



Durability and mechanical performance of a photo-catalytic water-based nanocomposite coating



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ABSTRACT

In this study, different combinations of nanoparticles including; TiO_2 , SiO_2 , silica grafted TiO_2 , titania grafted SiO_2 , physical blends of $\text{TiO}_2/\text{SiO}_2$ nanoparticles and nanocomposite particles made of titanium tetra-isopropoxide/tetraethylorthosilicate (TTIP/TEOS) precursors, were loaded into an acrylic emulsion coating. Photo-activity of the coatings was evaluated through the photo-degradation of Rhodamine B dyestuff, as a pollutant model, on the surface of the coatings under UVA irradiation. The coating films were exposed to accelerated weathering conditions for different time intervals. As the criteria for durability of the coatings, morphology and topology of coatings surface were studied using scanning electron microscopy (SEM) and atomic force microscopic (AFM) techniques, respectively. Mechanical properties of the coatings were assessed before and after exposure to accelerated weathering conditions. The results exhibited a favorable balance of photocatalytic activity and mechanical properties in the coatings containing TTIP/TEOS nano-composite particles even after exposing to the accelerated weathering conditions.

1. Introduction

Environmental contamination is growing all around the world and considered as a serious problem which should not to be neglected. Adsorbed dirt and pollutants on the exterior surface of structures, cause an unattractive view and lead to increase in cleaning costs [1]. Materials containing photo-active TiO_2 particles in different applications including; tile [2], cement [3], polymeric coatings [4], glasses [5], is one of the most promising approaches available to overcome the problem [6].

Nowadays, photo-active coatings containing well-designed TiO_2 nanoparticles have been developed in different categories including; inorganic [7], inorganic/organic hybrid [8], and organic [9–11], structures. However, organic photo-catalytic coatings have found limited industrial applications due to some shortcomings [12]. In general, spontaneous tendency of TiO_2 nanoparticles to the aggregation by attractive forces (e.g. van der Waals) provides undesired dispersion of the particles in the polymeric dispersing media [13]. Furthermore, poor mechanical properties and weak durability are the main disadvantages of organic photo-active coatings containing TiO_2 nanoparticles, which arise from photo-activity of titania nanoparticles and its damaging effect on the polymeric matrix [9,14].

Photo-activity adjustment of TiO_2 nanoparticles can be achieved via either surface treatment [15] or doping process [16]. Reduction in

photo-catalytic activity of TiO_2 results from changing the surface chemistry and hydrophilic character of the nanoparticles [17], and decreasing the effective surface area of TiO_2 available to both pollutants and UVA irradiation [18].

Mechanical properties such as tensile modulus, elongation, and toughness and other related parameters are important characteristics of organic coatings [19,20]. Exterior coatings must be durable and withstand the tensile and compressive forces that encounter during their service life [21]. Improving mechanical properties of organic coatings using nanomaterials have been reported in the literatures [22–24].

SiO_2 –based compounds which are usually used to adjust the photo-catalytic activity, [11] and to improve dispersion behavior [18,25] of TiO_2 nanoparticles in organic media, are one of the most promising materials in micro and nano particle forms for enhancing the mechanical properties of polymeric composites [26,27]. As a result of the literature survey, it is clear that silica compounds play a dual-edged role in the coatings performance. Based on our previous work [28], different combinations of Ti and Si elementals in titania/silica compounds, with different nanoparticles surface elemental compositions (i.e. presence or absence of Ti–O–Si band at the interface of catalyst and pollutants) lead to dissimilar photo-catalytic activities of the mentioned nanoparticles in an aqueous media [15].

Photo-activity and durability are two key factors which play a critical role in efficacy of photo-active coatings. However, there is a lack of

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studies for evaluating of various compositions of titania and silica spontaneously on both photo-activity and mechanical properties of acrylic as an organic coating. In our previous study [17], surface modification of titania nanoparticles with a hydrophobic fluorosilane compound in alkaline, acidic and neutral conditions was studied. The results revealed that fluorosilane treated nanoparticles migrate towards the coating surface during the film drying and increase photo-activity of the film with minimal negative effect on the polymeric matrix. In the current study, the effect of different combinations of TiO₂ and SiO₂ compounds including: untreated TiO₂ nanoparticles (UT), untreated SiO₂ nanoparticles (US), silica grafted TiO₂ (MT), titania grafted SiO₂ (MS), physical blend of TiO₂/SiO₂ nanoparticles (TSb), and TiO₂/SiO₂ nanocomposite particles (TSc) on the durability and mechanical properties of a water-based acrylic coating, before and after UVA irradiation were evaluated. In other words, a comprehensive study was conducted on the effect of physical and different chemical combinations of titania and silica nanoparticles on the photo-catalytic properties, durability, and mechanical properties of the waterborne coatings which the nanoparticles embedded in.

2. Experimental

2.1. Materials

Fumed silica (Aerosil 200) and TiO₂ (Aeroxide P25) nanoparticles were provided by Evonik Industries (Degussa GmbH, Germany). Titanium tetraisopropoxide (TTIP) and Tetraethylorthosilicate (TEOS) were purchased from Fluka, UK and used as precursors for surface treatment of SiO₂ and TiO₂ nanoparticles, respectively. Acrylic emulsion resin (Orgal P850W, 46 wt % solid content) was obtained from Celanese Emulsions, (U.S.). Texanol, as a coalescing agent was purchased from Eastman Chemical Co, (U.S.). Rhodamine B dyestuff (RhB), a pollutant model, was obtained from Ciba-Gigy, Switzerland and sodium dodecyl sulfate (SDS) was provided by Merck Chemicals, Germany. All chemicals were analytical grades and used as-received without further purification.

