher values as TEM evaluations. The fractal regime proposed by Beaucage was not observed [6][7].

References

- [1] R.J. Nussbaumer, W.Caseri, T. Tervoort, P. Smith, *J. Nanoparticle Res.*, 4, 319 - 323 (2002) and *Macromol. Matter. Eng.*, 288, 44 - 49 (2003)
- [2] P.P.E.A. de Moor, T.P.M. Beelen, R.A. van Santen, L.W. Beck, M.E. Davis, *J. Phys. Chem. B*, 104, 7600 - 7611, (2000)
- [3] M. Borsboom et al., *J. Synchrotron Rad.*, 5, 518 - 520 (1998)

- [4] G. N. Greaves , W. Bras, M. Overhuizen, S. M. Clark, Faraday Discuss., 2002, 122, 299 -314 (2002)
- [5] R.J. Nussbaumer et al., To be published
- [6] G. Beaucage, J. Appl. Cryst., 28, 717 - 728, (1995)
- [7] J. Hyeon - Lee, G. Beaucage, S. E. Pratsinis, S. Vemury, Langmuir, 14, 5751 -5756 (1998)