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Photostabilization of cationic UV-cured coatings in the presence of nanoTiO_2

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Abstract

The effect of TiO_2 nanoparticles for sun-weathering protection of UV-cured coatings is investigated. TiO_2 is either introduced in the form of nanoparticles in the photocurable formulations or generated in situ via sol–gel process. Cured films containing comparable amounts of TiO_2 were weathered for 800 h under UV irradiation and compared with free-TiO_2 coating. The TiO_2 presence induces a clear lower mass loss decrease during weathering as well as a lower gel content decrease. The TiO_2 screen effect is also confirmed by a lower alkyl-band reduction monitored by FT-IR during weathering. The TiO_2 generated in situ via sol–gel gives rise to transparent coatings without interfering with photopolymerization process and therefore without compromising UV-cured film properties.

Keywords: Sun-weathering of coatings; Photostabilization; Cationic UV curing; Sol–gel; TiO_2

1. Introduction

The primary and economically important purpose of application of organic coatings is to protect various substrates (metal, wood, plastics) from weathering in a harsh environment [1].

During outdoor service, coatings are exposed to environment, which affects negatively their physical or mechanical properties and chemical composition, by the formation of new functional moieties or fragmentation of the crosslinked macromolecules.

Physical and mechanical changes are consequence of minor chemical changes [2] and solar radiation is one of the principal reasons for the reduced durability of coatings.

Traditional choices for protecting coatings from sun-weathering involved the use of organic UV-absorber as hindered amine light stabilizers [3].

UV-absorbers are colorless or nearly colorless compounds having high absorption coefficients in the UV part of solar spectrum; they protect coatings against photoinduced damages by absorbing the harmful solar radiation [4]. The addition of organic UV-absorbers protects the substrate, but the effect is not permanent and such stabilizers tend to migrate or decompose during exposure.

In recent years there has been extensive interest in ultrafine or nanoparticle fillers and pigments, as alternative UV-blockers in coatings applications [5]. The photostabilizing effect of pigments can be attributed to screening of harmful radiation, selective absorption of the incident light and, to some extent, deactivation of photoexcited species [6].

Nevertheless, when photopolymerization technique is used for coating formation [7] both organic UV absorber or inorganic filler as TiO_2, can compete with photoinitiator absorption, with a consequent detrimental effect on final reactive group conversion, polymerization rate and mechanical properties of the cured network.

Therefore, in this work, we propose to generate TiO_2 nanoparticles for sun-weathering coating protection, only after UV curing. TiO_2 can be produced by sol–gel process after photopolymerization and its presence can protect the coatings against sun-weathering without compromising the UV curing process.

In order to compare the efficiency to ageing protection, cured coatings containing TiO_2 generated in situ were compared to coatings containing similar amount of TiO_2 dispersed in form of nanoparticles.

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2. Experimental

2.1. Materials

A cycloaliphatic epoxy silicone resin (Tego RC1406), gently given by Degussa, was employed as cationic photocurable resin. Titania nanopaticles were supplied by Degussa (TiO_2, P25, Degussa, Germany). For the samples containing TiO_2 generated via sol–gel process, 3-glycidoxypropyl trimethoxysilane (GPTS, Aldrich) was used as coupling agent, titanium tetra-isopropoxide (TIP, Aldrich) was the organic precursor for the ceramic phase. Diphenyliodonium hexafluorophosphate salt (Tego, PC1465, Degussa) was used at 2 wt% in each formulation, as photoinitiator.

2.2. Curing procedure

Cured coatings containing TiO_2 nanoparticles were obtained by adding 3 wt% of TiO_2 to the silicone resin, and 2 wt% of iodonium salt photoinitiator. The particles were dispersed with the aid of an ultrasonic bath. The formulations were coated onto a glass substrate using a wire-wound applicator, and following exposed to UV radiation with a Fusion lamp (H bulb) in air at a conveyor speed of 5 m/min, with radiation intensity on the surface of the sample of 280 mW/cm^2. The curing procedure was the same as reported in previous papers [8] obtaining films of about 100 μm.

