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Influence of TiO_2 nanoparticle synthesis on the properties of thin coatings

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ABSTRACT

Three different types of titania nanoparticles were used to fabricate coatings on glass substrates, comprising of two commercial products obtained from pyrolysis and precipitation as well as self-synthesized particles from a sol–gel-synthesis. The effect of different particle properties on the coating properties like film thickness, roughness, transparency and photocatalytic activity was investigated. Thereby, not only the primary particle size and crystal phase being the main differences of the chosen TiO_2 particles but especially the secondary particle size and morphology were found to affect the coating characteristics, first of all the photocatalytic activity. Furthermore, we were able to synthesize titania nanoparticles showing consistent properties independent of the agglomerate size, outperforming the commercial products in most investigated attributes.

1. Introduction

In the last century titanium dioxide has become a widely used material in a broad range of application fields, for example in inks and paints [1,2], in food and cosmetics [3,4] as well as in photovoltaics [5,6]. In particular, the photocatalytic properties of this material become increasingly important. Applications are, for example, air and water treatment [7–9] or self-cleaning of surfaces [10–15]. Photocatalytic coatings often contain TiO_2 as nanoparticles. In contrast to sol–gel coatings involving the reaction of molecular precursors, approaches emanating from pre-formed crystalline nanoparticles bear the intrinsic advantage of high photocatalytic activity even without any high-temperature crystallisation treatment, thus offering flexibility and compatibility with polymeric substrates. Often used are the commercial products AEROXIDE® TiO_2 P 25 (Evonik Industries) [16–18,12,19] and HOMBIKAT UV 100 (Sachtleben Chemie GmbH) [11,15]. On the other hand, extensive research efforts are still devoted towards the synthesis of advanced TiO_2 nanostructures showing improved properties, predominantly via wet chemistry methods [20].

Coating characteristics, which determine the scope of the coating application, strongly depend on the structure formation. This in turn is influenced by several procedures during the process chain, where the first step includes the dispersion of the nanoparticles into a solvent or a varnish formulation and in the second step the coating is produced by applying the varnish or suspension through coating methods such as dip, spin or coil coating. For example, the coating thickness is influenced by the viscosity of the suspension [21,22]. Furthermore, porosities are strongly affected by fractal dimensions of agglomerates or aggregates being higher with increased ramification of the particles [23]. Thus, primary and secondary particle sizes, size distributions, particle morphologies as well as particle–particle and particle–fluid interactions of the used formulations have to be considered regarding the coating process [24].

In the present work, we particularly focus on the comparison of titanium dioxide nanoparticles produced via different methods regarding their influences on coating characteristics. The self-made nanoparticles were synthesized by a nonaqueous sol–gel process, the so called benzyl alcohol route [25], as described elsewhere [26,27]. From the reaction of titanium isopropoxide with the solvent benzyl alcohol highly crystalline particles are directly obtained under relatively mild conditions. These particles are compared with commercially available products, the pyrogenic AEROXIDE® TiO_2 P 25 (Evonik Industries) and the precipitated HOMBIKAT UV 100 (Sachtleben Chemie GmbH). All investigated particles were suspended in ethanol in a planetary ball mill and stabilised with triethanolamine. Different agglomerate sizes were adjusted to be able to compare not only the effect of the primary sizes but also the secondary particle sizes on the properties of the suspensions as well as on the coatings produced from these suspensions. In contrast, other studies report results of just one of these characteristics [28,12], although both need to be taken into account due to their strong effect on the coating properties [29]. The resulting coatings were analysed with regard to coating thickness, roughness, transparency, haze and photocatalytic activity.

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2. Experimental procedure

2.1. Preparation

The self-prepared TiO_2 nanoparticles (named MZ 200 in the following) were synthesized from a reaction mixture of 168.3 g titanium(IV) isopropoxide (97%) and 1000 mL benzyl alcohol (99%), both obtained from Sigma Aldrich and used without further purification. The mixture was heated to 200 °C in a 1.5 L double walled stainless steel reactor (Polyclave type 3/1, Büchi Glas Uster, external thermostat: Huber Tango HT) while stirring with an agitator speed of 250 min^{-1}, and kept at this temperature for 7 h. The resulting particles were isolated through centrifugation for 10 min at 6500 *g* and washed twice with chloroform before being redispersed in ethanol. For the analysis of the pure particles, they were dried under reduced pressure for 24 h after being washed.

AEROXIDE® TiO_2 P 25 and HOMBIKAT UV 100 were purchased as dry powders from Evonik Industries and Sachtleben Chemie GmbH, respectively.

The three types of particles were dispersed in ethanol with a laboratory scale planetary ball mill (Retsch PM400, 200 rpm), varying the milling time to obtain different secondary particle sizes. As grinding media, yttrium stabilised zirconium oxide beads (Tosoh) with a median diameter of 185 μm were used. The filling ratio of the grinding media in the milling chamber was set to 50 vol.% for all experiments. The suspensions were dispersed at a solid mass content of 10% (volume fraction 2.26%) in batch mode. As a stabiliser 2.82 g triethanolamine (> 99%, Sigma Aldrich) in a 30 mL suspension was used. This corresponds to a molar ratio of 0.2 mol stabiliser per 1 mol TiO_2 or a weight ratio of 0.9:1.

