



Accelerated ageing of hybrid acrylic waterborne coatings containing metal oxide nanoparticles: Effect on the microstructure



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ABSTRACT

This work analyses the effect of UV radiation in a pure acrylic film, and two hybrid films, one with 1% CeO₂ nanoparticles and another with 1% of ZnO nanoparticles. The long term durability of the polymeric films was studied by accelerated UV exposure ageing. The changes occurring in the polymeric films were analyzed by measuring thermal properties, molecular weight distributions (MWD), formation of cross-linked or gel structures and the morphology by Transmission Electron Microscopy (TEM). The results revealed small changes (almost negligible) in the thermal properties and morphology whereas some differences were found when the microstructure was analyzed. Nevertheless, these differences were similar in the three studied films, discarding any additional degradation effect of CeO₂ and ZnO nanoparticles on acrylic films.

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1. Introduction

The UV light, ranging from 250 to 400 nm, represents about 5% of the total radiation reaching the earth's surface. UV radiation has detrimental effects on surfaces such as metal, glass, wood or human skin. All these surfaces can be protected against radiation with polymer coatings. Precisely, waterborne acrylic polymers are widely used in the formulation of varnishes and paints as protective coatings for different surfaces due to their low toxicity and good quality film forming properties [1]. Nevertheless, a common failure in outdoor acrylic coatings' applications is the photodegradation due to UV exposure, which causes structural changes and the consequent variation of the overall coating properties [2]. Though the polymer itself is non toxic and durable in outer environment, incorporation of UV absorbers and Hindered Amine Light Stabilizers (HALS) is necessary to increase the lifetime and improve the properties of the coating [3]. Therefore, due to the increasing pressure of the environmental legislation to reduce the volatile organic compounds (VOC) contents the use of non toxic UV absorbers, such as metal oxides, has increased considerably [4]. Titanium oxide (TiO₂), zinc oxide (ZnO) and cerium oxide (CeO₂) are widely used to block the solar radiation and to reduce the speed of photodegradation processes of the surfaces due to their broad UV spectrum attenuation properties and also their stability under radiation [5–9].

Nevertheless, it should be taken into consideration the photocatalytic activity of those metal oxides. TiO₂, CeO₂ and ZnO have almost the

same band gap energy (3.0–3.4 eV), and share the same UV absorption mechanism, under UV light the molecules get excited by absorbing a photon which creates an electron-hole pair. In the case of TiO₂ nanoparticles, these electron-hole pairs migrate to the surface of the particles and eventually reacts with oxygen, water or hydroxyls to form free radicals. This process is known as photocatalysis and it has been used to develop self-cleaning and antibacterial coatings and paints [10–12]. On the contrary, it has been proved that the photocatalytic activity of the CeO₂ and ZnO nanoparticles is lower than that of the TiO₂ [13]. Consequently, CeO₂ and ZnO seem to be good candidates due to their low photocatalytic activity to use as UV blocking material.

In our previous studies, it was reported the synthesis of high solids content acrylic/CeO₂ [8,14] and acrylic/ZnO [9] hybrid latexes to use as UV blocking binders. Those latexes were obtained by a two step polymerization process which led to encapsulation of the nanoparticles into acrylic polymer particles. The main advantage of having the nanofillers encapsulated inside the polymer particles was the lack of aggregation during film formation and leaching from the polymeric film. Therefore, good quality and transparent polymeric films were obtained with excellent UV absorption capacity. However, concerns were raised (at conferences and during publication procedure by reviewers) on the potential photodegradability of the coating matrix due to the photocatalytic or redox activity of the CeO₂ and ZnO used. This analysis was out of the scope of these papers, and it is the main objective of this work.

Photodegradation of hybrid acrylic coatings have been reported in the literature but in most of the cases the coatings were tested in substrates such as glass, stone or wood [2,6,7,15]. For instance, in the case of wood, lignin strongly absorbs in the UV-Vis region which leads to

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different chemical reactions and thus to photodegradation of the wood surface [16]. So once the UV light reaches the wood surface, formation of free radicals starts. Hence, there might be two sources of generation of radicals; one coming from the substrate itself and the other one from the metal oxides present in the hybrid acrylic films. In order to solve these concerns and to clarify the effect that the metal oxide nanoparticles have during photodegradation of acrylic binders, the degradation behavior of bare acrylic films was performed in this work.

Therefore, the objective of the present work was to analyze the effect that long exposure times to UV radiation of bare acrylic/CeO₂, acrylic/ZnO and pure acrylic polymeric films have on their microstructure and properties. Accelerated ageing test was used to assess the performance of the newly developed coatings.

2. Materials and methods

The acrylic polymer latexes containing 1% of CeO₂, 1% of ZnO and without inorganic nanoparticles were synthesized by seeded semibatch emulsion polymerization according to the procedure already described elsewhere [8,9]. The composition, the solids content, the average particle sizes and the polydispersity index of the latexes are presented in Table 1. The particles sizes were measured by Dynamic Light Scattering (DLS) using a Zetasizer Nano Series (Malvern Instrument).

Five films (20 × 5 × 0.12 mm) were cast in Teflon molds for each polymer latex at room temperature. Four of these films were exposed to accelerated weathering test and the fifth one was kept as reference.

Accelerated weathering test was conducted in a SolarBox 1500 with a Xenon lamp of 1500 W (UVA radiation) and having a constant irradiation at a power of 770 W/m². All the above mentioned samples were exposed to UV light for different time spans with maximum exposure time of 3200 h. Therefore, a sample for each coating was taken out of the SolarBox after 800 h, 1600 h, 2400 h and 3200 h of exposure.

