Accelerated degradation of water borne acrylic nanocomposites used in outdoor protective coatings

CrossMark

Thien Vuong Nguyen [a], Phuong Nguyen Tri [b, *], Tuan Dung Nguyen [a], Rachid El Aidani [c], Van Thanh Trinh [a], Christian Decker [d]

[a] Institute for Tropical Technology, VAST, Hanoi, Viet Nam
[b] Department of Chemistry, University of Montreal, Montreal, QC, Canada
[c] Department of Mechanical Engineering, ETS, Montreal, QC, Canada
[d] Photon and Polymer Society, 68460, Lutterbach, France

ABSTRACT

In this study, the degradation of a water-borne acrylic coating and the influence of rutile-TiO_2 (R–TiO_2) nanoparticles and a hindered amine light stabilizer (HALS) on its photo-stability in accelerated aging environment has been quantitatively studied by monitoring the chemical modifications occurring upon aging conditions. By using non-destructive analytical methods, like IR and UV-visible spectroscopy, 3D laser microscopy, SEM observations and weight loss measurements, it was possible to follow continuously the formation of photo-oxidative products and the loss of the binder functional groups on a sample undergoing accelerated aging. For the first time, numerous dark spots, randomly dispersed on the whole surface of the sample upon UV/condensation exposure are successfully observed and explained by using a novel technique 3D laser microscopy. Our findings also confirm that HALS greatly improved photo-stability to the coating thank to its free radical and hydrogen peroxide scavenging capacity. This work provides some useful information for a better understanding of the degradation behavior of water-borne acrylic coating under accelerated aging conditions.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Due to the low manufacturing costs, suitable bulk properties, versatility and aesthetic attributes, organic coatings are nowadays widely used to protect and decorate various metallic surfaces and buildings. Acrylic resins have attracted special interest of scientists and producers because of its distinct advantages characteristics, including its weathering durability, its optical clarity, its good mechanical properties and its chemical stability. The majority of commercial acrylic resins for industrial coatings are used in outdoor conditions. It is well known that the solvent-borne acrylic coatings which are largely employed in industrial maintenance such as steel structures, fuel tanks and automotive finishes consist the coatings based on thermoset acrylic binders (acrylic-melamine), 2 pack polyurethanes (acrylic-polyurethane) and based on thermoplastic acrylic polymers (acrylate-methacrylate copolymers) [1–11].

Nowadays, with the tightening of regulations relating the use of protective coatings associated with environmental occupations, coating industries are obliged to propose new solutions to minimize the levels of polluting substances released into the atmosphere. For this reason, end-users have tried to develop environmental friendly solvent-free coatings such as UV-cured systems, water-borne coatings [12,13]. The pure acrylic emulsions-based coatings are now commonly used for the exterior wall paints of buildings. The main advantages of these systems consist in their solvent-free formulation.

However, like other polymer materials, these coatings can be degraded upon outdoor exposure by environmental factors such as UV-light, oxygen, temperature, water and pollutants, which can deteriorate their bulk properties such as gloss, young's modulus and hardness and surface rugosity [13,14]. Among these factors, UV radiation is a major contributor to the degradation of such polymer materials. Even though UV-light ranging from 280 to 400 nm represents only 5% of the total radiation reaching the earth's surface, these energy-rich radiations induce photolysis and photo-oxidative reactions in the coatings by degrading their physico-mechanical, optical and other properties. The weathering

degradation of acrylic coatings has already been described in several publications [4,8].

The degradation of acrylic-urethane and acrylic-melamine coatings under UV-light exposure without water leads to polymer chain scissions and crosslinking. The cleavage of the urethane and ether chemical bonds by UV-light leads to the formation of free radicals, which may be the sources of a new crosslinking, are the main causes of the polymer degradation [4]. In the presence of water (moisture), the photodegradation of acrylic-melamine coatings is somewhat accelerated. Moisture enhances the degradation of partially-methylated melamine acrylic coatings with the production of formaldehyde by hydrolysis and formaldehyde molecules were absorbed UV light and dissociate to form free radicals following by hydrogen abstraction in the melamine chains and finally leads to the formation of amine and amide products [5–7]. The weathering degradation of the UV-cured acrylic coatings also includes chain scissions and crosslinking. However, due to the thick network structure, these coatings have been shown to be better resistant to weathering than acrylic-urethane and acrylic-melamine coatings [10–12].

