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Thin Coatings with Photo-Catalytic Activity Based on Inorganic-Organic Hybrid Polymers Modified with Anatase Nanoparticles

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Summary: Inorganic-organic hybrid polymer sols where modified with differently prepared as well as commercial titania nanoparticles, to obtain coatings exhibiting a photo-catalytic activity for the development of self-cleaning textiles. The particles synthesized using a sol-gel-approach where, amongst others, investigated by XRD to prove the existence of titania crystallized in the anatase structure. The photo-catalytic activity of the different particles as well of the coatings was compared by the decomposition of astrazone red induced by an irradiation with artificial and solar UV-radiation. With respect to the underlying aim of the investigation the durability of the effect against washing was tested by standardized washing experiments, showing promising results.

Keywords: anatase; fibers; nanocomposites; photo-catalytic activity; textile

Introduction

Titania crystallizes in three different crystal structures, rutile, anatase, and brookite. Titania particles crystallized in the rutile modification are used on a large scale as matting agent for polymeric fiber materials used in textile industry since many years. While rutile shows a strong absorption for ultraviolet radiation and simultaneously acts as a more or less inert white pigment, the anatase modification shows a strong so-called photo-activity if irradiated with ultraviolet radiation. The energy band gap of the semi-conductor is in the range of 3.2 eV, therefore the anatase absorbs radiation of a wavelength of about 387 nm. Due to the energetic position of the valence band of the anatase, the excited titania is able to oxidize available hydroxyl ions to the corresponding hydroxyl radicals.[1] Since these radicals are highly reactive species they will be able to decompose most organic materials. Although indications of a photo-catalytic activity of rutile are reported in literature[2] the activity of the anatase is much higher on all accounts. Recently, anatase-modified surfaces are of an enormous interest, due to this photo-catalytic behavior of the crystalline material.

The objective of this investigation was on one hand, the development of coatings based on inorganic-organic hybrid polymers modified with anatase nanoparticles that are applicable for textile finishing.[3–6] On the other hand, it was an aim to prepare titania particles, that show the needed photo-catalytic activity using the sol-gel-technique at ambient conditions,[7–10] and to use these for the mentioned finishing. The results of the study are expected to form the basis for the development of self-cleaning textiles or textiles that could, e.g., improve room-climates by oxidizing pollutants.

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Experimental Part

The inorganic-organic hybrid polymer sol used as a binder for the photo-catalytic nanoparticles was prepared by hydrolyzing

10 ml of (3-Glycidyloxypropyl)trimethoxysilane (GPTMS) with a stoichiometric amount of water after diluting the GPTMS with 180 ml isopropanol. The GPTMS based sol was either mixed with one of the sols described below or for comparison with anatase particles commercially available (AEROXIDE® TiO2 P 25 (*P25*), delivered from *Degussa*, 40% anatase). In case of P25, the particles were dispersed by using a disperser followed by an ultrasonic treatment. For all composites the share of titania was 3 wt.% relating to GPTMS. Before coating 1-methylimidazol was added to the sols for catalyzing the organic cross-linking. Different fabrics were dip-coated and dried afterwards at 110 °C for about one hour.

Sol-gel-derived titania nanoparticles were prepared following two different approaches. Titania sol A was prepared by mixing up of 80 ml of distilled water with 20 ml ethanol, 20 ml acetic acid, and 1 ml nitric acid under vigorous stirring. 5 ml of titanium (IV) isopropoxide (TIP) are added under further stirring. For sol B a mixture of 20 ml titanium (IV) ethoxide and 60 ml of ethanol were poured into a mixture of 60 ml distilled water and 140 ml ethanol.

The crystal structure of the titania particles developed in sols A and B were investigated by x-ray diffraction measurement (XRD). BET-measurements were carried out to evaluate the specific surface. Particle sizes were measured by dynamic light scattering employing a Zetasizer Nano S, Malvern. The photo-catalytic activity was characterized by placing particles as well as finished fabrics into a petri-dish filled with a defined dyestuff solution (astrazone red) and irradiating them with an UV-lamp spectrum. The extinctions of the differently treated solutions give information about the photo-catalytic activity. Washing tests were carried out according to DIN ISO 105 to investigate the durability of the coatings. For these tests a fabric is placed in a container made of stainless steel, several stainless steel globes and a solution containing a standardized washing powder are added additionally. To simulate the washing procedure the closed container is heated up to 40 °C and rotated for 45 min.