The glass transition temperature (T_g) was measured by Differential Scanning Calorimetry (DSC) in a Q2000, TA Instruments. The samples were cooled to −50 °C and then the analysis started by heating up to 150 °C at 10 °C/min; 2 cycles were completed for each sample. The reported T_gs correspond to the second cycle.

Thermogravimetric analysis (TGA) was performed to the coatings in a Q500, TA Instruments. The samples were heated from 0 to 800 °C with a heating rate of 10 °C/min under nitrogen atmosphere.

The gel fractions of the samples were measured via conventional Soxhlet extraction, using technical grade tetrahydrofuran (THF) as solvent. Molecular weight distributions of the soluble part were determined by Size Exclusion Chromatography (SEC). The samples were dried at room temperature and dissolved in THF. The solutions were filtered (polyamide 0.45 μm) before injection into the GPC, which consisted of a pump (Shimadzu LC-20AD), three columns (Styragel HR2, HR4 and HR6) and a refractive index detector (Waters 2410). Chromatograms were obtained at 35 °C using a THF flow rate of 1 mL/min.

For the Infrared (IR) analysis, a Bruker Hyperion 2000 microscope coupled to a Vertex 70 Fourier Transform Infrared Spectroscopy (FTIR) spectrometer was used, equipped with Attenuated Total Reflectance (ATR) module and a liquid-nitrogen-cooled mid-band mercury cadmium telluride detector. The ATR module (20× ATR objective, single internal reflection) comprised a germanium crystal with a diameter of about 100 mm at the point of contact with the sample and integrated pressure

sensor. The spectra were measured with a spectral resolution of 4 cm^{−1} and present an average over 250 scans.

The morphology of the films was analyzed by Transmission Electron Microscopy (TEM), TECNAI G2 20 TWIN (FEI), operating at an accelerating voltage of 200 keV in a bright field image mode. The films were trimmed at −40 °C using an ultramicrotome device (Leica EMFC6) equipped with a diamond knife. The ultrathin sections (100 nm) were placed on 300 mesh copper grids. Nanoparticles size distributions were obtained using Image Pro Plus 7.0 software counting 500 nanoparticles of each kind.

3. Results and discussion

As it can be seen in Fig. 1 the bare blank and the hybrid containing 1% of ZnO nanoparticles were totally transparent before starting the test, whereas the film containing 1% of CeO₂ nanoparticles was slightly yellowish. Nonetheless, as shown in Fig. 1, during the exposure time the neat acrylic film became yellowish and the color increased slightly in the film containing nanoceria, while the transparency and lack of color in the film containing ZnO nanoparticles was maintained. Besides, by Scanning Electron Microscopy (SEM) it was seen that the surfaces of the films did not present any damage or cracking during the exposure (images not shown here).

The thermal properties of the neat acrylic coating and coatings containing 1% of CeO₂ and ZnO nanoparticles were analyzed using DSC and TGA curves. Table 2 and Fig. 2 present the average values and the standard deviations of the T_g and DSC curves of the acrylic films after different periods of time in the UV chamber, two measurements were carried out for each sample. It can be seen that the T_g was only slightly altered during the UV exposure; an increase of 1 or 2 °C was observed in all cases. The T_g after 3200 h of exposure was of 21 °C while for the 1% CeO₂ and 1% ZnO films were of 19 °C and 17 °C respectively. The T_g slightly decreased with the addition of the nanoparticles, being the decrease more pronounced for the ZnO hybrid, likely due to larger sizes of the ZnO aggregates [9] (see Fig. 7) in the acrylic matrix that increased the free volume. This trend was maintained after the UV radiation exposure.

The TGA curves for the three samples before and after 3200 h of exposure are plotted in Fig. 3. The curves exhibit one step thermal degradation process, being the decomposition temperature around 380 °C in all of them. The decomposition temperature values are in good agreement with those found in the literature for pure acrylic binders [17].

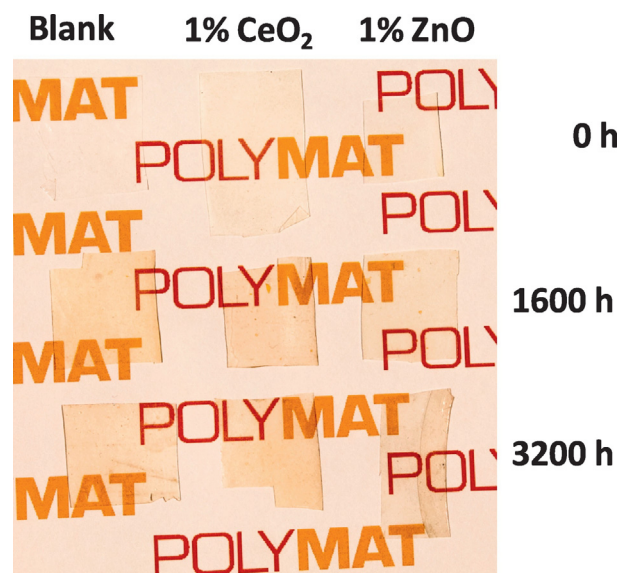


Fig. 1. Films appearance before starting the accelerated test, after 1600 h and after 3200 h of UV radiation exposure.

Table 1
Solids content (SC), average particle size (D_p), polydispersity index (PDI) and monomer composition of the three different latexes used to produce the films.

	SC (%)	D _p (nm)	PDI	MMA wt%	BA wt%	AA wt%
Blank	38	145	0.009	49.5	49.5	1
1% CeO ₂	40	173	0.021	49.5	49.5	1
1% ZnO	42	392	0.038	50	50	–

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