The hybrid films obtained via sol–gel process were prepared by adding to the epoxy resin 10 wt% of GPTS coupling agent and 10 wt% of TIP precursor, corresponding to the theoretical formation of 3 wt% TiO_2 after hydrolysis and condensation reactions. An amount of 2 wt% of iodonium salt photoinitiator was added to the obtained mixture, and the formulation applied to a glass substrate by using a wire-wound applicator. The photochemical curing was performed by using Fusion lamp. The subsequent hydrolysis and condensation reaction was performed by storing the photocured films in an oven at 80 °C for 4 h in a chamber with a constant humidity (95–98% relative humidity). The obtained samples after thermal treatment appeared transparent.

2.3. Characterization methods

The cured films were weathered using a UV-ASTM-G154 weatherometer chamber. The samples were treated with UV irradiation for 800 h at 50 °C.

Samples were prepared for TEM observation by Ar ion polishing system GATAN PIPS, working at 3.5 keV at an angle of 7°. They were examined in a 300 keV transmission electron microscope (TEM) Philips CM30. TEM micrographs were processed with a slow scan CCD camera and analyzed with the Digital Micrograph Program. The TEM observations were always performed using a very low electron flux in order to avoid any structural modification of the sample induced by the electron beam.

Mass loss measurements were recorded at appropriate irradiation time intervals. Samples were conditioned to constant weight in air in a dessiccator with silica gel for some hours before weighing. Gel content was determined on fresh cured and weathered films, by measuring the weight loss after 24 h extraction with chloroform at room temperature (ASTM D2765-84).

Chemical changes in the cured films under weathering conditions were monitored by FT-IR spectroscopy employing a Thermo-Nicolet 5700 instrument.

3. Results and discussion

Titania containing epoxy coatings were prepared via cationic photopolymerization by using a diphenyl iodonium salt as photoinitiator. Titania nanoparticles were dispersed or generated in situ through a sol–gel dual cure process, as previously reported [8,9].

It was demonstrated that, by increasing the TiO_2 nanoparticle concentration in the epoxy resin a decrease in photopolymerization rate and epoxy group conversion was induced [8]. This behavior has been attributed to the UV absorption competition between TiO_2 nanoparticles and the photoinitiator. For this reason we wanted to prepare coatings containing TiO_2 generated in situ after photopolymerization.

An in situ approach of preparing nanoparticles using metal-alkoxyde precursor and sol–gel process is appealing [10]. A coupling agent is usually added to provide bonding between the organic and the inorganic phases, thereby preventing macroscopic phase separation. Under proper conditions the size of the inorganic particles can be reduced to the nanolevel (<50 nm) [11].

The organic matrix is obtained by cationic ring-opening polymerization initiated by a photogenerated Brönsted acid; under this acidic condition a following hydrolysis and condensation reactions of alkoxytitanate groups, gives rise to TiO_2 network formation.

Because TiO_2 is formed only after UV-curing, it will not interfere with photoinitiation process, and therefore it will not compromise the UV curing rate and final epoxy group conversion, as it was previously demonstrated by real-time FT-IR kinetic investigations reported in a previous work [8].

Cured films containing 3 wt% of nanodispersed TiO_2 were hazy and cloudy. On the contrary, the cured films obtained by formulations containing 10 wt% TIP were fully transparent to visible light, indicating a uniform distribution of the in situ generated titania network without a significant macroscopic agglomeration; this was further confirmed by TEM analyses.

In the case of dispersed TiO_2, agglomerated clusters are formed above 100 nm (see Fig. 1). In the case of dual cured samples obtained by sol–gel, TiO_2 is well dispersed with no significant macroscopic agglomeration, and a size distribution ranging between 5 and 10 nm (see Fig. 2).

The free-TiO_2 epoxy cured network and the corresponding coatings containing dispersed or in situ generated TiO_2, were weathered for 800 h at 50 °C.

Mass loss measurements were recorded at appropriate time intervals during the irradiation period on coated substrate. In Fig. 3 the percentage mass loss as a function of weathering time is reported. A higher detrimental effect to the coating is evident in absence of TiO_2, with highest mass loss due to