Results and Discussion

General Characteristics of the Particles Prepared

Titania particles were prepared by a sol-gel-approach following two different routes. The size of these particles was investigated by dynamic light scattering (DLS). For sol A a hydrodynamic diameter of 29 nm was found, investigation of sol B failed, since the particles tend to agglomerate and the precipitation prevents the DLS measurements. The corresponding DLS-diagram for Sol A is shown in Figure 1. The specified particle size of the commercial particles is about 21 nm. Small particles might be of importance for two reasons. On one hand, the surface of the solid material is increased with decreasing particle size. Since the photo-catalytic oxidation of the hydroxyl ion occurs at the surface, a large surface is expected to be advantageous. On the other hand one has to keep in mind that the general aim of these investigations is the preparation of a photocatalytic finish for textiles. Filling the hybrid polymer with particles with sizes below 50 nm will guarantee transparent coatings (since no light scattering by the particles occurs). Therefore, the coatings will not or only slightly influence the product's appearance.

BET-measurements (compare Table 1) of the particles showed, that particles separated from Sol A have a specific surface of 218 m^2/g, the particles in Sol B 333 m^2/g. Compared to this the P25 particles show a specific area of only 46 m^2/g (product information: 50 ± 15 m^2/g).

To investigate the crystal structure of the particles synthesized, XRD-measurements were carried out. The corresponding XRD-spectra of the two laboratory prepared particles are depicted in Figure 2. The titania derived from Sol B shows very broad signals with a weak resolution, indicating a highly amorphous material. Nevertheless,

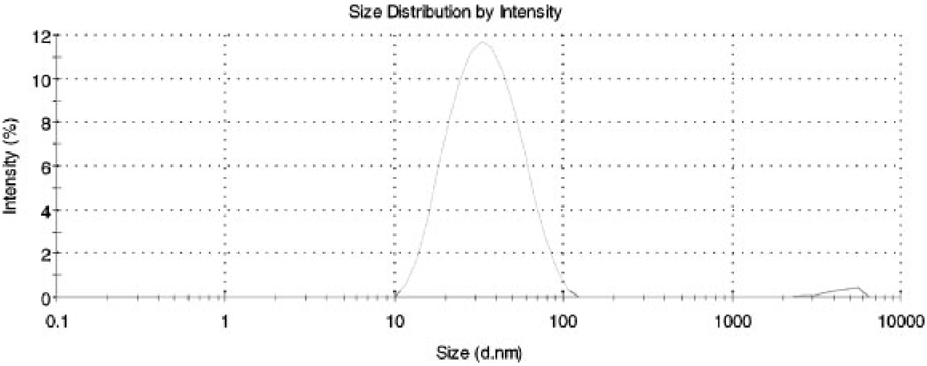

Figure 1.
Size distribution of particles in a sol A as measured by DLS.

Table 1.
BET Measurements of Titania Particles Used.

Particle	Particle size [nm]	Specific Surface [m^2/g]
TiO_2 (Sol A)	~29	218
TiO_2 (Sol B)	–	333
P25	21*	46

* (primary particle size, product information, according to experience strongly agglomerated particles).

the signals that can be observed show the existence of a certain share of anatase (the vertical lines show the expected position of the anatase signals). The results for the particles separated from Sol A are comparable, whereby the better resolution of the signals indicates a higher share of crystalline material. The higher specific surface of

