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Functional nanoscale additives for ultra-durable powder-coating polymers

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Abstract Surface-modified titania nanoparticles were prepared and their suitability as additives for the long-term UV-photoprotection of polymer materials was investigated. It was demonstrated that the functionalization of nano-TiO_2 with different fatty acid and phosphonate-based grafting reagents has a beneficial effect on the long-term stability of polyester composites under accelerated weathering conditions. These results are of considerable interest for the development of robust organic–inorganic hybrid systems that can be utilized as transparent but UV-resistant protective layers for outdoor applications.

Keywords Titanium dioxide · Nanochemistry · Polyester · Photodegradation · Surface · Phosphonates

Introduction

In the absence of a suitable protection or repair mechanism, organic matter will not resist permanent exposure to ultraviolet radiation or sunlight without incurring gradual damage. Therefore, commercial polymers usually contain small amounts of light stabilizers as functional additives [1]. Inorganic nanoparticles made of nonhazardous materials that are abundant in the earth, such as titanium dioxide (nanorutile), are frequently applied for this purpose [2], and the development of novel types of photoprotective agents based on inorganic additives is an important branch of current materials research [3].

A highly desirable feature in this context is the generation of tailor-made organic–inorganic hybrid systems that can be used as optically transparent but UV-resistant coatings. In order to achieve this goal, it is very important to control the size and the agglomeration behavior of the embedded nanoparticles. To realize nanocomposite materials with an appropriate optical appearance, particle diameters of less than 70 nm are required, provided that there is no significant formation of aggregates [4]. Nanoscale titanium dioxide (rutile) additives are already commercially available from various companies that also offer particle modifications such as surface coatings and doping. However, since these nanoparticles usually display a very high surface energy [5], powders of them tend to form aggregates. As a consequence of this aggregation, enhanced light scattering occurs, resulting in opaque rather than transparent systems when such materials are directly embedded into polymers. This even happens for rutile nanoparticles with a primary diameter of only 15 nm [6]. With this in mind, we decided to develop a surface modification procedure that enables better control over the optical properties of polymer composite materials carrying nanoscale titanium dioxide additives. Silane derivatives are widely used as functional grafting agents that modify the surface groups of rutile nanoparticles. During the course of the present study, we found that replacing silanes with alternative grafting reagents such as phosphonic acids [7] could have several advantages for our purposes; for example, surface-bound phosphonato groups are more stable to UV light and hydrolyzation than the corresponding silanized materials.

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Results and discussion

The powder coatings containing TiO$_2$ nanoparticles doped into a polyester matrix were synthesized starting from commercially available rutile samples (Rm200Wp, Fig. 1), which were added as a nanoparticle dispersion during the initial stage of the polyester synthesis. In order to produce outdoor-durable composite materials, it is very important to ensure that the particle distribution is sufficiently isotropic and to suppress destructive photocatalytic effects that are eventually caused by the embedded semiconductor additives. This can be partially achieved by selecting the optimal crystal structure of the incorporated material (in our case the rutile modification of TiO$_2$), and by avoiding nanoparticle agglomeration, which is especially important during the first steps in the formation of the polyester under elevated temperatures and relatively low viscosities.
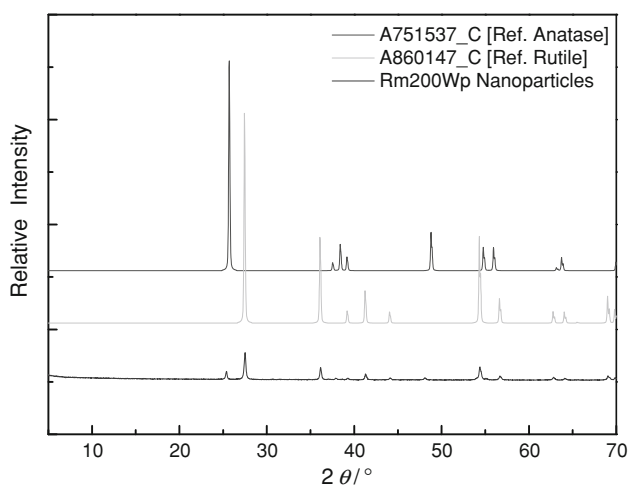

Fig. 1 Powder diffraction patterns obtained for Rm200Wp nanoparticles (*bottom*), as compared to the reference spectra of rutile (*center*) and anatase (*top*)

A top–down approach using an agitator bead mill was chosen to achieve a suitable rutile particle size (see the "Experimental" part). To further characterize the properties of the employed materials, disk centrifuge measurements were carried out to determine the grain size of the milled rutile particles. Nano-TiO$_2$ particles with an average diameter of about 60 nm that are highly suited to the production of composite materials with an appropriate optical appearance were obtained by applying top–down processing of the introduced nanopowders.

