Progress in Organic Coatings 74 (2012) 654–659

Contents lists available at SciVerse ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Review

# Polyhedral oligomeric silsesquioxanes as titanium dioxide surface modifiers for transparent acrylic UV blocking hybrid coating

J. Godnjavec [a,*], B. Znoj [a,b], N. Veronovski [c], P. Venturini [a,b]

[a] Center of Excellence for Polymer Materials and Technologies, Tehnoloski Park 24, 1000 Ljubljana, Slovenia
[b] HELIOS Domzale, d.d., Kolicevo 2, 1230 Domzale, Slovenia
[c] Cinkarna Celje, d.d., Kidriceva 26, 3001 Celje, Slovenia

ARTICLE INFO

*Article history:*
Received 6 June 2011
Received in revised form
12 September 2011
Accepted 22 September 2011
Available online 18 December 2011

*Keywords:*
Titanium dioxide
Inorganic UV absorber
Surface modification
POSS
Dispersibility
Nano-composite
UV protection

ABSTRACT

Architectural coatings are often recommended to enhance the durability of wood in exterior environment however the coatings itself are not UV stable enough for long term protection. For this reason inorganic UV absorbers like nano $TiO_2$ in rutile crystal form are of great research interest in last decade. It's advantage is UV reversible absorption activity in polymer composite like coating during weathering [1]. On the other side the $TiO_2$ surface has limited compatibility with polymers what can result in non-stable dispersion. To achieve a better compatibility between nano-particles and polymer matrix in coating, the use of different inorganic/organic surface modification of $TiO_2$ rutile nano-particles is recommended.

In order to improve dispersability of $TiO_2$ rutile nano-particles in acrylic water based coating, two step surface modification of $TiO_2$ nano-particles was investigated. First, $TiO_2$ nano-particle's surface was modified with $Al_2O_3$ and second polyhedral oligomeric silsesquioxanes (POSS) were used in order to improve $TiO_2$ dispersability and to enable higher UV absorption by reduction of nanoparticles agglomeration. Evaluation of physical properties before and after exposed weathering tests of coating samples with surface modified $TiO_2$ rutile nano-particles proved our prediction. The results can be used for further optimization of nano-composites in coating applications for long term UV protection.


**Contents**



## 1. Introduction

Wide-spread commercialization of polymer nanocomposite materials is not as fast as expected, mainly because of nanoparticle aggregation tendency and limited compatibility with polymer dispersions. High-quality dispersion of nanoparticles in different

* Corresponding author.
*E-mail address:* jerneja.godnjavec@polimat.si (J. Godnjavec).

0300-9440/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.porgcoat.2011.09.032

phases is necessary in the fabrication of homogeneous hybrid polymer nanocomposite materials used for making functional hybrid coatings, in our case for UV protection of wood. In order to overcome the problem of incompatibility of polymeric phases with high-surface-area inorganic structures, the surface of the particles should be modified first [2,3].

Nanoparticles of $TiO_2$ in rutile crystal form are usually surface treated by different inorganic oxides like $Al_2O_3$. The $Al_2O_3$ layer are expected to suppress the photocatalytic activity of $TiO_2$ nanoparticles responsible for the gradual yellowing and damage of polymer matrix [4,5]. Coating the nanoparticles is accomplished by precipitating white hydrated oxides onto the $TiO_2$ surface [6].

Surface modification can be further improved by non-covalent functionalization of the particles in the presence of a polymer surfactant, that becomes attached to the particle surface by preferential adsorption of the polar groups via electrostatic interactions or by chemical interactions between most common alkoxysilanes and the particles surface. The non-hydrolysable group (X-) of bi-functional alkoxysilanes (X-Si(OR)*n*) can be used to optimize the chemical and physical properties of the layers, while the hydrolysable alkoxy groups (–Si(OR)*n*–) in the presence of acid catalysts give reactive silanol groups (Si–OH) enabling the condensation of hydrolyzed silanes to gels by the formation of siloxane bonds (Si–O–Si) [7,8]. The functionalization of $TiO_2$ nanoparticles by grafting amino propyl trimethoxy silane is a typical example of using silane for modification of the particle surface in order to provide stable non-agglomerated dispersion of nano-particles and for tailoring their UV protection properties of the urethane clear coating [9].

Polyhedral oligomeric silsesquioxane (POSS) molecules are hybrids, intermediate between that of silica ($SiO_2$) and silicone ($R_2SiO$). POSS molecules consist of a Si–O–Si inorganic cage surrounded by an inorganic corona, represented by substituent R in $(RSiO_{1.5})_n$. The inorganic cage may be fully condensed closed or open structure. The most common are octasilsesquioxanes where $n = 8$. Trisilanol POSS is a novel dispersant [10]. In view of its open-cage-like structure with reactive silanol groups, trisilanol POSS is expected to possess several distinct advantages over traditional surface modifiers like silanes. Since it possesses three SiOH groups, they cannot react with one another by forming siloxane bonds (Si–O–Si) as in the case of ordinary trialkoxysilanes, where the surface mono-layers are difficult to make [11] and a particle/POSS interfacial bonding forms more robust bonds than typical silanes. In view of the structure of trisilanol POSS molecules, the POSS molecules are expected preferentially to interact with the particles surface rather than among themselves.