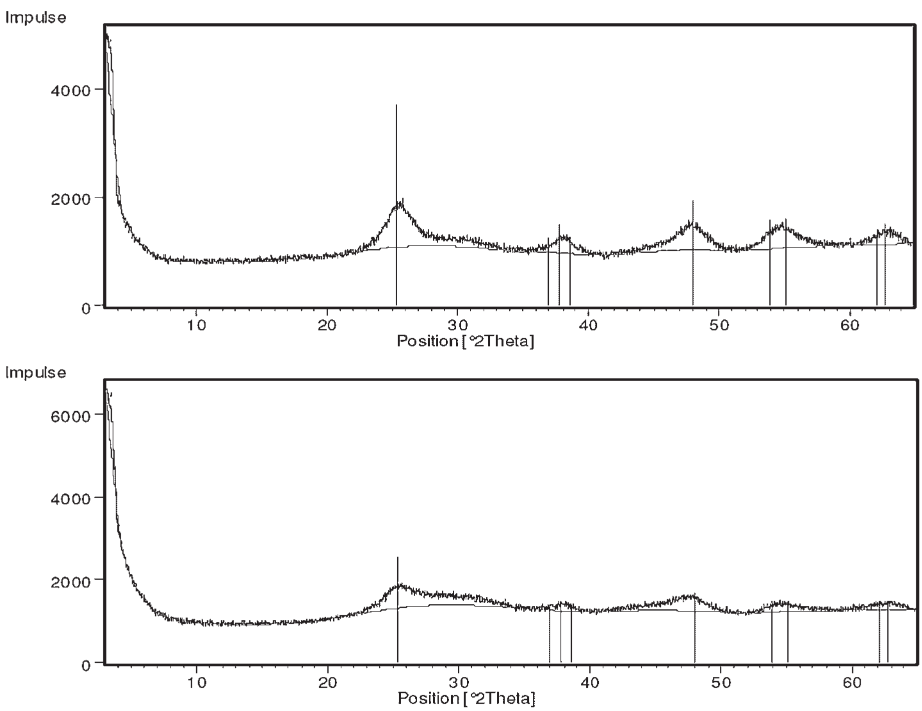

Figure 2.
XRD-spectra of the titania nanoparticles separated from Sol A (top) and Sol B (bottom). Vertical lines mark the expected positions of anatase signals.

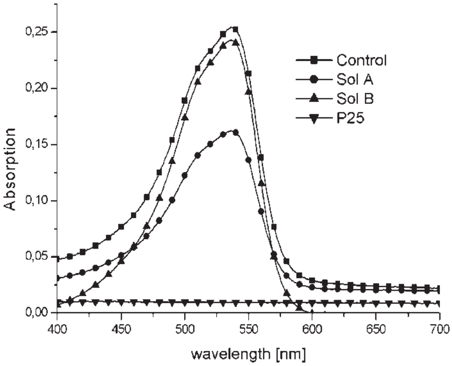

Figure 3.
Absorption spectra of the dyestuff solution after UV-irradiation in presence of an equal mass of different titania particles.

the particles at a similar particle size as P25 already indicated the higher amount of amorphous material for the sol-gel derived oxides.

Before carrying out coating experiments the photo-catalytic activity of the different particles was tested using powders. The particles were separated from the solvent before they were placed in a petri-dish with a defined dyestuff solution. Afterwards the petri-dish was irradiated with a UV-lamp for about one hour. The change of the solutions extinction was taken as a measure of the photo-catalytic activity. The measurements were done in order to check, whether there is a certain activity, and to compare it in relation to the commercial product. The corresponding results are summarized in Figure 3. Irradiating the particles separated from Sol B obviously lead to no photo-catalytic activity, whereby the dyestuff solution that was filled with particles of Sol A during irradiation shows a significantly weakened absorption. The commercial particles decolorized the solution completely within one hour. Due to the lower crystallinity a lower activity was to be expected. Simultaneously the higher photo-catalytic activity found for particles of sol A compared to B is in good agreement with the XRD-results presented that indicated a higher crystallinity for sol A.

Properties of Fabrics Finished With Modified the Hybrid Polymers

The basic procedure to finish textiles with hybrid polymers is as follows. After the partial hydrolyzation of the GPTMS subsequent condensation reactions take place, forming the inorganic-organic hybrid polymer sol that is modified with the anatase particles in a second step. The resulting dispersions are used for coating of textiles. In the curing step an amorphous inorganic-organic hybrid polymer network will be formed. Since in aqueous solution the surface of the oxide particles will be covered with a certain amount of hydroxy groups,[11] a condensation of the silanol and/or alkoxy silane groups at the particle surface can be expected. Simultaneously the gelation of the GPTMS-sol is increased. Parallel to this the epoxy groups are cross-linked forming the *organic domains* of the hybrid polymer network. The sketch depicted in Figure 4 shows the characteristic parts of resulting network schematically.