The polyester host matrix and the distribution of the embedded nano-TiO$_2$ additives within the novel nano-composite-based polymer coating materials were also characterized by electron microscopy. To do this, the samples used to record SEM and TEM photographs were carefully prepared by the focused ion beam (FIB) technique. Figure 2 shows typical examples of these studies, and illustrate the presence of nano-TiO$_2$ particles that are rather homogeneously distributed across the polymer host material. In other words, they do not leave large matrix regions unprotected, which frequently happens whenever additive particle agglomerates are formed.

In order to demonstrate the beneficial effects of adding photoprotective nanoparticles to powder-coating materials, the gradual loss of the surface gloss of a composite material, as caused by artificial weathering during permanent UV light exposure, is usually measured under standardized conditions [3]. In Fig. 3, the effects of different amounts of added TiO$_2$ nanoparticles on the final results of just such a QUV-B test are compared to the typical weathering behavior of an ultradurable polyester reference compound [3].

The best results were clearly obtained with ∼3% admixed rutile nanoparticles of the Rm200Wp type. Under these conditions, a significantly higher surface gloss was maintained with the nanocomposite-based polymer coating
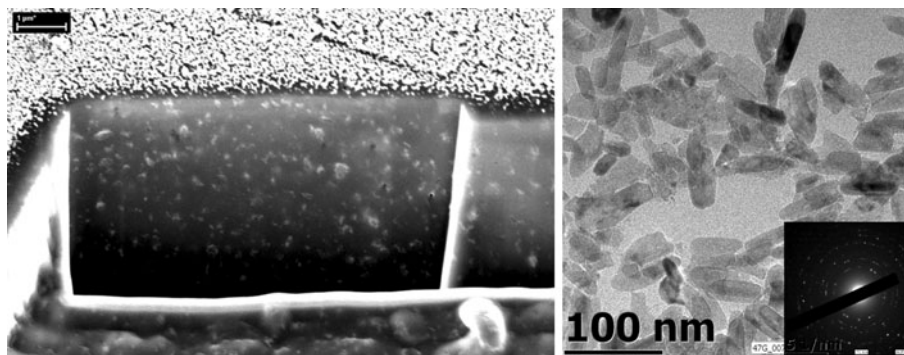

Fig. 2 Electron microscopy data characterizing the nano-TiO$_2$ particle distribution in the polymer host matrix. SEM and TEM pictures (*inset darkfield*) for a sample with 3% TiO$_2$ nanoparticles embedded into the polyester material. The FIB-imaging picture shown on the *left side* encompasses a section across the composite material with an area of approximately 30 μm^2. This section exhibits a sufficiently homogeneous nanoparticle dispersion without significant agglomeration
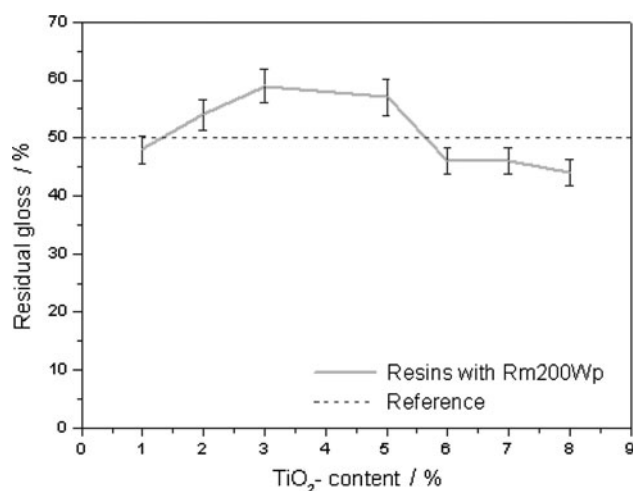
Fig. 3 Residual gloss of UV-exposed polyester samples containing various amounts of titania nanoparticle additives compared to the residual gloss of a UV-exposed ultradurable material, which displays 50% gloss retention after 900 h of accelerated weathering

Table 1 Silane reagents applied for TiO$_2$ nanoparticle surface modification

Compound	Abbreviation used[a]
3-Glycidoxypropyltrimethoxysilane	Geniosil GF 80
Isooctyltrimethoxysilane	Silane IO trimethoxy
Phenyltriethoxysilane	Silane P triethoxy[b]
N-Trimethoxysilylmethyl-O-methylcarbamate	Geniosil XL
Trimethylethoxysilane	Silane M3-ethoxy
3-Aminopropyltriethoxysilane	Geniosil GF 93

[a] Commercial trade name

[b] P-TES

materials tested, while the reference compound already exceeds the benchmark of 50% residual gloss.

