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Investigation of surface modification of rutile TiO_2 nanoparticles with SiO_2/Al_2O_3 on the properties of polyacrylic composite coating

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ABSTRACT

Surface modification and characterization of TiO_2 nanoparticles as an additive in a polyacrylic clear coating were investigated. For the improvement of nanoparticles dispersion and the decreasing of photocatalytic activity, the surface of nanoparticles was modified with binary SiO_2/Al_2O_3. The surface treatment of TiO_2 nanoparticles was characterized with FTIR. Microstructural analysis was done by AFM. The size, particle size distribution and zeta potential of TiO_2 nanoparticles in water dispersion was measured by DLS method. For the evaluation of particle size and the stability of nanoparticles in water dispersions with higher solid content the electroacoustic spectroscopy was made. To determine the applicability and evaluate the transmittance of the nano-TiO_2 composite coatings UV–VIS spectroscopy in the wavelength range of 200–800 nm was employed. The results showed that surface treatment of TiO_2 nanoparticles with SiO_2/Al_2O_3 improves nanoparticles dispersion and UV protection of the clear polyacrylic composite coating.

1. Introduction

Titanium dioxide has a wide spectrum of practical use. One of them is to increase the service life of wood substrates that are used in exterior environment. They are usually coated with various decorative or protective coatings to ensure its long term durability under weathering exposure where UV radiation, water and O_2 are three most crucial factors for coating's degradation [1].

One of the crystal structures of TiO_2 is rutile, which in nano size is a well-known inorganic UV absorber that increases the polymer stability and is used in coating formulations. It offers the most effective UV protection on the long-term exposure because it do not decompose and do not migrate in coating during weathering [2]. Three characteristics severely restrict the utilization of nano-sized TiO_2. First, the degree of dispersion of the rutile nanoparticles determines their UV protecting efficiency. Due to their large surface-area/particle-size ratio, strong polarity and their incompatibility with polymeric matrix, nanoparticles have significant tendency to agglomerate. Second, because of photochemical reactivity of TiO_2 we must prevent the formation of free radicals. One of the solutions of mentioned two drawbacks is modification of the TiO_2 nanoparticles surface with inorganic oxides that can additionally also diminish the difference in refractive index of the coating and TiO_2 nanoparticles what have also important influence on transparency of acrylic clear coating [3]. To overcome the before mentioned problems, TiO_2 needs to be coated with inert inorganic oxides, such as SiO_2 and Al_2O_3 or the combination of oxides, since the composition of coating materials affects the property of TiO_2 [3–6]. This was first done in the case of micron-sized TiO_2 which is being used as white pigment. SiO_2 can be easily deposited on TiO_2 surfaces, improving the weather ability of TiO_2. The negative effect of SiO_2 coating layers is that its lower polarity cannot significantly enhance the dispersibility of TiO_2 in polar water based media [4]. Contrary to SiO_2, Al_2O_3 lowers Van der Waals forces between particles by decreasing particle–particle attractions. Al_2O_3 coating with many —OH groups additionally provides active sites for further stabilization with organic compounds. The negative side of Al_2O_3 coating is that it has a tendency to loosely anchor at TiO_2 surfaces [7]. To overcome this problem, it is an alternative to successively coat TiO_2 with SiO_2 and Al_2O_3 coating layers via Si—O—Al bonds [8]. The effects of coating parameters on the dispersibility and pigmentary property of coated micron sized rutile TiO_2 with Al_2O_3/SiO_2 have been studied by Zhang and co-authors. Surface modification of pigmentary TiO_2 with multilayer SiO_2/Al_2O_3 enables high dispersibility in water and improved whiteness and brightness compared to unmodified and SiO_2-modified rutile TiO_2 [9].

Different processes were developed to optimize the surface modification of TiO_2 nanoparticles with SiO_2 or/and Al_2O_3. This Zhiping et al. report effective surface modification of TiO_2 with Al_2O_3 in ratio 10:28.5% to obtain high value added nano-powder

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with one-step hydrothermal method [10]. Rutile TiO_2 nanoparticles were surface treated by homogenous amorphous layer of SiO_2. Surface modification depressed photocatalytic activity of TiO_2. Practical application of surface treated rutile with SiO_2 can be found in wood protective coatings. Another usage of TiO_2 nanoparticles modified with SiO_2 synthesized by sol gel process is UV blocking applications in textiles and toiletries while avoiding the photodecomposition effects on the organic substrate materials [11,12]. There are also published patents regarding the surface treatment of TiO_2 nanoparticles which involve its coating with different inorganic oxides like SiO_2 KR20110032952 [13], Al_2O_3 EP1544256 (A2) [14] and different mixtures of oxides US2011259244 (A1), SI23029 (A) [15,16]. We can also find patents regarding coating of TiO_2 nanoparticles in a suspension with SiO_2 and Al_2O_3 but in this case it was used for cosmetic applications WP 0701809 [17]. However we could not find any information about surface treatment of TiO_2 nanoparticles with binary SiO_2–Al_2O_3, its stability and UV effectiveness in coatings for UV protection on wood substrate.

For this kind of application the solid content of nanoparticles is important parameter for studying the stabilization of TiO_2 nanoparticles in water or polymer dispersions. In most cases DLS method is used for particle size measurements however the samples should be diluted under 0.01 wt.% of solids. This is not the case in coating applications where the solid content of TiO_2 nanoparticles are more than 0.1 wt.%. For this purpose electro acoustic spectroscopy can be used. The determination of particle size by means of this method is carried out in two steps: measurement of acoustic attenuation spectrum and interpretation of the acoustic attenuation spectrum in terms of particle size distribution [18–20]. The technique has been employed in many studies for different applications: Richter et al. employed it for characterization of poly-disperse particles in micrometer range, Stolojanu and Prakash considered it for characterization of slurry systems, Tourbin and Frances used it for monitoring of aggregation process of dense colloidal silica suspensions [21–23].