Composites of the different particles with the epoxy-modified alkoxysilanes sol were prepared and applied to textile materials following this process. The textiles were used as received and finished in a dip-coating process as conventionally employed in textile industries. After that the coated fabrics were fixed in a frame and dried at 110 °C for about one hour. Experiments were carried out with technical polyester

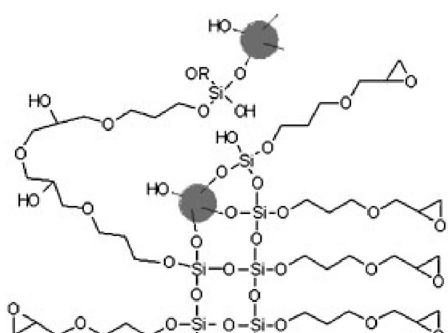

Figure 4.
Sketch showing the characteristic parts of the inorganic-organic hybrid polymer network as prepared in the presented work.

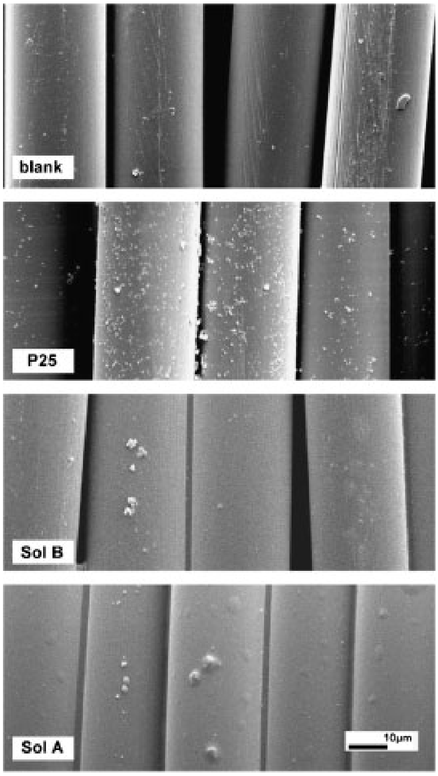

Figure 5.
SEM-micrographs of the differently treated polyamide fabric.

(polyethylene terephthalate) and polyamide (PA 6.6) fabrics. Results are only presented for the polyamide since the general of the results was comparable. The fabrics weight increased by 1–2 wt.% due to the finishing procedure, indicating very thin coatings. SEM-micrographs of the finished fabrics are shown in Figure 5. As one can observe, the hybrid polymer coatings form homogeneous thin films and smoothen the surface of the fibers. The blank fibers show grooves resulting from the spinning process, the coated fibers do not. The P 25 particles form comparably big agglomerates and can therefore be seen on the fiber surface. SEM-micrographs taken after ten washing cycles show comparable surfaces, indicating that the particles are not simply adhering loosely. Since the particles of Sol A and B are properly dispersed when added to the hybrid polymer sol, a comparable agglomeration of titania particles can not be observed. Nevertheless some big particles are on top of the fibers but might also be impurities brought by the technical textile materials.

The different textiles were tested with regard to their photo-catalytic activity. The general test was the same as described before for the powders. Textile samples of a defined diameter were placed in the dyestuff solution that was irradiated with a UV-lamp for one hour. The results of the treatment show the same tendencies as was observed for the powders. The highest activity is achieved with coatings modified with the highly crystalline P25 titania particles (nearly completely decolorized) but a certain activity can also be observed for the coatings filled with particles from Sol A. In accordance with the tests carried out with the powders no activity could be detected for Sol B. Since the presented investigations aim at a technical finish of textiles, the activity in combination with sun-light instead of artificial UV-light is of importance. The intensity compared to the lamp used in the laboratory is much lower, therefore corresponding tests were carried out for a longer time. The data presented in Figure 6 show the results for a 30-days storage at the window sill (from inside). The P25 sample decolorized the dyestuff

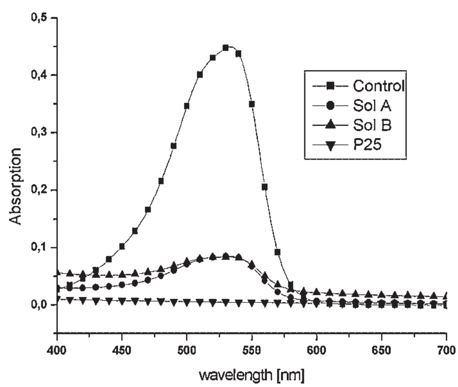

Figure 6.
Absorption spectra of the dyestuff solution after a storage at the window sill (inside) for one month in presence of fabrics (equal size) finished with different coatings.