2.2. Nanoparticles surface treatment

Various combinations of TiO₂ and SiO₂ nanoparticles were prepared using different routes [28]. TiO₂ and SiO₂ nanoparticles were separately treated with tetraethyl orthosilicate (TEOS) and titanium tetraisopropoxide (TTIP), via a two-step sol-gel procedure, respectively. SiO₂/TiO₂ nanocomposite was synthesized from TEOS/TTIP precursors using a sol-gel process followed by calcination at 600 °C for 3 h. Eventually, physical blending of 1:1 wt ratio of TiO₂:SiO₂ nanoparticles was prepared. The procedures details were reported elsewhere [28].

2.3. Preparation of acrylic-based coatings

0.46 g of different nanoparticles (neat and treated ones separately) were dispersed in 12 mL SDS solution (0.0003 g L⁻¹) via ultrasonic irradiation (Bandelin, SONO PULS-UW 2200, using KE-76 probe, 70 W power) for 15 min in the pulsation mode of 0.7 s on and 0.3 s off. The dispersions were then added to 100 g emulsion resin under mechanical stirring (Heidolph RZR 2102, Germany) at a constant rate of 600 rpm for 3 h. The excess water was removed from the sample by immersing the dispersion container in a temperature-controlled water bath on a programmable hotplate with external temperature probe at 60 °C. Finally, 1.6 g Texanol was added to the mixture and mechanical stirring was continued for further 30 min mixing at ambient temperature. The dispersion was then placed in a low pressure oven at 200 mbar for 30 min to remove the trapped air bubbles.

The dispersion was then applied on two series of degreased glass plates using a film applicator (Elcometer Doctor Blade) with 200 μm wet thickness (80 ± 10 μm DFT) for SEM and AFM sampling, and

Table 1
Sample coding for different specimens.

Row	Sample coding	Latex samples containing 1 wt % of different nanoparticles
1	N.La	Neat latex film
2	UT.La	Un-treated TiO ₂ nanoparticles
3	MT.La	TEOS treated TiO ₂ nanoparticles [18]
4	US.La	Un-treated SiO ₂ nanoparticles
5	MS.La	TTIP treated SiO ₂ nanoparticles [28]
6	TSb.La	Physical blend TiO ₂ /SiO ₂ nanoparticles
7	TSc.La	Synthesized TiO ₂ /SiO ₂ nanocomposite particles [28]

300 μm wet thickness (130 ± 20 μm DFT) for stress-strain analysis. The films were then left to dry at ambient temperature (23 ± 2 °C) for about 24 h. The coated glass plates were soaked in distilled water for about 1 h, and free-standing films were detached from the substrate and left to dry at room temperature for 24 h. Sample coding for different specimens is tabulates in Table 1.

2.4. Photo-activity of acrylic coatings

Dispersion status of different nanoparticles in the freestanding coating samples was studied using SEM micrographs. The different coating samples were mounted on a sample stage and sputter coated with a thin layer (≈ 10 nm) of gold for 60 s under argon atmosphere and examined using the scanning electron microscope (Cambridge Stereo scan S360) operated in the secondary electron mode at 10 kV.

Photo-catalytic activity of the coating samples containing 1 wt % of different nanoparticles was evaluated via assessment of photo-degradation of RhB dyestuff (deposited on the coatings surface) under UVA irradiation (OSRAM ULTRA-VITALUX[®], 300 W) [9]. For this purpose, a solution of 1 g L⁻¹ Rh.B dyestuff was casted on the coatings film and left to dry at ambient temperature and photo-degradation test was conducted after 48 h. Three replicate samples were tested for each exposure conditions. UVA lamp was placed at about 35 cm above the samples and the test was performed for 80 h, at 30 °C. The color coordinates measurements were carried out using Miniscan XE Plus colorimeter (0°/45° geometry, D65 illuminant and (10°) or 2° observation angle) before and during exposure to the UVA irradiation according to ASTM D 65 test practice. The total color change (ΔE) was calculated from the measured color coordinates as a function of the UVA exposure time, from CIE (Commission International de l'éclairage) (L*a*b*) 1976 formula using Eq. (1) [9]:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

where L^* represents the brightness and varies between 100 (white) and 0 (black); a^* (red- green) and b^* (yellow-blue) are the chromaticity coordinates.

Because of the red hue of RhB, chromatic coordinate a^* and the calculated color differences, ΔE, were utilized to evaluate the photo-catalytic efficiency of the samples. To this end, variation of a^* during the UV exposure times was utilized to determine the photo-catalytic efficiency of coating samples containing different nanoparticles.

2.5. Durability of photo-active coatings

Durability of the acrylic photo-active coatings containing different nanoparticles (1 wt.%) was evaluated via surface morphology and mechanical properties assessments, and through stress-strain analysis. For this purpose, the coating samples with 80 ± 10 μm dry film thickness (DFT) were exposed to the accelerated weathering conditions in a QUV chamber (QUV/Spray, Q-Panel Co.) for 24 h and 168 h in different tests, under cyclic conditions. The periodic test was performed under UVA irradiation (340 nm, 0.89 W m⁻²) at 60 °C for 8 h, followed by 4 h water condensation at 50 °C, according to ASTM G 154 test

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