The photo-oxidative behavior and the differences of stability of thermoplastic acrylic resin based coatings have also been reported in several publications [9,10,13,15–17]. The acrylate units were found to be more reactive to oxidation, in comparison with the methacrylate ones. With short alkyl side groups, chain scissions prevailed over cross-linking reactions both in acrylate and methacrylate samples. The degradation of poly(butyl methacrylate) proceeds in a completely different way, with extensive crosslinking and simultaneous fragmentation reactions. One of the most efficient methods to improve the weathering resistance of polymeric materials in general and particularly for acrylic coatings used in outdoor applications is integrating in the coating formulations several UV absorbers and stabilizing agents such as benzophenone or benzotriazole derivatives [1,2,18], or with oxide-based nanoparticles such as TiO_2, ZnO [19,20]. These agents act by different mechanisms, like the quenching of free radicals or the absorption of high energy radiation. However, for the use of those organic UV stabilizers show sometimes some drawbacks such as bad compatibility, migration and decomposition upon UV exposure. The loss of UV absorbers during photoaging is also an important parameter to evaluate the outdoor service lifetime of stabilized polymeric materials. This is particularly true for coated polymers where the decrease of the UV-filtering effect of the coating will enhance the photoinduced degradation of the underlying substrate [11]. So it is essential to slow down the UV absorber loss as much as possible. This problem can be partly overcome by using an acrylic copolymer where UV-absorbing groups are bonded to the polymer chains. Due to such chemical bonding, UV absorbers are less likely to escape from the coating [21].

In recent years, TiO_2 nanoparticles have attracted great attention and development in various fields of applications, in particular as UV absorbers for light stabilization, catalytic supports, photocatalysts for purifying water and air by degrading organic pollutants and killing bacteria, production of oxo-biodegradable plastics [20,22–29], as well as improving thermal and mechanical properties of polymer materials [30]. Compared to the instability of organic UV absorbers, TiO_2 nanoparticles are non-toxic inorganic compounds which show a good chemical stability upon exposure to both UV radiation and high temperatures. They offer a long lasting UV protection because they do not decompose and do not migrate in coatings during weathering [19,25,31]. The optical properties of nanocomposites depend on the size and concentration of the reinforcement particles. TiO_2 nanoparticles exhibit a high surface area, which causes a significant increase of their efficiency for the protection against UV radiations, compared to traditional TiO_2

microparticles [19,20]. The modified surface TiO_2 nanoparticles showed a better UV shielding efficiency than unmodified nanoparticles. The photo-catalytic activity of the particles is greatly suppressed after surface modification by trimethyl siloxane or several transition metal oxides [31,32]. However, the surface modified by organic compounds may reduce the dispersion of the modified particles in the hydrophilic environment, such as acrylic emulsion.

Hindered-amine light stabilizers (HALS) are often added to the formulation of weathering resistant coatings [1,2,11,12], because of their high radical scavenging effect. While there are a number of publications about the degradation and durability of solvent-based acrylic coatings, as well as of photocrosslinked acrylic coatings [8,9], there is a lack of information about the degradation and stability of water-borne acrylic coatings.

In this study, the photodegradation of a water-borne acrylic coating and the influence of R–TiO_2 nanoparticles and HALS were quantitatively studied by monitoring the chemical modifications occurring upon UV-B/condensation accelerated aging environment. By using non-destructive analytical methods, like IR and UV-visible spectroscopy, 3D laser microscopy, SEM observations and weight loss measurements, it was possible to follow continuously the formation of photo-oxidative products and the loss of the binder functional groups on a sample undergoing accelerated aging. This kind of study is considered to provide a reliable evaluation of the weathering resistance of a given polymer and of the stabilization effect of some additives, knowing that the physical and chemical changes observed in a photodegraded polymer are usually resulting from chain scission and cross-linking processes.

2. Experimental

2.1. Materials

PRIMAL™ AC-261, acrylic emulsions having a solid content of 50 wt% and Texanol (2, 2, 4-trimethyl-1, 3-pentanediol mono-isobutyrate) as a coalescing agent, were obtained from the Dow Chemical Company (Fig. 1). Rutile TiO_2 (R–TiO_2) nanoparticles, obtained from Sigma Aldrich (Singapore), have a mean diameter < 100 nm and a specific surface area of 18 m^2/g (Fig. 1), used as received without further treatment with other coating layers.

The hindered amine light stabilizer (HALS) used, namely Tinuvin 292 (T 292) from Ciba, is a mixture of bis (1, 2, 2, 6, 6-pentamethyl-4-piperidinyl) sebacate and methyl 1, 2, 2, 6, 6-pentamethyl-4-piperidyl sebacate (Fig. 1).

2.2. Samples preparation

To exclude any effect of some other additives on the photo-stabilization performance, all the formulations contained only 3% of 2, 2, 4-trimethyl-1, 3-pentanediol monoisobutyrate (Texanol) as a coalescing agent (optimal content for the best coalescing coating). The R–TiO_2 nanoparticles were added to the coating formulations at 1, 2, 4 and 6 wt%, with 1 wt% of T 292. The content of distilled water was 20 wt% (by weight on total solid resin).

The coating formulations were prepared by supersonic vibrations method using a supersonic equipment TPC-15 (Switzerland) to disperse the R–TiO_2 nanoparticles in distilled water (A mixture) and Texanol in the acrylic emulsion (B mixture). After 1 h of ultrasonication, the A and B solutions were mixed together and dispersed by 3 h of ultrasonication. Since T 292 is not soluble in water, it had to be pre-soluted in Texanol before dispersion in the acrylic emulsion by 3 h of ultrasonication.

The samples for UV-visible and IR analysis and for measurement of the weight loss during exposure were prepared on glass plates by