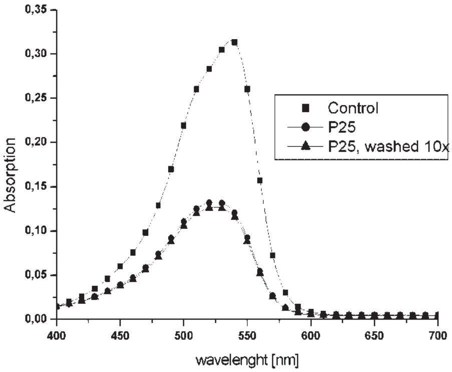

Figure 7.
Decomposition of astrozone red by a polyamide fabric finished with a hybrid polymer modified with P25 (irradiation for 15 min). The photo-catalytic activity of a sample before and after ten washing cycles (according to DIN ISO 105) are compared.

solution completely affirming the highest activity measured in all tests. Different from the tests before, a degradation of the dyestuff can also be observed for both sol-gel-derived particles after the long-time treatment with solar radiation.

After carrying out five to ten washing cycles the activity of the finished fabrics was tested. To speed up the tests, the comparison was done with P25 finished fabrics and the irradiation time was reduced to 15 min. As shown in Figure 7 even after ten washing cycles no significant change in the activity can be observed. SEM-micrographs of the washed sample look comparable to those of the virgin samples (compare Figure 8), emphasizing a promising durability of the finishings.

Conclusion

It has been shown that a photo-catalytic finishing of textiles can be carried out by applying inorganic-organic hybrid polymers modified with differently prepared anatase nanoparticles. The use of the commercially available P25 nano powders yielded the highest activity in the presented investigations, nevertheless the use of sol-gel-derived particles as synthesized offer certain advantages. Since the modification of the hybrid polymers can e.g. be carried out by a simple mixing with the titania sols no extensive dispersing of powders is

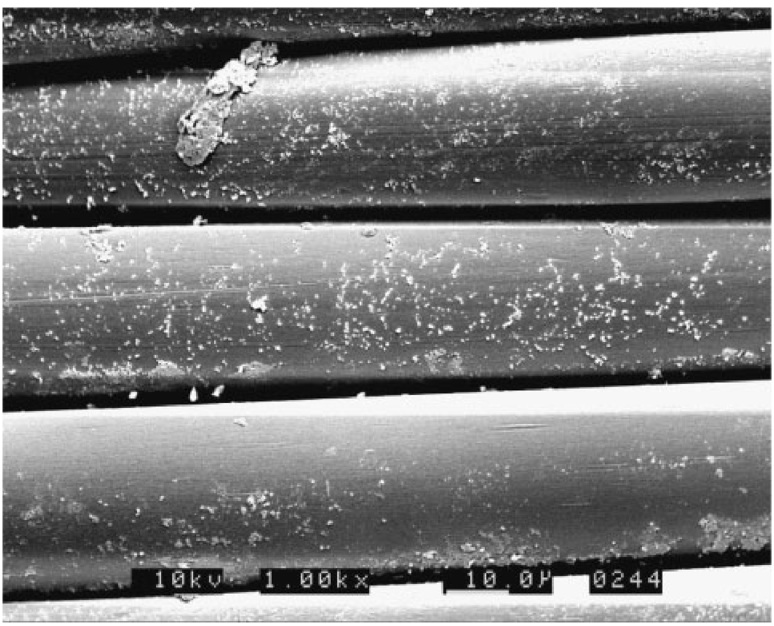

Figure 8.
SEM-micrograph of a polyamide sample finished with the P25-modified hybrid polymer after 10 washing cycles (compare Figure 5 showing the corresponding virgin sample).

needed. Future activities will deal with investigation to increase the crystalline share of anatase in the titania particles prepared by the presented approach, which would increase the photo-catalytic activity. Additionally modifications to protect the fiber material against possible decomposition will be examined. A possible decomposition of the organic domains of the hybrid polymer coating will also be investigated; potentially the amount of inorganic domains within the networks has to be increased to guarantee sufficient stability. It has to be stated that the introduction of sol-gel based hybrid polymer systems for textile finishing promises a variety of improvements as well as new applications. Combinations of the effect described here with other properties achieved, e.g., by using other nanoparticles or hybrid polymers are of high interest.

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