To further improve the performance of the UV-stabilizing titania nanoparticles, we have investigated the effects of modifying the surfaces of such additives with a series of grafting reagents, including silanes (Table 1), phosphonic and fatty acids (Table 2). The basic principle of this strategy is schematically illustrated for the silanization process in Fig. 4.

After successfully modifying surfaces of the rutile nanoparticles, they were examined with a series of complementary analytical techniques, including FTIR spectroscopy, energy-dispersive X-ray spectroscopy (EDX), and solid-state NMR. We started our investigations with different types of silane reagents (Table 1); adding these should lead to a more even distribution of nanoparticles throughout the polymer matrix and reduce the surface activities of these additives. Model substrate photodegradation tests (see the "Experimental" section) with the

Table 2 Phosphonic and carbonic acid derivatives applied for TiO$_2$ nanoparticle surface modification

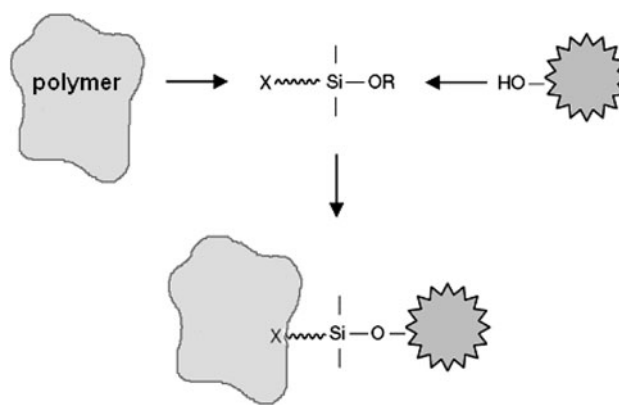| Compound	Abbreviation used
Phosphonoacetic acid[a]	PhphHAc
3-Phosphonopropionic acid[a]	PhphProp
N-(Phosphonomethyl)iminodiacetic acid[a]	PmiHAc
Lauric acid[b]	Lac
Myristic acid[b]	Mac
Palmitic acid[b]	Pac
Sebacic acid[b]	Sac

[a] Phosphonic acid

[b] Fatty acid

Fig. 4 Schematic representation of particle surface modification using silane grafting reagents

modified rutile nanoparticles were carried out, and these clearly demonstrated the beneficial effects of surface silanization for UV photoprotection, as they drastically reduced the remaining photocatalytic activity of these semiconductors. However, when incorporated into the polyester composite materials manufactured during the course of our work, some intrinsic problems occurred that hampered the utilization of this technique for practical purposes. On the one hand, when silanes are applied in aqueous media, they tend to react with each other in homocondensation processes rather than coupling to functional groups on the particle surface in a heterocondensation reaction. Therefore, an excess of the silane starting material was used, which had to be increased up to the manufacturing limit of the polymerization process in order to achieve a significant amount of particle surface modification. Even under such limiting conditions, the success of this technique was only moderate. While solid-state NMR measurements clearly indicated that the TiO$_2$ nanoparticles were silanized, the corresponding signal for the Si–O–C bond at 7.9 ppm was only very weak. More detailed EDX studies of the silanized nanoparticles revealed that typically only a small share of the original 25%
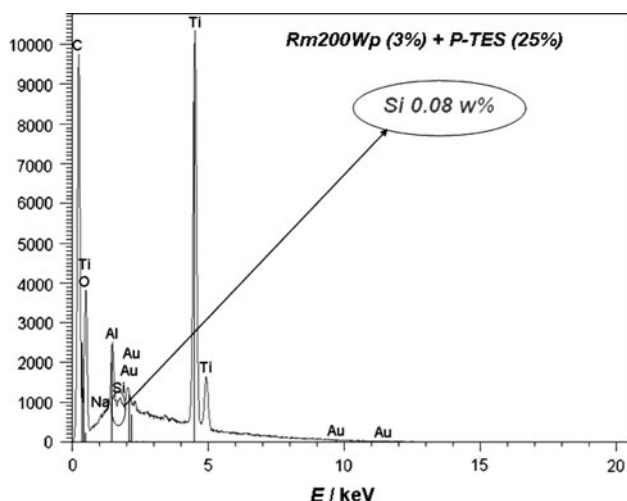
Fig. 5 EDX analysis of TiO₂ particles isolated from a polyester resin sample originally containing 3% rutile additives (Rm200Wp)—which were then modified with 25% phenyltriethoxysilane (P-TES)—in order to determine the amount of grafting reagent that had bonded directly to the particle surface
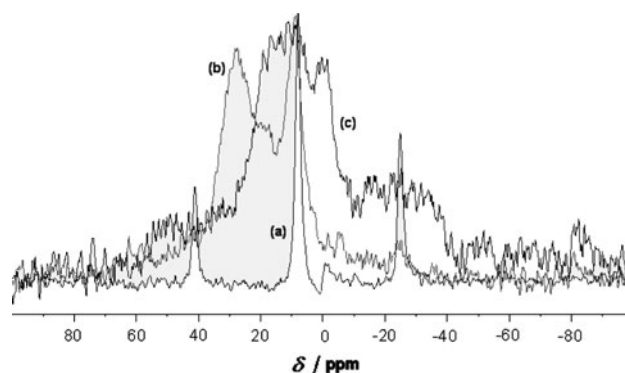