Heptaisobutyltrisilanol polyhedral oligomeric silsesquioxanes (trisilanol POSS, denoted as POSS) has incompletely condensed framework possesing a hybrid inorganic–organic, three-dimensional structure and containing three silanol (Si–OH) groups (Fig. 1). POSS with silanols groups are stable against condensation unlike most other silanols [12].

Only a few reports exist on trisilanol POSS molecules as dispersants. Trisilanol POSS has been already used in the modification of nanosized $TiO_2$ particles, which were then incorporated in polypropylene (PP) polymer [13]. Chemically similar trisilanol-phenyl POSS has also been used for the incorporation of $TiO_2$ particles in PMMA with good success [14] and blended into polycarbonate. Trisilanol isooctyl POSS makes bulk polycarbonate opaque, indicating poor dispersion of the POSS [15]. Gomathi et al. have reported that polyoctasilsesquioxane is a good reagent to covalently functionalize nanostructures of metal oxides as well as nano-carbons to prepare useful composites [16]. Another author reports about fluoropolymer based coatings that can be made from a pigment dispersion containing trisilanol isobutyl polyhedral oligomeric silsesquioxane modified black pigment particles

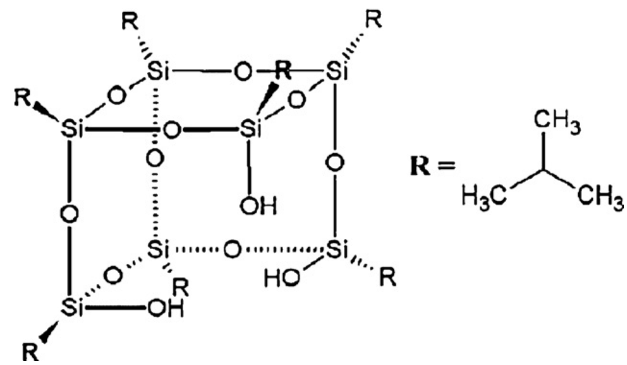


**Fig. 1.** Structure of heptaisobutyltrisilanol silsesquioxane [12].

[17]. However there was no report on improving colloidal stability of $TiO_2$ nanoparticles with POSS surface treatment and it's influence on transparency and UV stability of acrylic composite what is the goal of present work. The study is consequently focused on analysis of nano rutile $TiO_2$ surface treatment with trisilanol POSS molecules and it's influence on nano $TiO_2$ colloidal stability in water based acrylic coating. To anchor the POSS on $TiO_2$ nano-particle surface, we have exploited that metal oxide nanostructures posses surface hydroxyl groups [18]. We used $TiO_2$ nano-particles in rutile crystal form that were surface pretreated with $Al_2O_3$ to surpress the catalytic activity. Finally the transparency and UV stability of coating with surface treated nano $TiO_2$ in rutile crystal form was determined and the relation with colloidal stability was discussed.

## 2. Experimental

### *2.1. Sample preparation – surface modified $TiO_2$ nano-particles with POSS in water based dispersion*

$TiO_2$ nano-particles in rutile crystal structure form were synthesized using sulphate process and surface treated by precipitation with $Al_2O_3$ (sample denoted as $TiO_2$–$Al_2O_3$). The sample was prepared by Cinkarna Celje.

The dispersions of $TiO_2$–$Al_2O_3$ nano-particles grafted with POSS (sample denoted as $TiO_2$–$Al_2O_3$–POSS) were prepared according to the following procedure. $TiO_2$–$Al_2O_3$ nano-particles in rutile crystal structure in aqueous dispersion and POSS in wt. ratio $TiO_2$:POSS = 10:1 were added into water and hydrochloric acid (HCl) and put the mixture in the shaker for 2 min. Prepared mixture was than stirred for 6 h with a stir bar on a combined hot-plate magnetic-stirrer device at 70 °C. The content of $TiO_2$ nano-particles in the dispersion was ~30 wt.%.

### *2.2. Preparation of water based acrylic coating with integrated rutile crystalline $TiO_2$–$Al_2O_3$ and $TiO_2$–$Al_2O_3$–POSS nanoparticles*

Water based acrylic coating was prepared in the laboratory as described elsewhere [19]. In this case 0.6 wt.% of nano-particles in water based dispersion ($TiO_2$–$Al_2O_3$, $TiO_2$–$Al_2O_3$–POSS) were added to acrylic coating, stirred at approximately 1000 rpm for 20 min and prepared for the testing.

### *2.3. Characterization of the samples*

Particles morphologies were studied by transmission electron microscopy (TEM, JEOL 2100F, Japan).

Grafting of POSS on $TiO_2$ nano-particles was analyzed by FT-IR and TGA. The infrared spectra of original and modified $TiO_2$ were conducted using a FT-IR spectrometer (PERKIN ELMER Spectrum