The aim of our work was to prove significantly improved stability of surface modified nano TiO_2 with binary SiO_2/Al_2O_3 in water dispersion and it's positive influence on UV absorption and transparency in acrylic clear coating. We used surface modified TiO_2 nanoparticles that were coated by innovative method with SiO_2 and Al_2O_3 according to the patent SI 23547 A [24]. The research is based on thesis that surface modification has significant influence on TiO_2 nanoparticle size distribution and agglomeration tendency what consequently impact on the UV absorption properties and transparency of acrylic clear coating with integrated nanoparticles. Surface modified nanoparticles were first stabilized in water and dispersion was analyzed with DLS and electro acoustic spectrometer what enable us to determine the nanoparticle stability from low to high concentrated dispersions with nanoparticles what is unique approach in nanoparticle dispersion analysis according to literature data. Nanoparticle dispersion was then incorporated in acrylic clear dispersions and comparison of nanoparticle stabilization with UV absorption and transparency was evaluated.

2. Experimental work

2.1. Sample preparation of surface unmodified and modified TiO_2 nanoparticles with SiO_2 and Al_2O_3

TiO_2 nanoparticles in rutile crystal form were synthesized using sulfate process and delivered as water dispersions. First sample was not surface modified while the second one was surface treated by precipitation in two steps: with 1 wt.% of SiO_2 and afterwards with 3 wt.% Al_2O_3 (sample denoted as TiO_2–SiO_2/Al_2O_3) [13]. The pH values of modified nano TiO_2 (TiO_2–SiO_2/Al_2O_3) water based dispersion was 5.5–6 and of unmodified nano TiO_2 water based dispersion was 1.6–1.8. Both samples had 30 wt.% solid content of nanoparticles. The samples were prepared by company Cinkarna Celje d.d.

2.2. Preparation of polyacrylic coating with integrated surface modified and unmodified rutile crystalline nanoparticles

Water based polyacrylic dispersion is a commercial product Belinka Exterier 61 without UV absorbers (Helios Group). The samples of composite coatings with integrated TiO_2 nanoparticles were prepared by incorporation of 0.6 wt.% unmodified TiO_2 nanoparticles and 0.6, 1.2 and 1.8 wt.% of TiO_2–SiO_2/Al_2O_3 nanoparticles to polyacrylic coating, stirred at approximately 1000 rpm for 20 min and prepared for the testing.

2.3. Characterization of the samples

Modified and unmodified TiO_2 nanoparticles in water dispersions and polyacrylic dispersion with and without TiO_2 nanoparticles were washed several times with distilled water and separated by centrifuge. The nanoparticles were finally dried in an oven at 100 °C for 24 h. Prepared samples were analyzed by FT-IR (Thermo Nicolet 6700). FTIR spectroscopy was performed in potassium bromide pellet.

Surface morphology of unmodified TiO_2 and TiO_2–SiO_2/Al_2O_3 was studied by atomic force microscopy (AFM). AFM scanning were performed using Park XE100 with silica non-contact cantilever (PPP-NCHR).

Zeta potential, size and particle size distribution of diluted samples were obtained by Zetasizer Nano ZS series to investigate the surface character of TiO_2–SiO_2/Al_2O_3 nanoparticles and polyacrylic dispersion with and without TiO_2 nanoparticles. The sample (0.3 g) was dispersed in 50 g of distilled water.

Particle size distribution and zeta potential of high solid content nanoparticle dispersions were obtained with Electro-acoustic Spectrometer DT 1200 (Dispersion Technology). Electro-acoustic probes were calibrated with colloidal silica (Silica redox, $\zeta = -38 \pm 1$ mV).

UV–VIS transmittance of polyacrylic clear coatings without and with integrated nanoparticles was measured for estimating UV-shielding ability and transparency in the wavelength range 200–800 nm by UV-VIS spectrophotometer Varian Cary 100. The samples were prepared by mixing TiO_2 nanoparticle water based dispersions into polyacrylic coating and applied as 200 μm wet films.

3. Results and discussion

Microstructural analysis of unmodified TiO_2 and TiO_2–SiO_2/Al_2O_3 nanoparticles was done by AFM in order to determine predominantly the morphology. As seen from Fig. 1, individual particles are non-spherical and needle like shape. One selected particle was measured in dimensions below 100 nm in length and 40 nm in width. The shape and dimensions of unmodified TiO_2 and TiO_2–SiO_2/Al_2O_3 nanoparticles are comparable.

In next step FT-IR analysis was done to demonstrate surface modification of TiO_2 nanoparticles with binary SiO_2–Al_2O_3. Fig. 2 shows the FT-IR spectra of unmodified TiO_2 and TiO_2–SiO_2/Al_2O_3 nanoparticles and substraction result with bands wavenumbers. Detailed view of the bands in the 1700–900 cm^{-1} can also be seen in the Fig. 2. OH groups are described by bands at 3420 and 1630 cm^{-1}. The band appearing at 930 cm^{-1} is attributed to Si—O—Ti stretching vibration. The Al_2O_3 layers were probably anchored at the SiO_2 coated TiO_2 via Al—O—Si bond around 1080 cm^{-1} as denoted in