The coatings were fabricated by dip coating (Coater 4, IDLab) from suspensions consisting of the different TiO_2 types and different secondary particle sizes (defined as “initial” agglomerate sizes). The coatings were applied on a glass substrate (IDL, 76 × 26 mm) using a residence time of 60 s and a withdrawal velocity of 1 mm/s in ambient atmosphere. A subsequent heat treatment at 120 °C in ambient atmosphere was applied for 2 h to dry the coatings.

2.2. Characterisation

2.2.1. TiO_2 nanoparticles

The crystallite phases and sizes of the titania particles were determined by powder X-ray diffraction (PXRD) from the dry powders (Empyrean Cu LEF HR goniometer, Empyrean series 2, PIXcel-3D, PANalytical; Cu K_α, step size .05°). For PXRD analysis of the dispersed particles after the treatment in the planetary ball mill the suspensions were dried at room temperature to avoid sintering effects due to high temperatures. Transmission electron microscopy (TEM) images were obtained from the redispersed nanoparticles in ethanol (FEM-2100, JEOL, 10 kV) prepared on a Formvar-coated copper grid (Plano).

2.2.2. TiO_2 suspensions

Dynamic light scattering (DLS, Nanophox, Sympatec GmbH) was used to determine the secondary particle sizes and particle size distribution in the suspensions using ethanol as a dilutive solvent (300 to 500 kcps). The rheological behaviour of the suspensions was determined with a rotational viscometer (Searl type, Gemini 2, Malvern Instruments) at different shear rates. The viscosity at a shear rate of 10 s^{-1} was used to compare the viscosity for different particle sizes and types.

2.2.3. TiO_2 coatings

The coating thicknesses were determined by measuring profile and depth of a self applied scratch with a tactile profilometer (Dektak XTA, Bruker). The scratch was applied with defined load (1.962 N) and speed (4.5 mm/s) and the coating material was locally completely removed without damaging the substrate. The measurements of the roughness of the coating surfaces were conducted using a confocal laser scanning microscope [VK-9700K, Keyence (Institute of Joining and Welding, TU Braunschweig)] with a magnification of 150 in the surface profile mode. The measurement range and the quality were set to level and superfine, respectively. The measurements were performed without a further filter, a brightness of 900 and a z-step size of 0.02 μm. Additionally a disposition correction was used and the random noise was eliminated.

To generate SEM images of the coatings scanning electron microscopy [1550 Gemini, LEO, work distance 8 mm, voltage 5 kV (Institute of Material Science, TU Braunschweig)] was used. To avoid electric charging the coatings were sputtered with a thin layer of gold. Total transmittance and transmission haze were measured in conformity to ASTM D-1003 and ASTM D-1044 (Hazegard Plus, BYK-Gardner). Tested samples were referenced to blank glass substrates.

Photoactivity measurements were performed in accordance to ISO 10678 by the degradation of methylene blue (≥97%, Sigma Aldrich). The water used to make up the methylene blue solutions was double distilled and de-ionised. The photoreactor comprised of two optical glass cuvettes with light path = 55 mm fitted with Teflon substrate holders allowing a continuous stirring (fixed at 1500 rpm) of the solution, and one reference cuvette was used to perform a dark measurement without any UV irradiation. Irradiation was performed by two blacklight blue lamps from Sankyo Denki (315–400 nm, emission maximum = 352 nm) adjusted to 1 mW/cm^2 (thermopile sensor 3A-P-FS, Ophir Photonics). In-situ measurements were performed at 23 ± 3 °C by the use of a 100 W halogen bulb and a spectrophotometer setup, consisting of a ST-130 controller and a cooled 256 × 1024 pixel CCD-Array (both Princeton Instruments) with a Cut-On-Filter at 375 nm. The samples were preconditioned by UV for 24 h (Philips Actinic Black Light) with 2.3 mW/cm^2 at 365 nm and were treated with a conditioning solution of methylene blue (20 μmol/L) for at least 12 h in the dark. Afterwards, the solution was replaced by the test solution (120 mL, 10 μmol/L) and the sample cuvette was covered by a UV transparent glass pane. Additionally, the reference cuvette was covered with aluminium foil during the whole test. Irradiation started after a constant absorbance/time curve for at least 30 min. The total irradiation phase was set to 120 min. The photonic efficiency (1) was calculated by fitting the linear part of the absorption maximum λ = 662 nm during the UV activation phase.

$$\zeta_{MB} = \frac{R_{irr} - R_{dark}}{\frac{\lambda_{max} E}{hcN_a} \cdot 3600} \tag{1}$$

To verify the adhesion of the films during the photocatalytic measurement, we performed a blind test of the methylene blue solution after removing the coated substrate. No photocatalytic activity was detected after removal of the substrate, proving the good adhesion of the coatings to the substrate.

3. Results and discussion

3.1. TiO_2 nanoparticles

From the reaction of titanium(IV) isopropoxide and benzyl alcohol, highly crystalline anatase nanoparticles (MZ 200) were obtained, which have a crystallite size of 13.2 nm (calculated from the PXRD measurements using Scherrer's equation for the (011) reflection). In comparison with the TEM image in Fig. 1(a), these sizes evidently are primary particle sizes as the particles in the image show dimensions on the same scale (see also [26,27]).

In the same way, the TEM images of P 25 and UV 100 (Fig. 1(b) and (c), respectively) confirm the primary particle sizes of the materials declared by their data sheets. UV 100 is a precipitated product and only consists of the anatase crystal modification with a chemical purity