Fig. 6 Phosphorus NMR spectra of solid sodium hydrogen phosphate (a) used as a reference compound and rutile nanoparticles modified with 3-phosphonopropionic acid (b) or phosphonoacetic acid (c)

silanizing agent (P-TES) actually coupled to the rutile surface experimentally (Fig. 5).

More seriously, a significant proportion of the remaining silane groups were also incorporated into the polymer chain, which has a negative effect on the desired photostabilization of such materials, since Si–O–C bonds are known to be cleaved more easily than C–C bonds under the conditions of accelerated weathering. Therefore, it is not surprising that in the 900 h QUV-B tests performed with all of the silanized rutile additives studied in this work, we did not observe any significant improvement in the long-term stability over the already promising results obtained by applying unmodified TiO₂ nanoparticles only (Fig. 3). However, very different results were obtained when phosphonic and carbonic acids (Table 2) were applied as alternative grafting reagents in order to functionalize the rutile nanoparticle surface. The surface modifications were carried out by treating the TiO₂ particles with an aqueous solution of the compounds listed in Table 2 for several hours at elevated temperatures. After this process, the success of the grafting was studied by FTIR and solid-state NMR spectroscopy. The corresponding P=O and C=O stretching vibrations were observed at 1,366 and 1,748 cm^{-1}, respectively. In Fig. 6, the NMR spectra of rutile nanoparticles modified with various phosphonic acids (PhphProp and PhphHAc) at the 5% level are shown.

Spectrum (a) in Fig. 6 represents the NMR signal of the reference compound Na₂HPO₄, with a phosphorus peak at +8 ppm and satellite signals caused by the spinning rate of 4 kHz during the measurements (−58, −24, +42, and +76 ppm). The relatively broad peaks of the nanoparticle samples are caused by the large chemical shift anisotropy

(CAS). Additionally, the axes of the phosphorus bonds are oriented differently to the main axis of the rotor. Aside from the line broadening, there are different peaks for each sample, which are caused by different morphologies. Sample (b) in Fig. 6, which contained rutile nanoparticles modified with 3-phosphonopropionic acid, shows a larger shift to a higher field (PhphProp signal at +29 ppm) than seen for sample (c), which is functionalized with phosphonoacetic acid (PhphAc signal at +20 ppm). This indicates a higher degree of bidentate bound species in the case of PhphProp, while in the case of PhphAc the monodentate binding mode seems to be dominant. The remaining signals at around 8 ppm that are detected in both functionalized rutile samples represent the grafting agents that are not covalently bound to any particle surface. To quantify the percentage surface modification under these conditions, EDX measurements of particles isolated from the manufactured polymer composites were carried out, and these indicated that ∼12% of the inserted phosphonic acids reacted directly at the surface of a TiO₂ particle, while most of the remaining grafting agents were covalently linked to the backbone of the polyester matrix during the course of the polymer condensation process.

In addition to the FTIR measurements, some of the particles modified with carbonic acid were also characterized by solid-state NMR spectroscopy, as shown in Fig. 7.

The carbonyl group signal of the fatty acid with a chemical shift of 185 ppm as well as the additional signals in the region between 20 and 45 ppm resulting from the aliphatic groups again clearly indicate the presence of the desired grafting groups on the nanoparticle surfaces.

As already mentioned above, grafting phosphonic and carbonic acids onto the rutile particles had a very impressive beneficial effect on the long-term UV stability of the polymer materials containing these nanoparticles as photoprotective additives. In a series of experiments, the
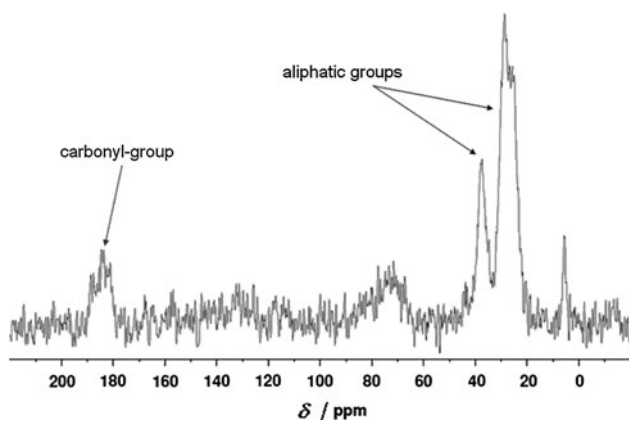
Fig. 7 Solid-state NMR (^{13}C CP-MAS, 4 kHz) spectrum of lauric acid functionalized rutile nanoparticles

optimized content of additives and grafting reagents was established. It turned out that, for the phosphonic acids tested, the best weathering results were achieved by incorporating 3% Rm200Wp rutile nanoparticles in combination with 3% of the respective grafting reagent. With the fatty acids, a typical ratio of 0.5 g of grafting reagent per gram of titanium dioxide nanoparticles was typically used, and the dispersion of the functionalized additives was added during the initial step of the polyester synthesis (see the "Experimental" section). Accelerated weathering experiments with the resulting powder-coating materials (900 h of light exposure in industrial Q-UVB test chambers) showed very significant improvements in the residual gloss retention in all cases, with values of up to almost 70% observed, as compared to the 50% benchmark of an ultradurable polymer reference compound [3]. Figure 8
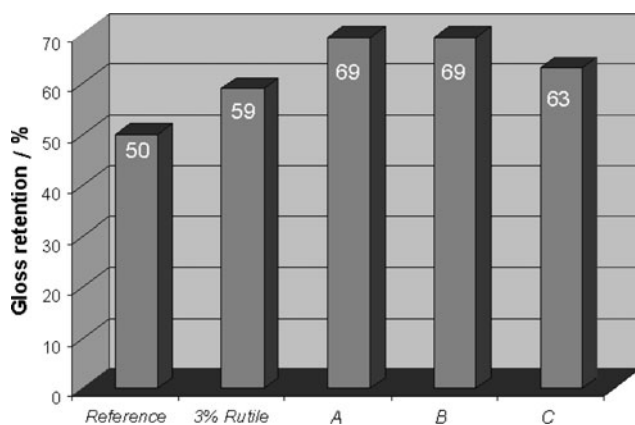

Fig. 8 Summary of the accelerated weathering tests (900 h of UV-light exposure) of powder-coating materials produced from polyester resins containing Rm200Wp TiO$_2$ nanoparticles only (3% rutile) and of samples that were additionally modified with different phosphonic acids at the 3% level, including phosphonoacetic acid (*A*), 3-phosphonopropionic acid (*B*), and *N*-(phosphonomethyl)iminodiacetic acid (*C*)

shows the final results for the phosphonic acids tested in the present work.

The results obtained confirm that decorating the rutile surface with various phosphonic acid derivatives results in an additional improvement in the long-term UV resistance of the polymers compared to samples containing only unmodified rutile additives, which typically achieve 59% gloss retention under these conditions (see also Fig. 3). Similar experiments performed for the fatty acid modified rutile nanoparticles resulted in gloss retention values of 67% (lauric acid), 69% (myristic acid), 68% (palmitic acid), and 62% (sebacic acid).

Conclusion

The present work clearly demonstrates the beneficial effects of surface-modified titanium dioxide nanoparticles as functional additives for the protection of polymer materials and powder coatings against UV-dependent degradation. Similar to certain recently established calcium phosphate nanoparticles [3], this alternative approach offers several advantages compared to conventional inorganic additives such as zinc oxide (ZnO) or unmodified titanium dioxide (TiO$_2$) that are already applied as broad-band UV-protection filters. Our first results—reported here—indicate very promising long-term UV-weathering stabilities of fatty acid and phosphonic acid modified nanorutile-containing polyester coating materials. When used in combination with improved top-down strategies to control the size of the nanoscale TiO$_2$, the design of transparent, ultradurable polymer materials could be targeted.

Experimental

Materials

All commercially available chemicals and solvents used for the present work had a purity of >99% and were applied as received without any further purification. Neopentylglycol was obtained from Polioli S.p.A., while isophthalic acid was purchased from Flint Hills Resources. The silanes and fatty acids used were obtained from Wacker. The phosphonic acids were delivered by Aldrich.

The rutile nanoparticles to be embedded in polymers were prepared with a top-down approach starting from Rm200Wp by a milling process using an agitator bead mill (Multilab Dyno-Mill from Bachofen AG with 0.2 mm ZrO$_2$/Y$_2$O$_3$ grinding elements). To avoid re-agglomeration of the ground material, the crushing process was performed in a matrix of neopentylglycol, water, and a suitable

dispersing additive (BYK 151, Byk Chemicals). The particle dispersion prepared from the top-down synthesis was applied to functionalize the rutile surface. The appropriate amount of grafting agent (3–5% with respect to rutile) was dissolved in distilled water (phosphonates, lauric and sebacic acid, and all silanes) or absolute ethanol (palmitic and myristic acid), and the solution containing the grafting agent was added dropwise under vigorous stirring to the dispersion. After stirring for approximately 24 h, the surface modification was complete and the whole mixture was added to the starting materials of the polyester synthesis, which was carried out as previously described [3].

Electron microscopy

Scanning and transmission electron microscopy (SEM and TEM) were used to determine the grain size of the obtained titanium dioxide nanoparticles. These techniques also served to characterize the particle distribution inside the polymer matrix. TEM measurements were carried out on a JEOL 2011 microscope, and a LEO Supra 35 FE-SEM was used. Sample preparation with the FIB technique was carried out with a Zeiss raster electron microscope equipped with a LEO XB 1540 (FIB-REM) unit.

Grain size determination

To characterize the grain sizes of the nanoparticles present in the dispersions obtained from top-down methods (Rm200Wp), a high-speed disk centrifuge (DC24000, CPS Instruments) was applied.

Spectroscopic characterization

Infrared absorption data were obtained with a Shimadzu IR-Affinity-1 FT-IR spectrophotometer. All NMR spectra were measured with a Bruker DPX 200 apparatus (liquid samples) or a Bruker DRX 300 spectrometer (solid-state materials).

X-ray diffraction

An X-ray diffractometer (X-Pert Pro from Phillips) was used to obtain powder diffraction spectra.

Photostability testing

Photoreactivity control experiments were carried out in a laboratory photochemical reactor (UV-RS-2, UV-Consulting Peschl) with an immersed 150 W medium-pressure mercury lamp (TQ 150, Heraeus Noblelight) equipped with a cooling jacket made of borosilicate glass ($T_{254 \text{ nm}} = 0\%$ and $T_{366 \text{ nm}} > 90\%$). The reactor was loaded with 450 cm^3 of water, 0.050 g of the corresponding TiO$_2$ sample (unmodified or functionalized with silane), 0.01 mol dm^{-3} of ascorbic acid as a donor molecule, and 5×10^{-5} mol dm^{-3} of the dye methyl orange. Under vigorous stirring and air exposure, the decomposition of methyl orange was followed by measuring the bleaching of the dye during the course of exposure to light. The remaining absorption at 453 nm was measured to quantify the amount of degraded methyl orange.

To carry out material aging tests under more drastic light-exposure conditions that simulate the requirements for real long-term outdoor applications, samples of the processed powder coatings were placed for up to 900 h in industrial-scale test chambers. These QUV-B chambers were equipped with fluorescent tube UV lamps emitting in the spectral region between 280 and 370 nm (maximum output in the UV-B region occurred around 313 nm). The time-dependent courses of the polymer degradation effects and the residual gloss retentions on the coatings could thus be evaluated under accelerated aging conditions, since UVB-313 lamps provide an enhanced short-wavelength radiation output which causes more severe effects than the ultraviolet portion of the solar spectrum that normally reaches the Earth's surface under ambient conditions [3].

For all of these measurements, the residual gloss of the samples was used to quantify the light-dependent material degradation. Therefore, the reflection of the material surface was investigated at an angle of 60° using a Micro-TRI glossmeter from BYK-Gardener.

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